Design, fabrication and characterization of organic-inorganic hybrid solar cells

Ahmed Ali Said Ahmed

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SINGAPORE

**DESIGN, FABRICATION AND CHARACTERIZATION OF
ORGANIC-INORGANIC HYBRID SOLAR CELLS**

AHMED ALI SAID AHMED

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2020

DESIGN, FABRICATION AND CHARACTERIZATION OF ORGANIC-INORGANIC HYBRID SOLAR CELLS

AHMED ALI SAID AHMED

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

.. 15/Jan/2020.....
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Ahmed Ali Said Ahmed

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

15/Jan/2020

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Date

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Zhang Qichun

Authorship Attribution Statement

This thesis contains material from (a) paper(s) published in a/the following peer-reviewed journal(s) where I was the first and/or corresponding author.

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The contributions of the co-authors are as follows:

A/Prof Q. Zhang provided the initial project direction and edited the manuscript drafts.

- I prepared and wrote the manuscript drafts. Dr. J. Xie co-wrote the manuscript draft.

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For Paper (1):

- A/Prof Q. Zhang provided the initial project direction and edited the manuscript drafts.

- I co-wrote the drafts of the manuscript. Fabrication of perovskite solar cell, XRD, UV- vis, PL. spectroscopy, AFM and SEM were proceeded by me.
- Dr. W. Q. Chen carried out electrochemical measurements.
- D. B. Shaikh, R. S. Bhosale, Dr. S. V. Bhosale, A. L. Puyad and Dr. S. V. Bhosale designed, synthesized and characterized DS1 and DS2 small molecules.

For Paper (2):

- A/Prof Q. Zhang conceived the idea and edited the manuscript drafts.
- I wrote the manuscript draft, fabricated perovskite solar cell and carried out XRD, UV-vis, PL spectroscopy, EQE measurements and measure J-V curves for perovskite material and perovskite solar cell. Dr. J. Xie performed SEM imaging, Dr. W. Q. Chen carried out electrochemical measurements and Dr. Z. Wang performed AFM imaging.
- S. M. Wagalgave, A. L. Puyad, Dr. S. V. Bhosale and Dr. S.V. Bhosale designed, synthesized and characterized PDPT and PMDPT small molecules.

For Paper (3):

- A/Prof Q. Zhang conceived the idea and edited the manuscript drafts.
- I wrote the manuscript draft, fabricated perovskite solar cell and carried out XRD, UV-vis, PL spectroscopy. Dr. Z. Wang, Y. Zhou, Dr. J. Xie, W. Liu, A/Prof W. Gao and K. Zhao performed OFET measurments, TRPL, SEM and CV measurments.
- D. B. Shaikh, P. S. Rao, R. S. Bhosale, A. M. Mak, S. V. Bhosale, S. V. Bhosale designed, synthesized and characterized NDI-BTH 1 and NDI-BTH 2 small molecules.

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- A/Prof Q. Zhang proposed the idea and edited the manuscript drafts.

- I co-wrote the manuscript draft, fabricated perovskite solar cell and carried out XRD, UV-vis spectroscopy, AFM, SEM imaging contact angle measurements, electrochemical impedance spectroscopy measurements and measure J-V curves (illuminated and dark) and stability for perovskite material and perovskite solar cell.
- Dr. Z. Wang carried out OFET measurements. Y. Zhou and A/Prof. W.-B. Gao performed TRPL. Measurements. W. Liu performed PL. spectroscopy measurements.
- Dr. W. Chen and Dr. M. Liu designed, synthesized and characterized PTTI1 and PTTI2 as small molecules. Dr. W. Chen wrote the paper.

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The contributions of the co-authors are as follows:

- A/Prof Q. Zhang proposed the idea and edited the manuscript drafts.
- I wrote the manuscript draft, fabricated perovskite solar cell and carried out XRD, UV-vis, PL. spectroscopy, SEM imaging contact angle measurements, EQE measurements and measure J-V curves (illuminated and dark) and stability for perovskite material and perovskite solar cell. Dr. J. Xie co-wrote the manuscript draft. Dr. Z. Wang carried out AFM imaging. K. Zhao had contribution in explaining some results regarding to effect of each ETL on performance of solar cell. Y. Zhou and A/Prof. W.-B. Gao performed TRPL measurements
- Dr. Y. Wang and T. Michinobu designed, synthesized and characterized pBTT, pBTTz and pSNT ETLs

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Date

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Ahmed Ali Said Ahmed

Abstract

Firstly, electron transporting materials have a critical role in achieving high power conversion efficiency in perovskite solar cell. High synthesis temperature of metal oxides as electron transporting materials hinders flexible solar cell technology and consumes huge energy. Thus, switching to organic electron transporting materials for low-temperature processing and energy-saving is necessary and highly-desirable. However, phenyl-C61-butyric acid methyl ester (PCBM) as a conventional electron transporting material lacks the tunability of frontier molecular orbitals, as well as its poor stability and high price, inspired scientists to explore novel organic electron transporting materials, which have been considered as good candidates to substitute PCBM. Organic transporting materials are distinguished by low synthesis price, tunable frontier molecular orbital, easy of film forming and stable toward air. Organic transporting materials can be classified into organic small molecules and N-type conjugated polymers. Secondly, lead-based perovskite solar cells achieved high performance. However, its toxicity and instability encourage scientists to develop stable and ecofriendly lead-free solar cells.

This project was designed to develop novel organic electron transporting materials, which can push inverted perovskite solar cells to high stability and high-power conversion efficiency. Developing stable and efficient lead-free solar cell is the second aim of this project. Thus, this thesis addresses the design, synthesis and characterization of novel organic transporting materials. Furthermore, they have been investigated as electron transporting layers in inverted perovskite solar cells. Importantly, this thesis also addresses the possibility of replacing lead-based solar cells with stable and efficient lead-free solar cells. Introduction on the research of organic electron transporting materials and lead-free solar cells is involved. The rationale, hypothesis and objectives are presented. Moreover, the strategies, methods and approaches to achieve the objectives are discussed in each chapter.

The literature review on recent progress of organic transporting materials in perovskite solar cells is provided, which includes the classification of organic transporting materials

according to their building block, the effect of their structure on their performance as electron transporting layer is included. Moreover, the literature review provides the information about different types of lead-free solar cells and their advantages and their drawbacks.

The achieved findings in this thesis include the following: (1) Six NDI-based molecules have been designed and synthesized as electron transporting layers in inverted perovskite solar cells; (2) Two pyrene-based molecules were designed and synthesized as electron transporting layers; (3) The effect of sulfur position in pyrene-based molecules was investigated (4) Three N-type conjugated polymers were explored as electron transporting layer (5) The effect of embedded sp^2 -nitrogen in donor and acceptors of conjugated polymer was explored and (6) Tellurium tetraiodide was explored as a promising light absorber in solar cells.

Finally, summary was provided, as well as the recommendations for current and future work were involved in last chapter.

Lay Summary

As revealed in the abstract, the aims of this thesis can be divided into two purposes; 1) developing novel organic electron transporting materials for inverted perovskite solar cells; and 2) developing stable efficient lead-free solar cells.

The achieved finding and the recommendations of current and future works are provided as following:

Firstly, six NDI-based molecules were synthesized by simple method and investigated as electron transporting layers in inverted perovskite solar cells. NDI-based molecules with embedded sulfur atoms (NDI-BTH2) has high electron mobility as well as the well-matched energy levels with conduction band and valence band of perovskite layer. The NDI-BTH2-based device achieved decent power conversion efficiency up to more than 15%.

Secondly, two pyrene-based molecules (PTTI 1 and PTTI 2) were synthesized and investigated as electron transporting layer in inverted perovskite solar cells. The only difference between the obtained molecules is the position of sulfur atoms in thieno[3,4-b]thiophene: PTTI 1 has a higher passivation power toward surface traps than PTTI 2. Therefore, PTTI1-based devices the higher exhibited power conversion efficiency than PTTI 2-based devices.

Thirdly, three N-type conjugated polymers (pBTT, pBTTz and pSNT) were investigated as electron transporting layers in inverted perovskite solar cells. The embedding sp^2 -nitrogen in donor unit of the polymer enhanced the performance of the polymer as electron transporting layer than that if embedded in acceptor unit. Interestingly, pBTTz-based device exhibited the higher stability than PCBM-based device.

Finally, overall summary of the project is provided by including the hypothesis and achieved outcomes. The recommendations for current (incomplete work) and future work are intensively provided.

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Figure 6.6 AFM images of (a) pBTT, (b) pBTTz and (c) pSNT.

Figure 6.7 I- V curves of pBTT, pBTTz, pSNT and PCBM-based devices under dark conditions.

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Figure 6.9 (a) J-V curves of PSCs with different concentrations of pBTTz as ETLs and PCBM (b) Distribution of PSCs efficiency with the optimum concentration of pBTTz.

Figure 6.10 EQE of champion pBTTz-based perovskite solar cell

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Figure 7.3 structure of pBTT, pBTTz and pSNT polymers

Figure 7.4 Device architecture of TeI₄ - based solar cell.

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Figure 7.6 J-V curves of TeI₄-based solar cell with different concentration of TeI₄

Figure 7.7 J-V curves of TeI₄-based devices fabricated with different dripping time

Abbreviations

AFM	Atomic Force Microscopy
BSE	Back Scatter Electrons
CBL	Cathode Buffer Layer
CV	Cyclic Voltammetry
DSSC	Dye sensitized Solar Cell
ETL	Electron Transporting Layer
EQE	External Quantum Efficiency
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectra
HOMO	Higher Occupied Molecular Orbital
HTL	Hole Transporting Layer
LUMO	Lower Unoccupied Molecular Orbital
NMR	Nuclear Magnetic resonance
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
WHO	World Health Organization
XRD	X-Ray Diffraction

Chapter 1

Introduction

Developing novel organic non- fullerene acceptors has received many scientists' attention, due to their ability to overcome the limitations of PCBM as the conventional electron transporting layer in inverted perovskite solar cells. Organic non- fullerene acceptors are distinguished by low synthesis cost, high stability, tunable energy levels and ability to passivate electron trap centers of perovskite surface. Furthermore, the toxicity and instability of lead-based perovskite solar cells inspired scientists to develop stable and efficient lead-free solar cells. In this chapter, the hypothesis and objectives are proposed to develop novel organic non- fullerene acceptors as electron transporting layers and develop stable and efficient lead-free solar cells. The dissertation overview and outcomes are also included.

1.1 Hypothesis

1.1.1 Non-Fullerene acceptors as electron transporting layer in p-i-n PSCs

The demand on energy for heating, lighting, manufacturing and transporting usually controls the thinking and mind of the humanity. The requirement of energy increases with the increasing number of people. However, more than 80% of the used energy is generated from non-renewable energy resources such as oil, coal, nuclear energy and natural gas. ^[1] In addition to their limitations and harmful effects on human beings and environments, they are also the main sources in response to the carbon dioxide increase, ^[2] therefore converting the Earth to a greenhouse. The temperature of the Earth will increase accordingly, resulting in global warming. Furthermore, acid rains will pollute the soil and the crops. ^[3] Although nuclear energy represents about 9 % of world energy consumption and it presents a huge amount of energy, a small accident during the utilization of this energy may cause a big disaster, e.g. the lessons from Chernobyl 1986, and Fukushima 2011. Due to all these harmful limitations of non-renewable energy resources, researchers and governments emphasized their concerns on renewable energy resources such as wind energy, geothermal heat, and wave energy for their advantages (e.g. unlimited and ecofriendly resources) over non-renewable energy resources. One promising renewable energy resource is solar energy, which is clean and unlimited. It can even reach the places, where the generation of electricity is a challenge. ^[1] Recently, solar energy can be used by four ways:

- a) Converting it to biochemical energy through photosynthesis in plant and artificial photosynthesis.
- b) Converting it to heat by using solar collector.
- c) Converting it to electricity by using solar cell.
- d) Converting it into chemical energy (e.g. water-splitting)

The advantages of solar energy strongly inspire researchers to convert it into electricity by developing solar cells or solar panels. So far, there are three generations of solar cells. For each generation, researchers wish to develop solar cells with low Watt per cost. The first generation is based on crystalline silicon solar cells, followed by the second generation

Figure 1.1 The architecture of a) regular perovskite solar cell (n-i-p) PSC, b) inverted perovskite solar cell (p-i-n) PSC

which is based on thin film solar cells, and finally the third generation, the representative is the organic-inorganic hybrid perovskite solar cells (PSCs) ^[4]. PSCs initiated a revolution in solar cell technology due to their unique properties, which inherited from inorganic solar cells, for examples, long diffusion length and long lifetime of charge carriers ^[5], weak exciton binding energy ^[6], high electron and hole mobility ^[7] and some additional properties from organic solar cells, such as high light absorption coefficient ^[8], low cost, and ease of processing. These properties pushed the efficiency of perovskite solar cells to a high record of 22 %. ^[9] PSCs configuration can be classified into two major groups: 1) regular PSCs (n-i-p PSCs), in which electron transporting layer (ETL) is spin-cast onto transparent conductive oxide electrode (TCO) and 2) inverted PSCs (p-i-n PSCs) in which hole transporting layer (HTL) is spin-cast onto TCO. ^[10] Therefore, each type of PSCs can be determined by the arrangement of deposited layers as shown in **Figure 1.1**. Actually n-i-p PSCs showed higher performance than p-i-n PSCs. ^[11-12] However, the later has received more attention from scientists and researchers. In fact, general configuration of n-i-p PSCs includes metal oxide as ETL, which requires high temperature to prepare. The high temperature to prepare metal oxide layers prevents the usage of most flexible substrates. Also, high temperature increases the fabrication cost. In addition, n-i-p PSCs suffer from the hysteresis phenomenon. Rigid substrate and hysteresis have been considered as the bottleneck toward commercialization.

Figure 1.2 Operation mechanism of p-i-n PSCs

The p-i-n PSCs fabricated from organic materials can enhance their ability to fabricate on flexible substrate in addition to low fabrication temperature, which leads to decrease in the cost of as-fabricated device. ^[13-15]

Figure 1.2 explains the operation mechanism of p-i-n PSCs. Incident light is absorbed by perovskite layer, where excitons (electron-hole pairs) are generated and dissociated into electrons and holes. Electrons are extracted by ETL and transfer into cathode, while holes are extracted by HTL and transfer to anode. The charge transporting layers play the crucial role to determine the performance of PSCs. HTLs are well studied by researchers and scientists. Different types of HTLs were studied, which include (organic small molecules, polymers and metal oxides) ^[16-20]. To enhance the performance of PSCs, it is desirable to select suitable charge transporting layers including HTL and ETL. HTLs such as small molecules, conjugated polymers and metal oxides were studied well in several publications. On the other hand, ETLs have relatively slow research progress. The ideal ETL in p-i-n PSCs should have following properties: 1) well-matched frontier molecular orbitals of perovskite layer are required in order to enhance the extraction of electrons from perovskite layer, while lower unoccupied molecular orbital (LUMO) of ETLs should be slightly deeper than conduction band of perovskite layer. In addition, high occupied molecular orbital (HOMO) of ETL should be deeper than valence band perovskite layer, which leads to blocking the movement of holes from perovskite layer to cathode these properties

decrease Voc loss and enhance fill factor (FF). 2) High electron mobilities of ETLs is highly desirable to improve the electron transport, which decreases series resistance and enhances short circuit current density (Jsc). 3) ETLs should be soluble in the solvents, which don't damage the perovskite layer, since p-i-n PSC is fabricated by the spinning of each layer alternatively. 4) Ideal ETL should show complete coverage over perovskite layer without pin holes or aggregation. Finally, ideal ETL should have the ability to passivate surface defect of perovskite layers. During the deposition of perovskite layer, antisolvent is dripped after definite time. As a result of antisolvent dripping, positively charged under coordinated Pb-atoms (electron deficient sites) are produced on the surface of perovskite layer.^[21-22] These atoms are considered as electron trap centers. ETLs, generally possessing electron rich centers such as sulfur and nitrogen, can act as Lewis base and the passivation of electron-trap centers could be replaced by the coordination of N-Pb and S-Pb. Therefore, ETLs with optimized passivation groups should get rid of non-radiative recombination and mitigate hysteresis.^[23] Furthermore, the ideal ETL should also have the property to block iodide migration and enhance device stability.

Fullerene (C_{60} , C_{70}) and the soluble form ([6, 6]-phenyl-C61-butyric acid methyl ester (PCBM)) are considered as conventional and common ETLs in p-i-n PSCs. PCBM has decent electron mobilities and acceptable LUMO and HOMO values regarding to the conduction band and valence band of perovskite layer, respectively. The passivation mechanism of PCBM is totally different from the mechanism of nitrogen and sulfur containing ETLs^[24]. PCBM is a Lewis-acid acceptor, which has the capability to passivate the perovskite layer by interacting with under-coordinated halide or Pb-I antisite defect PbI_3^- . PCBM was introduced for the first time as ETL in p-i-n PSC by Guo et.al.^[25] The as-fabricated device showed power conversion efficiency (PCE) 3.9 %. The relatively low PCE is attributed to low sophisticated fabrication technique of perovskite layer. After the optimization of PCBM layer thickness and the development of novel technique to fabricate perovskite layer. PCBM-based PSC showed PCE up to 21.1%. Due to the reliability of results showed by PCBM. PCBM was implemented as ETL by Snaith et.al. for exploring the charge carrier's lifetime of perovskite layer. To further understand the unprecedented PCE of PSC proceeded by adopting PCBM as ETL,^[5, 26] the scientists believed that PCBM could suppress halide ion migration from perovskite layer through π -halide non covalent

interaction. Such interactions will increase the electron transport in ETLs [27].

The change in PCE of PSCs with different scan direction and scan rate is known as Hysteresis. This phenomenon hinders PSC technology toward marketing. The origin of hysteresis is still in debate. However, it can be included in ferroelectricity nature of perovskite layer, and charge traps, which are generated inside and on the surface of the perovskite layer. [28] The ability of PCBM to passivate trap states of perovskite layer was discovered for the first time by Huang et.al. [29] This result was confirmed by photoluminescence (PL) spectroscopy measurement. The maximum PL peak of perovskite layer blue shifted after deposited PCBM. The importance of solvent annealing of PCBM was discovered by the same group. Heat treatment after deposition of PCBM in dichlorobenzene atmosphere enhances Voc. Solvent annealing at 100 °C for 60 minutes improves the ordering of PCBM and decreases the energy disorder and declines trap states, which increase Voc. PCBM was adopted in a lot of researches and provided decent PCEs. [30]

Although all previous devices with PCBM as ETLs provided decent results, PCBM doesn't match the requirement of ideal ETL due to poor morphology control, poor stability, fixed LUMO and HOMO values, and high cost of synthesis. [31-34] Thus, several methods were applied to improve the performance of PCBM as an ETL. These methods include the doping of PCBM with organic n-type dopants. The properties (e.g. energy levels, mobility and stability) of organic semiconductors can be improved by n-type doping. [35] Additional small amount of n-type dopants into PCBM enhances PCBM properties by synergistic effect. As a result of doping process, free charge carriers increased. Finally, the charge density and electrical conductivity of organic semiconductors enhanced. The doping of PCBM can be classified into several types according to the type of dopant and mechanism of doping. Graphdyine (GD, a π -delocalized graphene-like system) as a dopant of PCBM helps to enhance the film coverage that leads to the enhancement of Jsc and FF, [36-40] while reduced graphene oxides (RGOs) can increase electron transport. [41] Dumb-belled PCBM was also utilized as a dopant of PCBM. [42, 43] Doping can be produced by electron transfer between halide and fullerene by using fulleropyrrolidinium iodide (FPI) as a self- dopant [44]. Benefiting of Plasmonic effect, silver nanoparticle showed decent performance as a

dopant of PCBM. [45]

Another way to overcome the limitations of PCBM was modifying fullerene and PCBM to possess better properties as ETM than PCBM itself. Bolink et. al. modified PCBM by changing the terminal part of alkyl chain (e.g. by changing methyl group with butyl or hexyl group) to enhance the solubility of modified fullerene. Also, they tried to change the aromatic group. [46] The modified PCBM showed PCE up to 8%, which is higher than PCBM. By embedding diphenylmethanofullerene into C60 and C70 core, the resultant modified fullerenes showed higher passivation power toward electron trap states than PCBM, at the same time, the hysteresis also decreased [47]. To address poor stability of PCBM, cross-linkable silane fullerene molecules was synthesized and investigated as ETLs in p-i-n PSCs. The contact angle of C60-SAM is 40 degree higher than that of PCBM, which can improve the stability of devices. [48]

However, all these trials haven't achieved the researchers' requirements. Although most of modified fullerenes enhanced the PCE and the ability of the as-fabricated device, the cost increased, and the experiment became more complicated. It is desired to find the new replacement of fullerene and the modified fullerene molecules, which overcome all previous limitations. Non fullerene acceptors showed good experience in electronic devices such as organic solar cells and transistors and others.

Non fullerene acceptors can be classified into: organic small molecules and n-type conjugated polymers. Organic small molecules (perylene diimide, naphthalene diimide, azaacene, pyrene-based molecules) prepared through simple synthetic route have been demonstrated to possess tunable energy levels, even surface morphology, decent electron mobility, and decent stability. The performance of organic small molecules as ETLs in p-i-n PSC increased rapidly from 10 % to 20.5 %. Recent organic small molecules have been proven to show better performance than PCBM. PDI-based ETL showed decent performance since 3D SFX-PDI4-based device achieved good performance up to 15.3 %. 3D structure helps to decrease the aggregation. [49] Changing functional groups(e.g. FS-PDI2 and FA²⁺PDI2) also affected the performance as. [50] The increasing PDI groups (e.g. hPDI2-Pyr-hPDI2 and hPDI3-Pyr-hPDI3) also affects the performance of devices [51]. Although NDI-based molecules are relatively rare to be explored, the effect of the

functional groups on the performance of NDI-based molecules is significant while PCEs can be increased significantly by changing ending group. [52-54]

Azaacene –based small molecules showed decent performance. Especially, sulfur atoms in the framework of azaacene showed high performance through passivating the trap state of perovskite layer. [55-57] Fused aromatic rings-based small molecules have a promising performance as ETL in p-i-n PSCs. Fused aromatic rings-based small molecules characterized by rigid planar π conjugation structure with high electron affinity for efficient electron transport.

N-type conjugated polymers have the same advantage of organic small molecules in addition better film morphology since organic small molecules showed small cracks. The N-type conjugated polymer as ETLs in PSCs was first investigated by Wang et. al. and the as-obtained PCE was 8.7 %, which is considered relatively low. [58] Later on, the PCE can be increased to 16.54 % [59]. Recent progress in non-fullerene acceptors as ETLs in p-i-n PSCs will be discussed later in literature review section.

1.1.2 Lead-free perovskite solar cells as potential substituent of current technology

Lead-based perovskite solar cell exhibits high performance and this technology is being improved every day. Stability and toxicity are still two issues to block them toward marketing [60]. The solar cells are mainly designed to work outdoor, that means, it will be exposed to light, H₂O vapor and O₂. The main drawback of PSCs is the hygroscopic nature of organic cations that leads to the spontaneous degradation according to the following equations [61-64]:

In addition, MAPbI₃ showed relatively low stability toward the continuing exposure to high temperature. [65]

PbI₂ (s) is found to be the common degradation product, which for sure causes harmful effect on environment. Contrary to water-insoluble lead acid battery component (PbO and PbSO₄), PbI₂ has a solubility constant 4.4×10^{-9} in water at room temperature, which cause toxicity to the human and the environment. [66-67] It is difficult for lead-based PSCs to pass environmental standards as photovoltaic system, since the World Health Organization (WHO) determined that 50 % of lethal dose of lead (LD₅₀(Pb) is less than 5 mg/Kg of body weight and WHO stipulated that the highest lead blood level in children is 5 mg /L. [66- 69]

The toxicity caused by intrinsic instability of MAPbI₃ PSCs hinders the participation of PSCs in commercialization and marketing. [70-72] Thus, it is highly desirable to find environmentally-friendly and stable alternatives to replace lead element. Perovskite materials can be classified into three types: 1) inorganic oxide perovskite (BFO), alkali metal halide perovskite (CsPbI₃), and organic metal halide perovskite. All previous type have structure of ABX₃, where B is metal cation and X is anion (oxygen or halide). To design new perovskite structures, three important factors should be implemented: 1) Charge neutrality between cations and anions; 2) octahedral factor (μ), which represents the stability of BX₆ octahedra,

$$\mu = r_B / r_X$$

(r_B is ionic radius of cation B and r_X is ionic radius of anion X), and the perovskite structure is found to be stable when μ is between 0.442 and 0.895; and 3) Goldschmidt tolerance factor (t), which predicts the formation of perovskite structure, is a relationship between ionic radii of r_A (ionic radius of cation A), r_B and r_X according to the equation [73, 74].

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

The perovskite formation with different type of cations and anions can be predicted by implementing equation of octahedral factor of tolerance factor. ABX_3 structure has empirical tolerance coefficient between 0.8 and 1.0, since the t of ideal ABX_3 - perovskite with a cubic structure equals 1. Also, cubic structure can be predicted when t lies between 0.9 and 1.0. Different structures such as orthorhombic, tetragonal and rhombohedral can be empirically determined if t in the range of 0.8 to 0.89. If the cation A-site has too small ionic radius, t will be less than 0.8 and the resultant structure will be ilmenite –type instead of perovskite –type. While, if cation A has too large radius, hexagonal structure will be formed. [73, 75-79].

The new candidates to replace lead can be classified into homovalent elements (such as Sn and Germanium (Ge)) and heterovalent elements (such as Bismuth (Bi) and antimony (Sb)). According to the rule of charge neutrality, the heterovalent atom can be classified into two subgroups: ion-splitting and ordered vacancy. The ion-splitting subcategory can be further divided into mixed anion compounds with the formula of $AB(Ch,X)_3$, where Ch represents a chalcogen element, and X represents a halogen element, and mixed cation compounds with a formula of $A_2B(I)B(III)X_6$, which are commonly called double perovskites. The ordered vacancy subcategory can also be divided into the B(III) compounds with a formula of $A_3\square B(III)X_9$ and the B(IV) compounds with a formula of $A_2\square B(IV)X_6$ (the sign of $\square$ indicates vacancy), Te element can adopt this structure. Regrettably all reported lead free-based PSCs showed the efficiency smaller than lead-based PSCs. So, it is long journey to find novel replacement of Pb- element with high PCE and high stability. [80]

Figure 1.3 Schematic illustration of the approaches and consequences of potential Pb replacement.

[80]

1.2 Objectives and Scope

Organic molecules are recognized by several amazing properties: they can be synthesized with low-cost material through simple synthetic route; they can be synthesized without high technology equipment. Furthermore, the structure of organic molecules can be tuned and modified by simple solution processing way. Organic small molecules and conjugated polymers exhibited good performance in the application of organic electronics. Organic non-fullerene acceptors are widely investigated in organic solar cells. However, the number of the reported PSCs with organic small molecules as ETLs is still small. It is believed that, there are a lot of empty rooms to be discovered in this field. Clearly, developing novel

ETLs to achieve the higher PCE of perovskite solar cell is highly desirable.

This thesis will focus on the study the effect of organic non- fullerene acceptors as ETLs on the performance of p-i-n PSCs. Organic small molecules and N-type conjugated polymers will be designed, synthesized and characterized, then investigated as ETLs. Non-fullerene acceptors used in this thesis can be classified into NDI-based molecules, pyrene-based molecules, and N-type conjugated polymers. According to my results, I found that nitrogen atoms which embedded in NDI-based molecules can enhance electron transporting properties as ETLs in p-i-n PSCs. However, when S was used, the enhancement is even more. In pyrene -based molecules, the position of sulfur atoms plays an important role to determine the suitability of pyrene-based molecule as ETLs in p-i-n, while sulfur atoms passivate trap centers on the perovskite layer. Furthermore, the investigation of N-conjugated polymers as ETLs in p-i-n PSCs indicated that, the effect of embedded (sp^2 -nitrogen) sp^2 -N in acceptor unit is totally different from the effect of sp^2 -N in donor unit on the performance of the polymer as ETLs

Moreover, this thesis will also focus on finding novel lead-free solar cells. It was found that, tellurium tetraiodide has a promising performance as a light absorber in photovoltaic application.

The detailed objectives of the proposed project are listed below:

- 1- Design, synthesis and characterization of novel six NDI-based molecules with different structures containing nitrogen or sulfur atoms. Then, these materials have been utilized as ETLs in p-i-n PSCs
- 2- Design, synthesis and characterization of novel two pyrene-based molecules as ETLs. The sulfur position of each molecule has been investigated.
- 3- Investigation of the performance of three N-type conjugated polymers as ETLs in p-i-n PSCs. The effect of embedded sp^2 -N in donor and acceptor units has been studied.
- 4- Development of novel lead-free light absorber for photovoltaic application.

1.3 Dissertation Overview

The thesis addresses the design, synthesis and characterization of organic non- fullerene

acceptors as well as studying their performance as ETLs in p-i-n PSCs. Moreover, the thesis also addresses the development of novel lead-free light absorber for photovoltaic application.

Chapter 1 provides general introduction about the importance of solar cells, followed by the research on perovskite solar cells. Then, the information about the importance of electron transporting layers in perovskite solar cells and their different types has been provided.

Chapter 2 reviews the literature concerning different generations of solar cells, recent progress of organic non- fullerene acceptors in perovskite solar cells, and recent progress of lead-free perovskite solar cells.

Chapter 3 discusses the working principle of characterization equipment, which were used in this project. Methodology, materials and fabrication technique are discussed in this chapter.

Chapter 4 elaborates the design, synthesis, and characterization of six-NDI-based molecules as ETLs in pi-n PSCs. The effect of nitrogen atoms and sulfur atom in NDI-based molecules as ETLs was investigated.

Chapter 5 elaborates the design, synthesis, and characterization of two pyrene-based molecules as ETLs in p-i-n PSCs. The effect of sulfur atom position on the performance of pyrene-based ETL was investigated.

Chapter 6 elaborates the investigation of three N-type conjugated polymers as ETLs in p-i-n PSCs. The effect of embedded sp^2 -N position in acceptor unit and donor unit was investigated.

Chapter 7 provides a general summery the reported work in this thesis. Incomplete (current) work and proposed characterization to introduce tellurium tetraiodide as a light absorber in photovoltaic application. Recommended and proposed work to find novel lead-free solar cells and novel stable and high performance non- fullerene acceptors.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Six novel NDI-based molecules were developed as ETLs in p-i-n PSCs. The function of sulfur and nitrogen atoms in NDI-based molecules as ETLs was investigated.
2. Two novel pyrene-based molecules were developed as ETLs in p-i-n PSCs. The effect of sulfur atom position on the performance of pyrene-based ETL was investigated.
3. Three N-type conjugated polymers were explored as ETLs in p-i-n PSCs. The effect of embedded sp^2 -N position in acceptor unit and donor unit was investigated.
4. Tellurium tetraiodide was investigated as light absorber in solar cell for the first time.

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Chapter 2

Literature Review

This chapter includes review on the state of the art of three topics. First, the development of the generation of solar cells from silicon to perovskite is presented. Second, recent progress of organic non- fullerene acceptors in inverted perovskite solar cells is included. The motivation behind development of organic molecules in perovskite solar cells is provided. Different types of organic non-fullerene acceptors are included. The performance of inverted perovskite solar cells with non-fullerene acceptors are discussed. Finally, different types of lead-free perovskite solar cells with their performance are included.

2.1 Development of solar cells technology from silicon to perovskite solar cell

2.1.1 History

The technology of solar cells started after A. E. Becquerel discovered the photovoltage effect in 1839, by immersing an electrode in a conductive solution when exposing the system to light ^[1, 2]. The first solar cell was constructed from selenium element by Charles Fritts in 1883. The age of silicon wafers has started after the preparation of single crystal silicon by Jan Czochralski in 1918 ^[3]. The first commercial efficient silicon solar cell was fabricated by the team from the Bell Lab USA in 1954 with an efficiency about 6 % ^[4]. After a lot of researches in crystalline silicon-based solar cells have been developed, the efficiency increased but the price and payback time didn't decrease. Therefore, another technology of solar cell fabrication has been launched, which is known as the thin film technology. The first thin film solar cell was built in the university of Delaware in 1980 from Cu₂S/CdS, but this technology didn't achieve the goals of reducing the payback time and decreasing the Watt per cost. Organic semiconductor materials have low cost, ease of fabrication and high optical absorption, thus organic solar cells could participate as a promising candidate in third generation solar cells. As a fascinated contributor in third generation, the first dye-sensitized solar cell (DSSC) was fabricated in EPFL in 1991 by Michael Grätzel and O'Reagan ^[5]. DSSCs are considered as the ancestors of organic–inorganic hybrid halide perovskite solar cells, which started a new era in solar cell technology. The driving force of all these studies and trials in solar cells technology was from decreasing the cost and enhancing the efficiency. **Figure 2.1** shows each generation of solar cells ^[6].

Figure 2.1 Different generations of solar cells fabrication technology ^[6].

2.1.2 First generation solar cell

2.1.2.1 Crystalline silicon solar cell, C-Si (single crystal and polycrystalline)

It is the oldest technology of solar cells. C-Si solar cell technology is currently dominant in the market of solar cells. It represents about 90 % of the global photovoltaic module production ^[7]. C-Si solar cell is distinguished by its reliability and high performance. However, it has a long payback time and a high Watt per cost due to its sophisticated and complicated fabrication. Single crystalline solar cells are fabricated by Czochralski process. Each cell is a single crystal of silicon, so it provides a high extraction of charge carriers. Polycrystalline solar cells are constructed by the casting of pure molten silicon ^[8], and each cell consists of more than one crystal, resulting in a lot of grain boundaries which could increase the charge recombination processes. Therefore, polycrystalline silicon solar cells are less efficient than single crystalline silicon solar cells. The highest lab-efficiencies of single crystalline silicon solar cell and polycrystalline silicon solar cell are 25.6% and 20.4%, respectively ^[9]. At the module-level design, the highest efficiencies of single crystalline and polycrystalline silicon solar cells are 20.8% and 18.5 %, respectively ^[10].

2.1.3. Second generation solar cells

2.1.3.1 Cadmium telluride (CdTe)

The main advantage of CdTe thin film solar cells is its direct band gap, 1.45 eV, which is an optimum band gap for high performance solar cells ^[11]. The production cost of this type of solar cells is less than that of the crystalline silicon solar cell, but the later has a higher efficiency ^[11, 12]. Due to its optimum direct band gap, CdTe thin film solar cell has a high optical absorption coefficient, with efficiencies as high as 21% and 17.5% for lab cells and modules respectively ^[9, 10]. The drawbacks of CdTe thin film solar cells are the toxicity of cadmium ^[13] and the high temperature requirement (600 °C) for production ^[11].

2.1.3.2 Copper zinc tin sulfide (CZTS)

This type of solar cells solves the main drawback of CdTe solar cells in the toxicity and rarity, because it depends on abundant and ecofriendly materials. Moreover, it has an optimum direct band gap and a high optical absorption ^[14]. However, the efficiency is still lower than that of CdTe solar cells. The recorded lab CZTS solar cell efficiency was 12.6 % ^[15].

2.1.4. Third generation solar cells

This type of solar cell technology isn't economically famous, but it is a promising candidate in solar cell communities, owing to its dependence on low cost production, ease of fabrication, and short payback time with reasonable efficiencies.

2.1.4.1 Organic solar cells

Distinctive properties like low production cost and ease of fabrication in addition to its dependence on the earth abundant materials enable it to be promising solar cells for the future. Organic solar cell mainly depends on the blending of electron donor materials and

electron acceptor materials (polymers or organic small molecules). After the absorption of light by electron donor material, excitons are born, then dissociate on the interface between the two different materials, forming electrons and holes which are collected to external circuit by two electrodes ^[16, 17]. The highest lab efficiency of organic solar cell is more than 16 %.

2.1.4.2. Dye sensitized solar cells (DSSCs)

As a result of their different colors, low production cost, and ease of fabrication, DSSCs are used as electricity-generated facades in buildings. In addition, DSSCs are more efficient than silicon solar cells in indoor applications ^[18]. The first efficient DSSC was fabricated by Brian O'Regan and Michael Grätzel in 1991, where they succeeded to employ mesoscopic titanium oxide as photoanode ^[5]. The efficiency of DSSCs improved from 7.9 % in 1991 ^[5] to 14.3 % in 2015 ^[19]. However, these cells suffer from long term stability and their electrolytes may leak after strong hit. Finally, DSSCs are considered as ancestors of perovskite solar cells.

2.1.4.3 Organic-Inorganic Hybrid Perovskite Solar Cells (PSCs)

So far, organic-inorganic hybrid perovskite solar cells (PSC) is not only a last member in third generation solar cells, but also a most important member. PSCs hauled the mind of researchers and scientists, from 2009 to 2016. The number of publications doubles every year and thousands of papers have been published within seven years ^[20] from first paper published by Miyasaka's group in 2009 ^[21]. The term perovskite refers to the crystal structure of the absorbing material of a solar cell. It adopts the formula of ABX_3 as shown in **Figure 2.2**, where A site is a monovalent cation ($CH_3NH_3^+$, Cs^+ or $CH(NH_2)_2^+$), B site is a divalent cation (Pb^{2+} or Sn^{2+}) and X site is a halogen (Cl^- , Br^- or I^-) ^[22, 23]. The fascinating properties of PSCs combines both the advantages of inorganic solar cells, like long diffusion length, long lifetimes of charges carriers ^[24], weak exciton binding energy ^[25] in addition to high charge carrier mobility ^[26] and organic solar cells such as high optical absorption coefficient ^[27], low cost, besides ease of processing.

Figure 2.2 Structure of perovskite materials

2.1.4.3.1 Regular perovskite solar cells

The first inspiration of PSC was initiated in Japan by Miyasaka's group in 2009 when perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was utilized as an absorbing material and a photosensitizer in DSSCs. The efficiency of this solar cell was 3.9 %. However, this solar cell rapidly degraded, due to the degradation of perovskite materials by electrolytes ^[21]. After two years, Park's group exploited $\text{CH}_3\text{NH}_3\text{PbI}_3$ quantum dots as sensitizing materials on different thicknesses of titanium oxide, and they achieved an efficiency of 6.2% ^[28]. In 2012, the electrolyte was substituted by hole transporting material 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (*spiro*-MeOTAD) and the efficiency was increased to 9 % ^[29]. In 2013, Lee group replaced the TiO_2 electron transporting layer by Al_2O_3 , and surprisingly they got an efficiency of up to 10.9%, although Al_2O_3 is considered as an insulator. **Figure 2.3** shows the transfer process of electrons from perovskite material to FTO in TiO_2 and Al_2O_3 - based perovskite solar cells ^[30]. The vapor deposition technique was used for the first time to fabricate $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite film by Snaith group and they got an efficiency of 15.4 % ^[31]. The same group fabricated PSC at a relatively low temperature of 150 °C instead of 500 °C by using Al_2O_3 particles on compact TiO_2 layer and got an efficiency of 12.3 % ^[32]. Mohammad K. Nazeeruddin and Michael Grätzel achieved a breakthrough in the fabrication of perovskite films by using two-step method

technique, which resulted in large grains of perovskite layer with lab efficiency equaled to 15% [33].

Figure 2.3 Electrons transfer in the case of TiO_2 and Al_2O_3 as electrons transporting layers ⁽³⁰⁾.

In 2014, Snaith and Nicholas et al incorporated graphene layer between TiO_2 and FTO. This layer introduced a step energy level of electrons and facilitated the transfer of electrons to FTO, resulting in a high efficiency of 15.6% [34]. Sang Il Seok's group employed polytriarylamine (PTAA) as a HTL due to its high hole mobility. Moreover, its HOMO energy is well matched with the valance band of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, therefore they obtained a high open circuit voltage (V_{OC}) of 1.02 V and an efficiency up to 16.4% [35]. Jaemin Lee and Sang Il Seok made some modifications in spiro-MeOTAD layer by using pm-spiro- MeOTAD, po-spiro-MeOTAD and pp-spiro-MeOTAD as HTLs in PSCs. The highest efficiency of 16.7% was achieved by using pp-spiro-MeOTAD as a HTL [36]. Sang Il Seok et al. accomplished a breakthrough in fabrication of perovskite solar cell by dripping toluene as an antisolvent on the perovskite layer during spin coating. They attained an efficiency of 16.7%, and their method enabled researchers to get high dense

perovskite films with large grains and very small roughness. [37] Thomas Moehl et al used porous TiO_2 as an electron transporting layer, and the pores permitted the perovskite film to contact with FTO, which increased the rectifying behavior and they got an efficiency of 17.2 % [38]. Yang Yang's group made modifications on ITO by poly-ethyleneimine ethoxylated (PEIE), which changed the work function from 4.6 eV to 4.0 eV, and they used Yttrium-doped TiO_2 (Y- TiO_2) as an electron transporting layer with a conduction band minimum up to 4.0 eV. So, they obtained a high V_{oc} up to 1.12 V and a high efficiency of 19.3 % [39]. In 2015, Sang Il Seok et al. replaced methylammonium iodide (MAI) with formamidinium iodide (FAI). The resultant formamidinium lead iodide perovskite had a band gap with a larger absorption than that of methylammonium lead iodide perovskite, and the efficiency was 20 %. [40] In the same year, Anders Hagfeldt et al. got an efficiency of 18.4 %, and they replaced TiO_2 ETL with SnO_2 ETL, which was fabricated by a low temperature atomic layer deposition. They synthesized mixed cations and mixed anions perovskite layer. The conduction band of the synthetic perovskite layer was well matched with the conduction band of SnO_2 ETL, leading to a high V_{oc} of 1.19 V [41]. In 2016, Michael Grätzel et al. applied a new perovskite composition, $\text{FA}_{0.81}\text{MA}_{0.15}\text{PbI}_{2.51}\text{Br}_{0.45}$ with DMSO (1:1) in molar ratio, and they attained an efficiency of 20.61% [42]. Also in the same year, Michael Grätzel et al. prepared a new lead perovskite composition with triple monovalent cations (Cs^+ , MA^+ and FA^+) and mixed halide (I^- and Br^-). This composition improved the stability of perovskite solar cells, resulting in an efficiency of 21.1 % [43]. The same group achieved an efficiency of perovskite solar cell up to 21.8 % after the incorporation of Rb^+ ion into the perovskite precursor [44]. The highest efficiency of perovskite cell now is around 22.1% by Sang Il Seok group, and this result was achieved by decreasing of the defects in perovskite layer [45].

2.1.4.3.2 Inverted perovskite solar cells

The first inverted perovskite solar cell was fabricated by Guo et. al. in 2013. They were inspired by the idea from polymer solar cells. They achieved an efficiency of 3.9%. **Figure 2.4 (a)** shows the architecture of the first inverted perovskite solar cell and **Figure 2.4 (b)** shows the energy levels diagram of each layer of this device [46]. In the same year, the

efficiency was increased to 9.8 % by Snaith et al. after the optimization of the fabrication parameters ^[47]. Mohammad K. Nazeeruddin and Henk J. Bolink et al. improved the efficiency to 12 % by introducing an interfacial layer of Poly [N, N'-bis (4-butylphenyl)-N, N'-bisphenylbenzidine] polyTPD between the perovskite layer and HTL. PolyTPD was introduced as an energy level step of holes to keep high V_{oc} ^[48].

Figure 2.4 (a) Architecture of the first inverted perovskite solar cell. (b) Energy levels diagram for each layer used in the device. ^[46]

In 2014, a flexible perovskite solar cell was fabricated by Yang Yang's group with an efficiency of 9.2 % after 20 bending, therefore they proved that perovskite solar cells are promising flexible solar cells. ^[49] In the same year, Sang Il Seok et. al. proved that a thinner PCBM layer can lead to a higher efficiency. They got an efficiency up to 14.1% for a small unit cell (0.09 cm²) and 8% for a module with an active area equaled to 60 cm². ^[50] Yang Yang et al. fabricated an efficient inverted solar cell in ambient atmosphere with an efficiency up to 17 %. They ascribed the high efficiency to the accumulation of moisture at the grain boundaries of perovskite layer during the heat treatment. This phenomenon motivated the grain boundaries to creep and merge with adjacent grain boundaries, resulting in an increase of the size of the grains and a reduction of the number of pin holes. ^[51] From the stability point of view, inorganic hole transporting materials are better than PEDOT:PSS or other organic materials. Alex Jen's group fabricated an efficient inverted solar cell by using a Cu-doped NiO HTL with an efficiency of 15.4%. ^[52] In 2015, Paul

Meredith et al. fabricated several inverted perovskite solar cells, with different ultrathin p-type polymeric semiconductor interlayers with different ionization potentials: P3HT (-5.0 eV), PCPDTBT (-5.0 eV), DPP-DTT (-5.2 eV) and PCPTBT (-5.3 eV) to modify the interface between PEDOT:PSS, HTL and perovskite layer. The best efficient PSC was fabricated by PCDTBT interlayer and the efficiency was 11.7%. Moreover, they performed theoretical calculation to get the optimum conditions to fabricate perovskite solar cell. After they combined the optoelectronic theoretical calculations of perovskite material with the experimental preparation parameters, they got an efficiency of 16 % ^[53]. Aditya D. Mohite et al. used a hot casting technique for perovskite layer deposition. The resultant perovskite layer had large grains and pin holes free, leading to an efficiency of 18%. ^[54] In 2017, the efficiency was rapidly increased to 19.9% by incorporating p-type Cu(thiourea)I in perovskite layer, which made passivation of trap states in perovskite layer. ^[55] By utilizing the synergistic effect between H₂O and DMF, Chun-Guey Wu et al. fabricated large grains of CH₃NH₃PbI₃ via a two-step method, with a high efficiency equaled to 20.1% ^[56]. Recently, P-i-n-based device approached 21%. ^[57]

2.2 Recent progress in non-fullerene acceptors in p-i-n PSCs

2.2.1 Non-fullerene acceptors as ETLs in inverted PSCs

The doping and modification of PCBM will increase the cost of final devices, which frustrates scientists a lot for practical applications. Thus, searching new organic materials to replace PCBM or its derivatives is very important and highly desirable.

2.2.1.1 Perylene diimides as ETLs in inverted PSCs

Due to the ease of synthesis and good thermal and chemical stability of PDIs as well as their well-matched LUMO and HOMO with conduction band and valence band of perovskite layer, ^[58-61] PDI and its derivatives as ETLs have received many scientists' attention. Jo et al. introduced diPDI as an electron ETL in p-i-n PSC and found that the quenched PL. of diPDI-based PSC was similar to the quenched PL. of PCBM-based

devices.^[62] Furthermore, they found that the electron lifetime (1.2 ns) of diPDI-based PSCs is lower than that of PCBM-based PSCs. Also, the PCE (7.1 %) of diPDI-based PSCs was smaller, which might be caused by the low conductivity of diPDI (4.7×10^{-12} S/cm). Inspired by their previous work that the conductivity of PCBM can be enhanced from 3.8×10^{-9} S/cm to 6.1×10^{-5} S/cm by DMBI doping,^[62] the addition of small amount of DMBI to diPDI also increased the conductivity of diPDI from 4.7×10^{-12} S/cm to 7.6×10^{-8} S/cm and the PCE was improved to 10 %.^[63]

Modified PDI with dipentyl chains was introduced as an ETL in p-i-n PSC by Chu and Wang et al. Although the Voc of PDI-based devices was 0.06 V lower than that of the PCBM-based device, the efficiency of the PDI-based devices showed a higher value than the PCBM-based devices, because the planarity and high smoothness of PDI layers allow good contact between PDI as ETL and electrode. In addition, the planarity of PDI facilitated electron transport, which is helpful to achieve the higher values of Jsc and FF comparing to PCBM. However, the Voc of PDI-based devices is lower than that of PCBM-based devices, which might be ascribed to the small grain boundaries of the perovskite layers. Moreover, the relationship between Voc and the intensity of light confirmed that the perovskite/PDI interface has less trap-assisted recombination than perovskite/PCBM interface. Such factors suggested that PDI is a potential replacement of PCBM as ETLs in PSCs.^[64]

Chen et al. also synthesized another three different PDI-based molecules (X-PDI, where X is H, F or Br). These molecules have been employed as ETLs in p-i-n PSCs and their performance have been compared with PCBM. Although F-PDI layer has well-matched LUMO and HOMO with the conduction band and valence band of perovskite layer, respectively, F-PDI-based perovskite solar cell didn't show any photovoltaic performance. The strong interactions (π - π , F- π and F-F) in F-PDI film might cause strong aggregation, which resulted in an inhomogeneous and incomplete film of F-PDI layer on perovskite layer, leading to the declined shunt resistance and the deteriorated photovoltaic performance. Moreover, the conductivity and electron mobility of F-PDI were the lowest among other X-PDI ETLs. The investigation on steady-state PL of H-PDI, Br-PDI and PCBM showed blue shift from 781 nm to 774 nm to 773 nm, respectively, which explained

the passivation ability of Br-PDI to the trap centers of perovskite layer as depicted in **Figure 2.5 (a)**. After applying ZnO nanoparticle as a cathode buffer layer (CBL) ^[65,66] on different ETLs, the PCE of F-PDI-based device didn't show any performance, while the PCEs of the devices based on H-PDI, Br-PDI and PCBM were comprehensively increased from the original 1%, 3.23% and 4.13% to 7.78%, 10.5% and 11.07%, respectively. These enhancements were attributed to ZnO nanoparticles, which declined direct contact between ETLs and cathode, leading to the increased shunt resistance and the enhanced photovoltaic parameters. ^[67]

PDIN as an alcohol soluble non fullerene acceptor has been used as an ETL in n-i-p PSCs with a high PCE (17.66%), because PDIN has amino as terminal group, which could decrease the work function of the cathode as well as the energy barrier. Moreover, PDIN can also passivate trap centers on the surface of perovskite layer. Therefore, Meng and Yang et al. tried to apply PDIN as ETLs in PSCs, however, they had to address the erosion issue of perovskite layer, which could be occurred in case of using conventional alcohol such as methanol or ethanol or the toxicity by using chlorocarbon as solvents. By introducing a green orthogonal solvent (2,2,2-trifluoroethanol) ^[68] they found that the highest PCE could reach 15.28%, which further suggests the possibility of using a green orthogonal solvent for ETL in p-i-n PSCs. ^[69]

Figure 2.5 a) Steady-state PL of PDI-X/ perovskite bilayer and PCBM/ perovskite bilayer, reproduced with permission. ^[67] b) steady-state and TRPL of perovskite/PCBM and perovskite TPE-PDI₄ bilayers, c) AFM images of perovskite layer, PCBM on perovskite layer and TPE-PDI₄ on perovskite layer. Reproduced with permission. ^[74]

Cheng and Sun et al. prepared two different PDI dimers for application in ETLs (3, 30-(9H-fluorene-9,9-diyl)bis(N,N-dimethylpropan-1-amine) (FA) and 3,30-(9H-fluorene-9,9-diyl) bis(N-ethyl-N,N-dimethylpropan-1-aminium) bromide (FA²⁺)). The main difference between two molecules is the end of alky chains, where FA-PDI2 has a terminal amine group while FA²⁺-PDI2 molecule ends with tertiary ammonium group, balanced by counter ions Br⁻. Note that Br⁻ as a counter ion didn't have any influence on the optoelectronic properties of FA²⁺-PDI2. Furthermore, FA²⁺-PDI2 showed an electron mobility similar to that of PCBM but higher than that of FA-PDI2. In addition to its higher mobility and conductivity, FA²⁺-PDI2 also exhibited higher suitability toward electron extraction from perovskite layer than FA-PDI2, which was confirmed by steady-state PL. Such results and properties resulted in a decent PCE, where the PCE of FA²⁺-PDI2-based devices could

reach 17.1 %, which is higher than that of FA-PDI2-based device (13.5%) and slightly less than that of PCBM-based devices (17.5%). The FA²⁺-PDI2-based devices retained about 80 % of its initial efficiency after 15 days in air, dark and humidity (less than 20 %), which are higher than those of PCBM-based devices and FA-PDI2-based devices. This high stability was attributed to the high hydrophobicity of FA²⁺-PDI2, confirmed by the contact angle measurements. [70]

For the first time, Nuckolls and Echegoyen et al. introduced graphene nanoribbons as ETLs in p-i-n PSCs. Two graphene nanoribbons hPDI2-Pyr-hPDI2 and hPDI3-Pyr-hPDI3 were synthesized for ETLs. The well-matched LUMO and HOMO of hPDI3-Pyr-hPDI3 with the conduction and valence band of perovskite layer, as well as its high mobility and high light absorption gave the PCE of as-fabricated devices up to 16.5%, which was higher than that of the devices based on hPDI2-Pyr-hPDI2 (15.6%) and PCBM (14.9%). [71]

It is well known that PDI-based molecules suffer from self-aggregation, which hinders electron transport properties. Sun et al. tried to overcome this issue by designing and synthesizing a 3D twisted PDI-based molecule. Their novel molecule was termed as SFX-PDI4, where spiro[fluorene-9,9'-xanthene] (SFX) building blocks were connected to four PDI-molecules. PCBM-based devices exhibited a higher PCE (16.9 %) than SFX-PDI4-based device (15.3%). To further understand the reason behind these results, energy levels, electron mobility, PL quenching, and the surface roughness of ETLs were investigated on each material. The LUMO and HOMO of SFX-PDI4 are similar to those of PCBM, while the electron mobility of SFX-PDI4 was slightly smaller than that of PCBM, but in the same order of magnitude. The PL quenching study of SFX-PDI4 gave a slightly lower value than PCBM layer, even PCBM has a poor roughness than that of SFX-PDI4 layer. Although SFX-PDI4-based devices showed lower PCE than PCBM-based devices, SFX-PDI4-based ETL was still considered as a potential and novel ETL in p-i-n PSCs. [72]

Hsu, Wong and Chu et al. synthesized different PDI-based molecules and employed them as ETLs to replace PCBM in p-i-n PSCs. The as-synthesized molecules were benzo[ghi]perylene triimide (BPTI) derivative and twisted dimer benzo[ghi]perylene triimide (t-BPTI) derivative. Although the PCEs of (BPTI)-based

devices and (t-BPTI)–based devices were less than those of PCBM-based devices, the blend of two as-synthesized molecules as ETL in p-i-n PSCs could reduce the hysteresis effect of PSCs. ^[73]

Due to its decent performance as a non-fullerene acceptor in polymer solar cells, it is reasonable to employ TPE-PDI4 (tetraphenylethylene core connecting to four PDI-molecules) as ETL in p-i-n PSCs. More importantly, its LUMO and HOMO are similar to those of PCBM, and it exhibited decent electron mobility of $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to that of PCBM ($2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Steady-state PL has been conducted to confirm the equal ability of TPE-PDI4 and PCBM toward PL quenching. However, TRPL showed that the lifetime of the electron from the perovskite layer to TPE-PDI4 was shorter than that from the perovskite to PCBM as shown in **Figure 2.5 (b)**. Therefore, this result suggested that the electron extraction ability of TPE-PDI4 was higher than that of PCBM. In addition, the investigation on surface morphology of TPE-PDI4/perovskite bilayer and PCBM/perovskite bilayer indicated that the roughness of TPE-PDI4/perovskite bilayer was lower than PCBM/perovskite bilayer as shown in **Figure 2.5 (c)**. Such merits resulted in efficient TPE-PDI4 in p-i-n PSCs. TPE-PDI4-based devices showed a higher PCE than that of PCBM-based devices. In addition, TPE-PDI4 gave a high performance as interfacial layer for C60 as ETL in the structure ITO/P3CT-Na/Perovskite/TPE-PDI4/C60/BCP/Ag, suggesting that TPE-PDI4 facilitated the electron transporting from perovskite to C60, which reflected on all photovoltaic parameters of fabricated solar cell and PCE enhanced from 16.56 % to 18.78%. ^[74] All chemical structures of PDI-based ETLs, which presented in this section, are shown in Figure 2.6. In addition, the photovoltaic parameters of PDI-based PSCs are presented in **Table 2.1**.

Figure 2.6 Chemical structures of PDIs, which are discussed in this chapter.

Table 2.1 Photovoltaic parameters of PDI-based PSCs

PDI-based ETLs	Jsc (mA/cm ²)	Voc (V)	FF %	PCE %	Mobility (cm ² /V.s)	Ref.
diPDI	17.2	0.8	51	7.1	-----	63
Doped-diPDI	21.6	0.86	54	10	-----	63
PDI	19.3	0.93	61.48	11.04	1.2×10 ⁻⁴	64
H-PDI	6.65	0.64	15.4	0.66	1.12×10 ⁻⁴	67
ZnO doped HPDI	7.78	0.73	59.9	7.78	4.57X10 ⁻⁴	67
Br-PDI	14.64	0.75	29.5	3.23	1.08x10 ⁻³	67
ZnO doped Br-PDI	18.90	0.83	66.9	10.50	1.84 X10 ⁻²	67
PDIN	20.34	1.03	73.31	15.28	-----	69
FA-PDI2	20.5	1.03	63.8	13.5	8.93X10 ⁻⁵	70
FA ²⁺ -PDI2	21.3	1.08	74.5	17.1	1.12X 10 ⁻⁴	70
hPDI2-Pyr-hPDI2	21.17	0.93	79	15.6	10 ⁻⁴	71
hPDI3-Pyr-hPDI3	22.68	0.93	78	16.5	10 ⁻⁴	71
SFX-PDI4	19.9	1.08	71.4	15.3	1.80X10 ⁻⁴	72
BPTI	16.97	0.87	63.66	9.29	3.19x10 ⁻²	73
t-BPTI	19.80	0.97	60.55	11.63	2.67x10 ⁻²	73
TPE-PDI ₄	21.68	1.013	74	16.29	1x 10 ⁻³	74

2.2.1.2 Naphthalene diimides as ETLs in inverted PSCs.

Because of its low price, ease of synthesis, high solubility in different organic solvents, and commercial availability, Naphthalene diimide (NDI) has been widely used as an efficient building block in organic synthesis community. NDI-based materials can be synthesized in short steps with high yields and have been demonstrated to show high electron mobility and thermal stability. ^[75-77] So far, only a few papers about NDI-based molecules as ETLs in p-i-n PSCs were reported. The first NDI-based ETL (NDI-PM) in p-i-n PSCs was introduced by Kwon and Im et al. ^[78] NDI-PM was distinguished by its high mobility of 0.72 cm²/V.s and good conductivity of 0.0150 mS/cm (PCBM: 0.0164 mS/cm). To investigate NDI-PM as an efficient ETL, the average lifetime of electrons in NDI-PM/MAPbI₃ bilayer and PCBM/MAPbI₃ bilayer were investigated. TRPL showed that the average lifetimes of electrons in PCBM/MAPbI₃ bilayer and NDI-PM/MAPbI₃ bilayer were 2.42 ns and 4.18 ns, respectively. By employing a structure of

glass/ITO/PEDOT:PSS/MAPbI₃/NDI-PM/Al, NDI-PM-based devices showed a high PCE (18.4%), while under the same condition, the PCE of PCBM-based devices could reach 18.9%. To confirm the universality of NDI-PM as an ETL in p-i-n PSCs, the devices containing NDI-PM with different perovskite composition (glass/ITO/PEDOT:PSS/FAPbI_{3-x}Br_x/NDI-PM/Al) have been fabricated and the results were in agreement with the previous case. The PCEs were increased to 19.6% for NDI-PM and 20% for PCBM. Although the PCE of NDI-PM was slightly lower than that of PCBM-based devices, NDI-PM provided the devices with higher stability than that of PCBM. [78] Few month later, the same group designed and synthesized a new ETL material, which has a slightly different structure from the previously mentioned NDI-PM. They replaced the terminal groups phenyl methyl with 1-indanyl and the new molecule is termed as NDI-ID. NDI-ID-based devices showed a PCE of 20.2%, which is higher than that of NDI-PM-based devices (19.6%) and PCBM-based devices (20%). This enhancement was attributed to the superior electron transport property of NDI-ID. Additionally, NDI-ID was designed containing alicyclic and aromatic groups without the flexible alkyl chain to overcome the phase transition of this material. Moreover, the alicyclic group can increase the solubility, which is helpful to the solution processing. [79] When replacing 1-inadanyl with 1-phenylethyl, a new compound was obtained as NDI-PhE. This novel material could form a good film with 3D isotropic electron transport properties, which can explain the reason of the high PCE of NDI-PhE-based PSCs (20.5 %). [80]

Gao et al also prepared two NDI-based molecules for ETLs: coplanar NDI3HU-DTYM2 and twisted (DTYM-NDI-DTYA)2. (DTYM-NDI-DTYA)2-based devices can yield a decent PCE due to the good electron mobility (0.45 cm²/V.s) and well-matched LUMO of (DTYM-NDI-DTYA)2 with the conduction band of the perovskite layer. Although a PCE of (DTYM-NDI-DTYA)2-based device is smaller than that of PCBM-based device (14.3%), (DTYM-NDI-DTYA)2 was still considered as a promising candidate for potential ETL. [81]

Our group also focused on developing new NDI-based ETLs. Two NDI-based compounds (PDPT and PMDPT) have been synthesized and demonstrated as ETLs in p-i-n PSCs with the structure of ITO/PEDOT:PSS/CH₃NH₃PbI_{3-x}Cl_x/ETL/Ag. PMDPT-based devices

achieved higher PCEs than PDPT-based devices. This higher performance might be attributed to the excess number of nitrogen atoms in PMDPT-based ETLs, which could passivate the electron trap centers in perovskite surface. Note that due to the low mismatch of LUMO and HOMO of two ETLs with the conduction band and valence band of the perovskite layer, respectively, both PCEs of PDPT and PMDPT-based devices exhibited poor efficiency.^[82] Benefiting from the passivation nature of sulfur atoms, the under-coordinated Pb-atoms on the perovskite surface can be passivated. Based on these results, two new ETLs based on NDI-small molecules (DS1 and DS2) have been prepared, where DS1 molecules contain one NDI and one thiophene group while DS2 possesses one NDI and two thiophene groups. DS2-based devices showed a decent PCE (11.4 %) compared with PCBM-based devices (13.5 %) and DS1-based devices (9.6 %).^[83] The chemical structures of NDI-based compounds for ETLs are shown in **Figure 2.7**. The photovoltaic parameters of NDI-based PSCs are presented in **Table 2.2**

Figure 2.7 Chemical structures of NDIs, which are discussed in this chapter.

Table 2.2 Photovoltaic parameters of NDI-based PSCs

NDI-based ETLs	J _{sc} (mA/cm ²)	V _{oc} (V)	FF %	PCE %	Mobility (cm ² /V.s)	Ref.
NDI-PM/MAPbI ₃	21.1	1.1	79.1	18.4	0.72	78
NDI-PM/MAPbI ₃ - _x Br _x	22.8	1.08	79.6	19.6	0.72	78
NDI-ID	23.0	1.1	80	20.2	1.5X10 ⁻⁵	79
NDI-PhE	23.1	1.1	80.8	20.5	1.5X10 ⁻⁵	80
NDI3HU-DTYM2	18.56	0.96	48.85	8.7	7.50×10 ⁻⁴	81
(DTYM-NDI- DTYA)2	22.80	0.9	62.86	12.9	6.26×10 ⁻³	81
PDPT	22.9	0.76	44	7.6	-----	82
PMDPT	22.4	0.84	49	9.2	-----	82
DS1	23.41	0.74	55.4	9.6	-----	83
DS2	22.65	0.8	63	11.4	-----	83

2.2.1.3 Azaacenes as ETLs in inverted PSCs.

Our group is one of the pioneer groups in synthetically approaching azaacene-based derivatives. ^[84-95] It is believed that azaacenes possess high electron mobility and have a lot of applications in organic electronics. ^[84-95] this knowledge makes researchers believed that azaacenes should be an excellent replacement of PCBM as ETLs in p-i-n PCSs. Employing a new azaacene derivative (QCAPZ), whose LUMO of QCAPZ was -3.7 eV slightly higher than the conduction band of the perovskite layer, a decent efficiency (10.26 %) was obtained. ^[96] After recognizing the importance of sulfur-Pb interaction as well as sulfur's passivation of surface trap of perovskite layer, another new azaacene-based derivative (HATNT) with the mobility of 1.73x10⁻² cm/V.s has been synthesized. Due to well-matched LUMO and HOMO with conduction band and valence band of the perovskite layer, respectively, the PCE of the devices based on HATNT as ETL has reached 18.2 % without hysteresis. ^[97] Continuing on this research, another new azaacene-based derivative (TDTP) was designed, synthesized and implemented as an ETL in PSCs by the author's group. Due to its high mobility as well as well-matched energy levels with the bands of

perovskite layer, PCE up to 18.2% was obtained, which is higher than that of the device based on PCBM. Inspired by these results, the author's group also prepared several new azaacenes as ETLs to enhance the efficiency of PSCs. ^[98] Hexaazatrinaphthalene derivatives can be used as ETLs, due to the low cost of their synthesis, high mobility and large band gap. ^[98-102]

Jen et al. also focused on N-doped polycyclic aromatic compound HATNA-F6 ^[103-104] for ETLs. When they replaced three F atoms in HATNA-F6 with alkylsulfonyl chains, they found that both the solubility of the as-prepared compound and the ability of the devices based on the new compound to passivate trap centers on perovskite layer were increased. Later, Jen et al modified HATNAs with different alkylsulfonyl groups to form different compounds (e.g. HATNAS3C4, HATNAS3C7, HATNAS3C7-C3h, HATNAS3C7-Cs, HATNASOC7-Cs and HATNASO2C7-Cst) for controlling the energy level of ETLs in p-i-n PSC with the structure of ITO/NiOx(30 nm)/MAPbI₃(350 nm)/ETLs (80 nm)/Ag. It was found that PCE can be improved from 4.69 % for HATNA-F6 to 17.62% for HATNASOC7-Cs, due to the increased solubility and the increased hole blocking ability of the as-prepared compound. Steady-state PL measurement showed that the ability of HATNASOC7-Cs to extract electron from perovskite layer was higher than PCBM as depicted in **Figure 2.8 (a)**. Moreover, TRPL measurements determined that the PL decay of HATNASOC7-Cs was shorter than that of PCBM as shown in **Figure 2.8 (b)**. More importantly, the device based on HATNASOC7-Cs can maintain about 80 % of its original PCE after 30 days, while PCBM-based devices can only keep about 30 % of its initial PCE within the same time as presented in **Figure 2.8 (c)**. Furthermore, contact angle measurement suggests that the high stability of HATNASOC7-Cs-based devices might come from its high contact angle (89.4 o), while the contact angle of PCBM was 70.8 o (**Figure 2.8 (d)**). ^[105] The chemical structure of azaacenes as ETLs, which presented in this section, are shown in **Figure 2.9** and the photovoltaic parameters of azaacene-based PSCs are provided in **Table 2.3**.

Figure 2.8 a) Steady-state PL of perovskite layer, PCBM/perovskite bilayer and HATNASOC7Cs/perovskite bilayer, b) TRPL. of perovskite layer, PCBM/perovskite bilayer and HATNASOC7Cs/perovskite bilayer, c) stability of PCBM-based devices and stability of HATNASOC7Cs-based devices with time, d) contact angle of PCBM and HATNASOC7Cs. ^[105]

Figure 2.9 Chemical structures of azaacenes, which are discussed in this review.

Table 2.3 Photovoltaic parameters of azaacene-based PSCs

Azaacene –based ETLs	J _{sc} (mA/cm ²)	V _{oc} (V)	FF %	PCE %	Mobility cm ² /(V.s)	Ref.
QCAPZ	16.55	0.86	72.1	10.26	4.7X10 ⁻⁴	96
HATNT	21.83	1.07	77.8	18.1	1.73X10 ⁻²	97
TDTP	22.4	1.05	77.7	18.2	4.6X10 ⁻³	98
HATNAS3C4	16.81	0.95	72.8	11.59	0.83X10 ⁻³	105
HATNAS3C7	18.28	0.95	76.1	13.49	1.45X10 ⁻³	105
HATNAS3C7-C3h	18.31	0.96	76.3	13.38	1.58X10 ⁻³	105
HATNAS3C7-Cs	19.69	0.94	75.8	13.95	1.36X10 ⁻³	105
HATNASOC7-Cs	20.73	1.08	78.6	17.62	5.13X10 ⁻³	105
HATNASO2C7-Cs	19.44	1.00	74.2	14.42	2.34X10 ⁻³	105

2.2.1.4 Crosslinked azaacenes as ETLs in inverted PSCs

To address the effect from water, oxygen or heat on the stability of p-i-n PSCs, Jen et al. designed and synthesized novel crosslinked ETLs (c-HATNA) as shown in **Figure 2.10** (a) through three steps: 1) preparing hydrophobic hexaazatrinaphthylene (HATNA); 2) Crosslinking HATNA (c-HATNA) together to improve its photo and thermal stability by low-temperature initiator PETMP; 3) Doping crosslinked HATNA with Et₃N to further enhance its mobility. The c-HATNA showed higher hydrophobicity than that of PCBM layer, which was confirmed by the contact angle measurements (c-HATNA: 96° and PCBM: 68°, **Figure 2.10** (b)). This higher contact angle was ascribed to the embedded alkyl thiol co-crosslinking group. To investigate the waterproof reliability of c-HATNA, c-HATNA film was treated under harsh condition. The color of droplet water on the sandwiched perovskite with c-HATNA didn't change after 5 minutes, while in PCBM-based device, the color changed in 5s as depicted in **Figure 2.10** (c). The efficiency of c-HATNA-based device was 11.97 % with a VOC of 1.05 V, a JSC of 16.79 mA/cm², and a FF of 67.9%. The low PCE might come from the low electron mobility of c-HATNA

($6.92 \times 10^{-5} \text{ cm}^2/\text{V.s}$). After the addition of 3% Et_3N , the mobility was enhanced to $1.14 \times 10^{-3} \text{ cm}^2/\text{V.s}$, leading to the enhancement in PCE (18.2%).^[106]

Figure 2.10 a) Structure of c-HATNA, b) contact angle of PCBM and HATNA, c) photograph of PCBM-based device (left) and c-HATNA-based device (right) after exposure to water.^[106]

2.2.1.5 Other organic small molecules as ETLs in inverted PSCs.

Yang et al. prepared two novel π -conjugated small molecules containing indacenodithiophene as cores with different substituted groups (the molecule with

substituted thiophenes called as ITCPTC-Th, while with substituted selenophenes termed as ITCPTC-Se) as shown in **Figure 2.11**. Both materials have been employed as ETLs in p-i-n PSCs. They found that ITCPTC-Th layer has a higher electron extraction property, a smoother surface, and a higher electron mobility comparing with ITCPTC-Se. These results led to a high PCE (17.11 %) in ITCPTC-Th-based device while 16.12 % for ITCPTC-Se-based PSCs.^[107] other molecules such as ITCPTC,^[108] hexadecafluorophthalocyaninatocopper (F16CuPc),^[109] benzobis (thiadiazole)-based^[110] and triphenyl amine-based derivatives (TPA3CN)^[111] were also used as ETLs in p-i-n PSCs, exhibiting PCEs ranged from 12 % to 19 %.

Figure 2.11. Chemical structures of ITCPTC, ITCPTC-Se and ITCPTC-Th.

2.2.2 N-type conjugated polymers as ETLs in inverted PSCs.

Uneven surface and poor morphology control of organic small molecules, as well as the crack formation encouraged scientists to find new candidates as ETLs to address this issue. A lot of researches were carried out to develop n-type conjugated polymer-based ETLs. Wang and Ma et al. published the first paper to demonstrate that different polymers could be used as ETLs in p-i-n PSCs,^[112] where polymer N2200 was first introduced as an ETL in p-i-n PSCs. Although N2200 has a high mobility and well-matched LUMO and HOMO with valence band and conduction band of the perovskite layer, the as-obtained PCE was quite low (8.78%). Other polymers such as PVNT-8 and PNDI2OD-TT were also

investigated as ETLs in p-i-n PSCs to check the universality of this method, and PCE could only reach 7.74% and 6.47%, respectively. ^[112]

Yip and Huang et al. designed and synthesized different conjugated polymers using NDI and fluorene as the main building blocks in all polymers. The main difference between polymers P1, P2, P3 and P4 is the pendant groups that were attached onto fluorene. These pendant groups were dimethylamino, N-methylbenzylamino, dibenzylamino, and pure alkyl chains for P1, P2, P3 and P4, respectively. P4-based ETL showed a higher performance compared with other polymers. Obviously, the electron-donating properties decreased as the steric hindrance of amine groups increased. The effect of each polymer on the work function of Ag electrode was studied. The work function of Ag decreased from -4.66 eV to -4.00, -4.13, -4.24 and -4.36 eV for P1, P2, P3 and P4, respectively. These results confirmed that all the polymers have some effect on the work function of Ag. Slight variation on the Voc of devices on the basis of each polymer confirmed that the work function of Ag wasn't the main reason for the deterioration of the PCE in the case of P2, P3 and P4. The passivation power of each polymer was also investigated by steady-state and TRPL. The PL peak of perovskite was detected at 776 nm. However, when the polymers attached onto the surface of perovskite, it can cause the PL of perovskite shift. The highest blue shift was observed by P1, which indicated that P1 has a higher passivation power than P2 and P3. However, P4 didn't show any shift. All results exhibited by TRPL are in agreement with the efficiencies of each polymer-based devices. ^[113]

Loi et al. prepared three different n-type conjugated polymers with NDI and bisthiophene as building blocks, termed as P(NDI2OD-T2), P(NDI2DT-T2) and P(NDI2OD-TET). The LUMO and HOMO of P(NDI2OD-T2) and P(NDI2DT-T2) are almost similar to each other. However, the ethyl group in backbone of P(NDI2OD-TET) reduced the conjugation and increased the band gap slightly. The PCEs of P(NDI2OD-T2), P(NDI2DT-T2), P(NDI2OD-TET)- based devices were 10.82 %, 10.83 % and 0.18%. It is worthy to point that, the LUMO and HOMO of P(NDI2OD-TET) were not responsible to the poor PCE, because these two energy levels still matched with the conduction and valence band of the perovskite layer. The investigation on bimolecular recombination revealed that P(NDI2OD-TET)-based devices suffered from this type of recombination. Also, the series

resistance in P(NDI2OD-TET)-based devices was very high ($3411 \Omega/\text{cm}^2$, in contrast with P(NDI2OD-T2, $7.8 \Omega/\text{cm}^2$) and PNDI2DT-T2 ($9.2 \Omega/\text{cm}^2$)-based devices. Therefore, the reason for poor PCE of P(NDI2OD-TET)-based device was the low electron mobility ($1 \times 10^{-8} \text{ cm}^2/\text{V.s}$).^[114] F8BT, combining with C60, was also used as an ETL in p-i-n PSCs.^[115] A decent PCE of 13.9 % was achieved by F8BT-C60-based devices. This PCE could be further increased to 15.9 % by using F8BT:PCBM mixture as an ETL. Notably, F8BT has a significant effect on reducing the hysteresis.^[115]

Hayat and Tan et al. conducted a research on exploring the origin of the effectiveness of polymer-based ETL. These polymers contained a PDI-building block and different conjugated units such as vinylene (V), thiophene (T), selenophene (Se), dibenzosilole (DBS), and cyclopenta[1,2-b:5,4-b']dithiophene (CPDT). The electron mobility and energy offset between LUMO and the conduction band of each polymer and perovskite layer, as well as the surface morphology were investigated by different technique.^[116]

Naphthodiperylenetetraimide-vinylene-based polymer (NDP-V) was also implemented in p-i-n PSCs as an ETL. The LUMO and HOMO of NDP-V have the same value of such levels of PCBM. The planar structure and pi-conjugation system of NDP-V enhanced the packing of molecules, then improved the electron transport. Because the electron mobility of NDP-V ($2.5 \times 10^{-3} \text{ cm}^2/\text{V.s}$) was higher than that of PCBM ($2 \times 10^{-3} \text{ cm}^2/\text{V.s}$), the PCE of NDP-V based devices (16.54%) was higher than that of the PCBM-based device (15.27%).^[117]

Our group also employed three n-type (D–A1–D–A2) conjugated polymers (pBTT, pBTTz, and pSNT) as ETLs because these polymers exhibited high mobility values (0.92, 0.46, and $4.87 \text{ cm}^2/(\text{Vs})$, respectively) compared with PCBM. To be highlighted, for the first time, the effect of sp²-N position on polymer properties as ETLs in p-i-n PSCs was investigated. The pBTTz-based devices gave the highest PCE (14.4 %) while pSNT-based devices displayed the lowest PCE (12%). The contact angle measurement confirmed that pBTTz (108.6 °C) has the highest hydrophobicity, which can explain the higher stability of pBTTz-based devices than PCBM-based devices.^[118] Recently, p-i-n PSCs based on P(NDI2DT-TTCN)) as ETLs has been reported to exhibit a decent PCE (17 %).^[119]

Note that the performance of n-type conjugated polymer (ETL)-based perovskite can be enhanced by doping. For example, PCE of N-2200-based device (15.02 %) can be improved to 16.84 % after N-2200 was doped with PFN-Ox ^[120]. In another case, the PCE of PNDI-2T-based devices (6.5%) was enhanced after doping with N-DMBI. ^[121] The chemical structures of polymer-based ETLs, which presented in this section, are shown in **Figure 2.12**. The photovoltaic parameters of polymer-based PSCs are provided in **Table 2.4**.

Figure 2.12 Chemical structures of n-type conjugated polymers, which are discussed in this chapter.

Table 2.4. Photovoltaic parameters of n-type conjugated polymer-based PSCs.

Polymer-based ETLs	J _{sc} (mA/cm ²)	V _{oc} (V)	FF %	PCE %	Mobility cm ² /(V.s)	Ref.
P1	21.5	0.94	75	15.2	2.98×10^{-4}	113
P2	20.6	0.94	60	11.5	7.1×10^{-5}	113
P3	19.5	0.93	45	7.7	2.5×10^{-5}	113
P4	9.6	0.86	28	1.5	9.8×10^{-5}	113
P(NDI2OD-T2)	16.90	0.884	73	10.82	2.3×10^{-4}	114
P(NDI2DT-T2)	17.10	0.899	71	10.83	1.2×10^{-5}	114
P(NDI2OD-TET)	1.41	0.715	17.5	0.18	1×10^{-8}	114
F8BT/C60	22.40	0.971	63.8	13.9	-----	115
PV-PDI	16.6	0.931	65.6	10.14	2.3×10^{-3}	116
PT-PDI	14.7	0.898	47.4	6.24	8.9×10^{-4}	116
PSe-PDI	14.0	0.901	42.6	5.37	7.4×10^{-4}	116
PDBS-PDI	19.0	0.894	33.8	5.73	8.8×10^{-4}	116
PCPDT-PDI	6.62	0.921	31.3	1.91	2.8×10^{-5}	116
NDP-V	21.41	1.043	74	16.54	2.5×10^{-3}	117
pBTT	22.5	0.88	64.4	12.8	0.92	118
pBTTz	21.95	0.91	72.3	14.4	0.46	118
pSNT	20.5	0.88	66.5	12	4.87	118
P(NDI2DT-TTCN))	22.0	1.00	77.4	17.0	7.71×10^{-4}	119
N2200	19.3	1.06	73.4	15.02	6.9×10^{-4}	120
PFN-Ox-doped N2200	20.5	1.09	75.4	16.84	8.2×10^{-4}	120

2.3 Lead- Free perovskite solar cells

2.3.1 Tin based- perovskite

It is considered as the most investigated for lead replacement in perovskite solar cell. While both have lone-pair s orbital. ^[122, 123] Kagan et. al. demonstrated the first high charge carriers tin-based field effect transistor. ^[124] Sn-based perovskite has excellent optoelectronic properties, such as high carrier mobilities 10^2 - 10^3 $\text{cm}^2/\text{V.s}$ which presented by Stoumpos et.al. ^[125] Wu et. al. demonstrated that, the high-quality single crystal ingot of CsSnI_3 has diffusion length up to 1 micro meter with bulk carrier lifetimes approaching 6.6 ns. ^[126] Sn-based perovskite has narrow (1.2-1.4 eV) direct band gap. The preparation method determines the value of band gap. ^[125]

2.3.1.1 Methylammonium tin halides (MASnX_3 , $\text{X}=\text{Cl, Br, I}$)

Kanatidis et.al. and Snaith et. al. demonstrated $\text{MASnI}_{3-x}\text{Br}_x$ as an absorbing material in photovoltaic application. Then their research were followed by a lot of reports via changing solvents to approach the highest efficiency of Sn-based perovskite solar cells. Kanatzidis et. al tuned the band gap of $\text{MASnI}_{3-x}\text{Br}_x$ -based perovskite solar cell between 1.3 to 2.15 eV by changing the ratio of I/Br. While stoichiometric ratio of MAI and SnX ($\text{X}=\text{Br, I}$) were mixed together, the as-resulted materials can be dissolved in DMF. The color of as-prepared material varied between dark brown to transparent yellow ^[127]. Snaith can push V_{oc} of Sn-based perovskite solar cell up to 0.88 with V_{oc} loss 0.35 eV, regarding that the band gap of fabricated absorber was 1.23 eV. ^[128]

Kanatidis et. al. fabricated pin-hole- free ultra-smooth Sn-based perovskite film by using DMSO as a solvent instead of DMF. The $\text{SnI}_3 \cdot 3\text{DMSO}$ intermediate, which was confirmed by XRD and FTIR, has a crucial rule for achieving homogeneous nucleation and optimum growth rate. N-methyl-2-pyrrolidone (NMP) as solvent exhibited intermediate stable phase during thin film fabrication. ^[129] Less toxic mixture of methanol and 1, 4 dioxane were employed by Greul et al. as a solvent for MASnI_3 and $\text{MASnBr}_x\text{I}_{3-x}$. The resultant film were dense and homogenous due to the coordination between dioxane and Sn^{2+} , The as-

prepared film showed the longer lifetime of charge carrier than that fabricated with DMF and DMSO. This was attributed to lower defects density. All these results reflected on the PCE, which approaching 1.05 % higher than that fabricated by DMF (PCE= 0.04 %) and DMSO (PCE= 0.01 %).^[130] Sn-based perovskites showed easily oxidation of Sn^{2+} to Sn^{4+} , which is considered as p-type dopant^[131] and deteriorates the performance of Sn-based solar cell. Kanatzidis et. al fabricated lower defect Sn-based perovskite film by exploring the fabricated film to hydrazine vapor (as reducing agent).^[132] PCE of Sn-based perovskite solar cells with the treatment of hydrazine vapor was significantly enhanced to 3.89 % while Sn-based PSCs without the treatment of hydrazine vapor only exhibited poor PCE (0.02%). Addition of SnF_2 into MASnI_3 can suppress the oxidation of Sn^{2+} to Sn^{4+} . 20 mol % of SnF_2 in MASnI_3 decreased the concentration of doped holes by two order of magnitude.^[133]

2.3.1.2 Formamidinium tin halides (FASnX_3)

Formamidinium iodide was utilized as an organic cation for the first time in tin-based system by Koh et al. in 2015. Optimized fabrication of FASnI_3 with 20 mol % of SnF_2 showed PCE= 2.10 %.^[134] Gu et al. replaced SnF_2 with Sn powder in FASnI_3 to suppress the oxidation of Sn^{2+} to Sn^{4+} . By optimizing fabrication parameters, annealing time reaction time, the annealing temperature, as well as the tuning of the composition of the FASnI_3 films, a PCE was achieved to 6.75%^[135] Lee et. al. developed new fabrication method by the addition of a SnF_2 -pyrazine complex into DMF and DMSO. During the fabrication, toluene was dripped as antisolvent. After the characterization by X-ray photoelectron spectroscopy (XPS), it was found that pyrazine has a crucial role to decrease the amount of Sn^{4+} by 5-14 % in different depth, comparing with film, which was fabricated by same method without pyrazine. Optimization of the device fabrication led to a PCE as high as 4.8%.^[136] Liao et. al. demonstrated an effective method by the addition of SnF_2 and diethyl ether as antisolvent. This method led to a uniform, high quality and fully covered film. These properties can push PCE up to 6.22%.^[137] The first flexible solar cell based on FASnI_3 was fabricated on a polyethylene naphthalate-ITO flexible substrate by Xi et al, while the FASnI_3 film was deposited by novel multichannel interdiffusion protocol, which

involved annealing the stacked layers composed of an initial water-based spin-coated FAI/PEDOT: PSS, followed by an evaporated SnI_2 film. High coverage, homogeneous FASnI_3 films could be easily obtained by controlling the PEDOT:PSS concentrations in FAI/PEDOT:PSS aqueous solutions. The dense tiny FAI crystals locally restrained by PEDOT:PSS could provide films with multichannel available for interdiffusion between layers to form FASnI_3 films. Flexible solar cells based on FASnI_3 perovskite achieved a PCE of 3.12%, with a V_{OC} of 0.31 V, a J_{SC} of 16.07 mA cm^{-2} and an FF of 62.6%. This launch of multichannel interdiffusion strategy for the fabrication of flexible PSCs announced the incipience of a new epoch of eco-friendly photovoltaic technique.^[138]

2.3.1.3 Cesium tin halides (CsSnX_3)

Initially, CsSnI_3 was known in photovoltaic as a HTL in DSSCs by Chung et. al.^[139] The configuration structure of this solid-state solar cell was CsSnI_3 , nano-porous TiO_2 and dye N719 as the light absorber. The achieved PCE was 3.72%. Interestingly, 5% fluorine doped $\text{CsSnI}_{2.95}\text{F}_{0.05}$ improved the photovoltaic parameters, since PCE = 9.28%.^[139] Chen et. al. in 2012 illustrated CsSnI_3 as an absorber material in Schottky solar cell with structure of ITO/ CsSnI_3 /Au/Ti, and the as-obtained PCE was 0.9 %.^[140] Then, CsSnI_3 was employed as an absorbing material in perovskite solar cell with configuration of FTO/ compact TiO_2 /mesoporous TiO_2 / CsSnI_3 /HTM/Au. This solar cell was fabricated at low temperature by mixing CsI, SnI_2 , and SnF_2 in appropriate solvents and cast by spin-coating, followed by the annealing at 70 °C. The achieved PCE was 2.02%^[141]. Hypophosphorous acid (HPA) was applied to decrease the Sn vacancies density. HPA has a function as an accelerator of the nucleation and reducing agent toward Sn^{4+} .^[142] The champion cell based on CsSnI_3 quantum rods showed PCE up to 12.96 %. The configuration of this cell was ITO/ TiO_2 / CsSnX_3 /spiro-OMeTAD/Au.^[143]

2.3.1.4 Tin halides with mixed cations

Benefitting of the reported work based on mixing monovalent organic cations in APbI_3 , this strategy was applied by Zhao et. al. on Sn-based PSC with the novel structure $\text{FA}_x\text{MA}_{1-x}\text{SnI}_3$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.00). The as-synthesized material exhibited band gap

reached to 1.26, 1.28, 1.3, 1.33 and 1.36 eV, respectively. The best performance (8.12 %) was achieved by the composition of $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$. This material showed decent stability, while it retained about 80 % of its initial performance after 400 hr. inside glove box. The achieved results were ascribed to the mixing of two cations, which improved the film morphology and reduced charge carrier recombination. ^[144] Lie et. al. examined the antisolvent effect on the performance of mixed cation tin based perovskite, by utilizing diethyl ether, toluene and chlorobenzene as antisolvents. The best PCE achieved was 9.06 % ^[145]. The reproducibility of the mixed cations based tin perovskite solar cell gave this novel structure with higher priority than FASnI_3 and MASnI_3 -based solar cells.

The expression of 3D-hollow structure, introduced for the first time by Kanatzidis et. al., was synthesized by incorporating small amount of ethylenediammonium (*en*) into ASnI_3 crystal. Because of the large size of *en*, the unit cell increased and SnI_2 vacancies created, which led to a larger band gap, longer lifetime and reduced trap states. The combination between this strategy and hydrazine vapor as an atmosphere for fabrication led to the best PCE of (*en*) MASnI_3 -based device was 6.63%. The device based on (*en*) FASnI_3 showed better PCE (7.14%) with good stability since the device retained its initial stability up to 6.37 % after 1000 hr. ^[146-148]

2.3.2 Germanium-based perovskites

Ge-based perovskite received many researchers' attention, due to its promising theoretical PCE. By using SLME mathematical model, the theoretical PCE of CsGeI_3 -based device can be as high as 27.9% ^[149]. The calculated theoretical band gap of Ge-based perovskites were 1.6 eV for CsGeI_3 , 1.9 eV for MAGeI_3 and 2.2 eV for FAGeI_3 . The calculated band gap indicated the suitability of Ge-based perovskite as absorbing materials in photovoltaic application. ^[150]

Regretfully, the experimental PCEs of CsGeI_3 and MAGeI_3 -based devices only have 0.11% and 0.20%, respectively. The poor PCEs were ascribed to the relatively poor film morphology, ^[151] Mixed anions strategy was applied as a trial to improve the performance

of Ge-based PSCs. However, the performance is still low, since $\text{MAGeI}_{2.7}\text{Br}_{0.3}$ -based PSC achieved PCE equaled to 0.57% ^[152].

2.3.3 Bismuth-based perovskites

The great attention was devoted to Bi-based PSCs due to its long-term stability. Moreover, the similar electronic structure and ionic radius of Pb^{2+} might lead to similar optoelectronic properties. $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{MA}_3\text{Bi}_2\text{I}_9$ were reported for the first time as an absorber material for photovoltaic application by Park et.al. However, two materials exhibited poor performance. In fact, the low PCEs of two different materials were ascribed to the possible phase impurities within the films and intrinsic properties of the materials. This intrinsic feature was explained by Pazoki et al., which included high effective mass of electrons and holes ^[153, 154]. To enhance the properties of Bi-based perovskite, Zhang et. al, employed new fabrication technique based on two steps. High vacuum deposition of BiI_3 , followed by low vacuum evaporation of MAI. Pin-hole free and large grain film of $\text{MA}_3\text{Bi}_2\text{I}_9$ was obtained and the achieved PCE of as-fabricated solar cell was 1.6 %. ^[155] Ran et. al. adopted the same previous method by evaporation BiI_3 and MAI deposited via spin coating technique. Although the as-fabricated film of $\text{MA}_3\text{Bi}_2\text{I}_9$ had pin-holes free with high quality, the highest PCE was only 0.39 % ^[156]. The effect of ETL on the Bi-based perovskite growth was investigated by utilizing three types of ETLs, planar, brookite, and anatase mesoporous TiO_2 . The best performance and more stable device was achieved by mesoporous TiO_2 -based PSC, since the Bi-based perovskite was grown uniformly on mesoporous TiO_2 . ^[157] By introducing Ag^+ instead of MA^+ or Cs^+ , 3D bismuth derivative AgBi_2I_7 was produced. Furthermore, other derivatives were produced such as AgBiI_4 , Ag_2BiI_5 , and Ag_3BiI_6 , which were proposed to be specified as the rudorffite structure (AaBbX_x ($x=a+3b$)) after Walter Rudorff ^[158-164]. AgBi_2I_7 -based solar cell showed amazing moisture and air stability with PCE equaled to 1.22 %. The device retained 92.6 % of its initial stability under ambient condition. ^[158] Ag_3BiI_6 -based devices showed higher performance (4.3 %) compared with AgBi_2I_7 ^[158]. The presence of BiI_3 in Ag_2BiI_5 plays an important role in charge separation in Ag_2BiI_5 . The pure Ag_2BiI_5 -based device showed PCE up to 1.74%. Interestingly, $\text{BiI}_3/\text{Ag}_2\text{BiI}_5$ -based device achieved PCE of 2.31 % ^[163-165]. AgBiI_4 has a suitable band gap

(1.64 eV), which is suitable for solar cell application. Solar cell based on AgBiI₄ showed PCE of 2.1 %. Also, the PCE was retained up to 96% of the initial value after 1000 h at relative humidity of 26%.^[164]

2.3.4 Antimony-based perovskites

Trivalent antimony-based perovskites exhibit the similar electronic properties of divalent Sn-based perovskite, due to the similar band structure. The typical formula of Sb-based perovskite is A₃Sb₂I₉. These perovskites have 0D octahedral anionic metal halide units (Sb₂I₉)³⁻, surrounded by three A cations and connected via a hydrogen-bonding interaction. Cs₃Sb₂I₉-based PSC was prepared by Saparov et al. However, the PCE was relatively low, less than 1 %. The low PCE was attributed to deep defects in band gap, which causes non-radiative recombination.^[166] The addition of HI enhanced the optical absorption by reducing the band gap of Cs₃Sb₂I₉ and MA₃Sb₂I₉. HI improved the phase purity and crystallinity. With the HI additive, PCE of MA₃Sb₂I₉-based device enhanced from 1.11% to 2.04%. Furthermore, PCE of Cs₃Sb₂I₉-based devices improved by 25%,^[167] and MA₃Bi₂I_{9-x}Cl_x- based PSC showed interesting PCE up to 2.19%, due to the enhancement of the film coverage^[168].

2.3.5 Metal halide double perovskites

As mentioned above, the typical structure of antimony and bismuth –based perovskites is A₃B₂X₉, which lacks three dimensionality and exhibits lower dimensional structure, which leads to higher band gap. Interestingly, 3D structure can be retained by the incorporation of monovalent cation B' (Ag⁺, Cu⁺) in B site. The new structure is named as double perovskite containing the structure formula A₂B'BX₆ with varied band gap which can be tuned for photovoltaic application^[169]. The first double perovskite-based PSC was demonstrated by Greul et al. The as-fabricated solar cell adopted the structure of FTO/compact TiO₂/mesoporous TiO₂/Cs₂BiAgBr₆/spiro-OMeTAD/Au. The achieved PCE was up to 2 % with the unprecentnted Voc up to 1.0 V, compared with other Bi-based perovskites as absorber materials.^[170] By adopting isopropanol as an anti-solvent, the as-

deposited film distinguished by micro-sized grains and high crystallinity, leading to the PCE up to 2.23%. ^[171] MA₂BiAgBr₆-based perovskites were synthesized and showed an indirect bandgap of 2.02 eV, good air and moisture stabilities, and a decomposition temperature higher than MAPbBr₃. ^[172] To the best of our knowledge, the first prepared hybrid tellurium based perovskite material for optoelectronic application was introduced by Ju et.al. Family of Te-based single crystals perovskite was synthesized including A₂TeX₆: A= MA (Methyl ammonium), FA (formamidinium) or BA (benzyl amine), X= Br or I. Surprisingly, MA₂TeI₆ and FA₂TeI₆ showed broad UV-vis absorption of about 843 and 871 nm, respectively. The synthesized single crystal MA₂TeBr₆ has band gap 2.00 eV with long carrier lifetime up to 6 μs, these features are ideal for photodetector and solar cells, these crystals shows decent stability without change for one month. ^[173] Cs₂TeI₆ thick film was fabricated as an active material for X-ray detector. The fabrication process depends on low temperature solution process electrospraying. The morphology of Cs₂TeI₆ thick film was enhanced by optimizing the growing parameters such as solvent, applied electric field. ^[174-175]

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Chapter 3

Experimental Methodology

The working principle of used characterization technique are included. In details, characterization of synthesized organic molecules (FT-IR, ^1H NMR, ^{13}C NMR, TGA and CV) for the confirming the purity, for investigating morphology (SEM and AFM), for crystallinity analysis (XRD), for optoelectronic properties (UV-vis, PL, TRPL spectroscopy), for photovoltaic parameters of solar cell (EQE, illuminated and dark I-V curves), for electrochemical properties of solar cell (EIS), and for wettability (contact angle measurement). Fabrication method of solar cells is also included.

3.1 Rationale for selection

The presented work in this thesis is classified into two part: (1) investigating the performance of novel organic non-fullerene acceptors as ETLs in p-i-n PSCs; and. (2) Fabrication of novel lead-free solar cell based on tellurium tetra-iodide as a photo-absorbing material in p-i-n solar cell. Therefore, the selected characterization techniques have the specific roles to prove the crystallographic structure of the as-prepared materials by XRD, interface morphology by UV-vis spectroscopy, PL. spectroscopy and optoelectronic properties by IPCE, and J-V curves of fabricated devices. In addition to the characterization by electrochemical impedance spectroscopy, the most important results in presented work is power PCE. Therefore, the most repeated characterization method is illuminated J-V curves.

3.2 Materials Characterization

3.2.1 Scanning Electron Microscopy (SEM)

SEM is a non-destructive tool to characterize the morphology and elemental composition of different samples including: organic, inorganic, and conductive and insulator materials. Comparing to optical microscope, SEM shows higher magnification and larger depth of field. The scanning process starts by the interaction of electrons beam with the atoms of the sample producing different signals, which can be translated into image on the attached display. These signals include: (1) low energy secondary electrons (< 50 eV), which produced from very close to the sample surface, (2) high energy back scatter electrons (BSE), which are deflected electron beam after elastic scattering of the samples, and (3)X-rays, which generated, when the electron beam removes the electron of the inner shell and then the empty orbital filled with the high energy electron. Each type of these signals was detected by specific types of detectors. Everhart-Thornley detector was used to detect secondary electrons by attracting them towards an electrically biased grid at about +400 V. The brightness of the signal depends on the number of secondary electrons reaching the detector. Everhart-Thornley detector is not applicable to detect back scattered electrons because of its high energy. Heavy elements backscatter electrons stronger than light

elements and thus appear brighter in the image. BSEs are used to detect the contrast between areas with different chemical compositions. SEMs can be classified into thermionic SEM and field emission SEM (FESEM). The main difference between two types is the source of ejected electrons. In thermionic SEM, the energy of electron beam generated by heating the filament is higher than the work function to emit electron outside material. Electrons beam in FESEM is generated due to the voltage gradient in the electrodes. The formed image of SEM depends on the area of electron beam and wavelength of incident electrons. Although the resolution of SEM isn't enough to detect atomic scale. However, SEM has a lot of advantages such as scanning large area, with different topology and chemical composition. The schematic structure of JEOL JSM 5410 is shown in **Figure 3.1**.^[1]

Figure 3.1 Schematic illustration of an example of a SEM instrument.^[1] The model is JEOL JSM 5410.

3.2.2 X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is a non-destructive analytical technique that exposes information about the crystal structure as well as its purity. This technique is based on detecting the scattered intensity of an X-ray beam striking a sample as a function of incident and scattered angle as depicted in **Figure 3.2**. The Bragg's law formula equation is used to measure the space between diffraction planes by using the equation ($n\lambda = 2d \sin \theta$), where d is the space between parallel plane of atoms.

Figure 3.2 Diffraction of X-rays from a crystal. ^[2]

XRD is suitable for powder, small crystals and thin films. Some precautions should be followed before starting the measurements;

- 1) In case of small crystals, the sample should be grinded to some certain size to be suitable for measurements (optimum size less than 10 μm).
- 2) Specific holder should be used during the measurement to obtain accurate results. Also, the height of the sample should be the same of the edge of the holder.
- 3) The sample should be mounted precisely in goniometer circle between the source of X-ray and detectors.
- 4) The sample surface, and the receiving slit axes should be parallel to each other and all perpendicular to the plane of the diffractometer circle. The surface of the specimen

should be coincident with the diffractometer axis. The receiving slit should lie on the diffractometer circle

Each XRD equipment has its specific software. The software facilitates to input the following parameters; the range of the scan should be detected, including starting and ending 2θ (2Θ), step size of 0.02 degrees (2Θ) for collection data as well as spinning of the sample or not. Incident X-rays wave is ejected from the source, then falls on the sample, which reflects the waves to the detectors. The detector collects the diffracted waves and the data is analyzed and solved by complex mathematics methods to diffraction pattern. Match is specific software, which was designed to identify the phases of the sample by interpreting the diffraction pattern of the sample. The diffraction pattern is produced as the interaction between the incident X-ray waves and closed backed parallel planes in the sample. The diffraction pattern is analyzed to characterize the unknown planes, which determine information on crystal structures, orientations, grain size, crystallinity, and crystal defects. By applying Bragg's law, the distance between parallel planes can be determined.

3.2.3 Atomic Force Microscopy (AFM)

AFM is an imaging technique belongs to the family of probe scanning microscopy. AFM is a useful tool to characterize and image the morphology, thickness and topography of the material surface. These materials include insulator, semiconductor and metals. The as-formed image is 3D with very high resolution up to atomic scale. The main part of AFM is a very sharp tip, which connected to the end of flexible cantilever. The dimension of the cantilever is in micrometer. However, the radius of the tip is a few nanometers. The dimension of tip is important, because the resolution of the image depends on the tip. The force is produced between the tip and the surface of the sample, when the tip closes to the surface of the sample. The produced force leads the cantilever to bend or deflect.

The bending of cantilever is detected by laser beam and transferred to the detector. The laser beam falls on the cantilever, then reflecting onto the detector. The bending and deflection of the cantilever cause the movement of the reflected laser on the detector as shown in **Figure 3.3** ^[3]

AFM can operate in different modes, which include: contact mode, non-contact mode and tapping mode. In contact mode the tip is pulled very close to the sample surface. The feature of sample surface can be measured by the deflection of the cantilever. The cantilever should have low stiffness (low spring constant, k) to be sensitive to low force.

Non-contact mode: in contrast to contact mode. In this mode, the tip doesn't approach to the sample surface and the cantilever oscillates in a few nanometers to pico meters on the sample surface. The attraction forces on the sample surface decrease the frequency of oscillation. The difference in oscillation is combined with electronic circuit loop to produce the image.

Tapping mode: tapping mode or AC mode is the most utilized mode in AFM measurements. Tapping mode was developed to address the problems of contact mode, such as the formation of meniscus layer during measurements in ambient conditions. In this mode, the cantilever oscillates to resonance frequency. The frequency and amplitude are kept constant, then the repulsion forces decrease the amplitude of the oscillation, which can be converted to image. In all modes, the force can be calculated by using Hook's law ($F = kz$, where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent).

Figure 3.3 General operation mechanism of AFM ^[3]

3.2.4 Ultra Violet-visible absorption spectroscopy.

Ultra Violet-visible absorption spectroscopy was used to measure the amount of absorbed light, which is incident on the sample. The UV-vis absorption takes place after falling of light on the materials, due to electronic transition between bonding orbital and anti-bonding orbital (HOMO and LUMO) and valence band and conduction band in case of solid materials. The absorption takes place, if the energy of light is equal or more than the band gap energy as depicted in **Figure 3.4**.

According to Beer-Lambert law: $A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon cL$, where, A is absorbance, I_0 is intensity of incident light, I is the intensity of transmitted light, ϵ is extinction coefficient, c is concentration of absorbing material and L is path length.

UV-visible absorption technique can be used to determine optical band gap of the material, thickness of material and its concentration. The main parts of UV-visible absorption spectrophotometer include: light source (tungsten lamp, xenon lamp and deuterium arc lamp), diffraction grating to separate different wavelength and detector (photomultiplier tube).

There are different types of UV-visible spectrophotometer including:

Single-beam UV-Vis spectrometers: Firstly, the reference should be measured and removed. Then, the sample was mounted and measured. The final absorption spectra processed and the analysis displays on the attached screen

Double-beam UV-Vis spectrometers: the light beam split into two parallel light beams, one passes into the reference and other passes into the sample. Then, the absorption spectra are displayed on the attached screen after the detection of the transmitted light intensity. ^[4]

Figure 3.4 Figure Schematic diagram showing possible molecular levels electronic transitions, and vibrational and rotational energy ^[4]

3.2.5 Photoluminescence spectrophotometer

In solid materials, electrons in valence band transfer to conduction band by absorbing light. Then excited electrons in conduction band tend to relax by radiative recombination (photoluminescence) or non-radiative recombination. The intensity of photoluminescence depends on the intensity of excitation. Photoluminescence can be applied in a lot of applications such as LEDs. As shown in **Figure 3.5**, the photoluminescence in semiconductor can be produced by different ways: ^[5]

Processes **A** and **B** describe the excitation process of the electrons from valence band to conduction. Then thermal relation of excited electrons moves to minimum of conduction band.

Process **C** describes the emitting of photoluminescence by recombination of excited electron in conduction band with hole in valence band.

Process **D** describes a special case of radiative recombination at very low temperature in pure crystal

Processes **E** and **F** describe popular process in solid, in which the transitions take place between band edges and donors and acceptors.

Process **H** describes the radiative recombination of electron from neutral donor and neutral acceptor.

Figure 3.5 Transitions producing emission of photons in solids.

The measurement starts by selecting the excitation wavelength by monochromator. The emitted radiation identified by detector, then translated to emission spectra. Photoluminescence has an important role to determine the band gap of the material. Furthermore, trap states can be discovered by photoluminescence measurements. ^[6]

Figure 3.6 Schematic illustration of PL. spectrophotometer.

3.2.6 Time-resolved Photoluminescence (TRPL)

This technique is very important to determine the lifetime of charges. In a semiconductor, electrons are excited and transfer from the valence band to the conduction band by absorbing light with an appropriate wavelength. Then the electron relaxes to the valence band by radiative decay. The lifetime of charge carriers can be detected by investigation of the lifetime of emission decay. [7]

3.2.7 Contact angle measurements.

Contact angle technique is a simple way to measure the hydrophobicity or the hydrophilicity of the thin film. While the contact angle value increases, the hydrophobicity increases and the hydrophilicity decreases. This method is mainly based on measurement of the angle between the liquid and the substrate (Θ_{AC}). The stability of the thin film towards moisture can be predicted by the contact angle measurement. Since the stability towards moisture is directly proportional with the value of the contact angle.

Θ_{AC} can be measured by dropping a droplet of water on the sample surface as depicted in **Figure 3.7**. This process is controlled by a camera, which is attached to a display to adjust the position of the water droplet on the surface. By using a software, which is designed to draw a tangent line on the image of the droplet, the contact angle can be determined. [8]

Figure 3.7 Contact angle measurement by water droplet.

3.2. 8 Electrochemical Impedance spectroscopy (EIS)

It is known that Ohm's law $R=E/I$, where R is electrical resistance, E is a potential and I is electrical current. Ohm's law describes the ability of circuit to resist the electrical currents. But this law can be compatible with simple circuit and idea resistor. The resistance of ideal resistor doesn't affect by frequency, as well as current and optional in the same phase. In complex systems and circuits can't be applied. Therefore, impedance (Z) replaced the resistance. While the excitation with sinusoidal potential and then a sinusoidal current is measured.

$$* Z = E/I$$

$$* E(t) = |E| \sin(\omega t)$$

$$* I(t) = |I| \sin(\omega t + \theta)$$

$$* Z = E(t)/I(t) = |E| \sin(\omega t)/|I| \sin(\omega t + \theta) = |Z| \sin(\omega t) / \sin(\omega t + \theta)$$

* $|E|$ is the amplitude of the voltage signal, $|I|$ is amplitude of the current and $\omega=2\pi f$ (the angular frequency).

Mathematical impedance can be represented by complex number: $Z = Z' + Z''$, where, Z' is real part and Z'' is imaginary part.

However, EIS is a powerful technique to detect the dynamic of charge carriers in electrochemical system.

EIS can be presented by Nyquist plot, where X-axis represents the real part and Y-axis represents imaginary part.

EIS is utilized in perovskite solar cells to study the dynamic of charge carriers, the applied frequency is in range of 1 to 1M Hz, as well as the applied initial voltage varies.

Nyquist plot shows two semicircles at low frequency and at high frequency. Semicircle at high frequency represents charge transfer resistance in bulk materials and charge transfer layers. Semicircle at low frequency represents charge recombination resistance. Series resistance can be determined. However, series resistance has only one component on X-axis.

The typical solar cell should have very small series resistance. The semicircle at high frequency should be very small, while it represents charge transfer resistance. In contrast, the semicircle at low frequency should have high value. ^[9]

3.2.9 External quantum efficiency measurements.

EQE is a ration between produced electrical current and number of incident photons of specific wavelength on solar cell. Therefore, EQE is a function of the wavelength of incident light. The EQE is produced by absorbing light with energy equal or higher than the band gap of solar cell. Therefore, EQE equals zero, indicating that the light energy is less than energy of the band gap. For the ideal solar cell, EQE appears as a square (100%). However, EQE of real solar cells drops, due to optical losses including transmission or reflection of incident light and a lot of charge carriers' recombination, while the charge carriers have shorter diffusion length and low lifetime as shown in **Figure 3.8**. ^[10]

Figure 3.8 EQE curve of ideal and real solar cell ^[10]

3.2.10 Characterization of solar cell efficiency.

The most powerful characterization method of solar cells is to measure its efficiency, which is known as power conversion efficiency (PCE). It is a strong tool to compare between different solar cells. To unite the results all over the world, some standards should be followed during measurements:

- 1) Solar cell for terrestrial application should be measured at AM 1.5 G, and solar cell for space application should be measured at AM 0, which is light path before atmosphere. The Air Mass is the path length which light takes through the atmosphere normalized to the shortest possible path length (that is, when the sun is directly overhead). The Air Mass quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust. The Air Mass is defined as: $AM = \frac{1}{\cos \theta}$ where θ is the angle from the vertical
- 2) The temperature of the solar cell should be 25 °C
- 3) The light source should be calibrated to 100 mW/cm² (it is known one sun)

Elements to measure the efficiency of the solar cell:

- 1- Calibrated solar simulator
- 2- Keithley 2400 SourceMeter
- 3- Software (tracer 2)

Figure 3.9 illuminated I-V curve of solar cell ^[11]

Power conversion efficiency (PCE) is the ration between output energy from solar cell and input energy from the Sun. PCE can be determined by measuring illuminated J-V curves.

$$P_{\max} = V_{oc} * J_{sc} * FF$$

$$PCE = V_{oc} * J_{sc} * FF / P_{in}$$

Where,

V_{oc} is open-circuit voltage, voltage of solar cell is obtained when the current passes through solar cell equals zero. It is maximum voltage of the solar cell.

J_{sc} is short-circuit current density, current density when the voltage across solar cell equals zero.

FF is fill factor, which is a ration of maximum power of the solar cell and the multiply product of J_{sc} and V_{oc}.

$$FF = \frac{V_{mp} * J_{mp}}{V_{oc} * J_{sc}} = \frac{P_{in}}{V_{oc} * J_{sc}}$$

As shown in the figure, FF is the ratio between area of square (A) and area of square (B) [11, 12]

Figure 3.10 FF of illuminated solar cell determine by the ratio of area of square A and area of square B. [13]

Dark I-V Curves:

The main function of solar cell to convert light energy to electrical energy. Therefore, the investigation of solar cell under dark condition is rare. However, dark I-V curve presents various information about the quality of fabricated solar cell. Leakage current can be determined from dark I-V curves. Leakage current is considered as an indicator of shun resistance.

Figure 3.11 Linear I-V curve of solar cell ^[13]

Figure 3.12 Semi Log I-V curve of solar cell ^[13]

3.3. Fabrication of inverted perovskite solar cell:

Table 3.1 Materials used in this project

Materials and solvents	Company
PEDOT:PSS Clevious TM, Al 4083	Heraeus
Lead iodide, PbI_2 99.999 % perovskite grade	Sigma Aldrich
Lead chloride, PbCl_2 , 99.999%, beads	Sigma Aldrich
Methyl ammonium iodide $\text{CH}_3\text{NH}_3\text{I}$	Greatcell Solar
Formamidinium iodide	Greatcell Solar
PCBM, 99.0 %	American Dye Source

Dimethyl sulfoxide 99.9 %, anhydrous (DMSO)	Sigma Aldrich
γ -Butyrolactone (GBL)	Sigma Aldrich
1, 2-Dichlorobenzene, 99%, anhydrous (DCB)	Sigma Aldrich
Silver, shot, 99.99%	Sigma Aldrich

3.3.1 Preparation of solution:

- a. Perovskite solution is prepared by mixing 1.26 M PbI_2 , 0.14 M PbCl_2 , 1.08 M methylammonium iodide and 0.27 M formamidinium iodide in DMSO and GBL (3:7 V/V). Then stirring the mixture for 12 hr. at 60 °C.
- b. PCBM solution is prepared by stirring 22 mg of PCBM in DCB for 12 hr at 60 °C.

3.3.2 Fabrication method

1. Washing ITO slides by Deionized water using ultra-sonic for 20 minutes. This step repeats three times.
2. Washing ITO slides by acetone and isopropanol in Ultra-sonic, respectively for 20 minutes. Each step repeats three times.
3. Blowing ITO substrate by nitrogen and dry in oven.
4. ITO substrates are treated in plasma cleaner for 20 minutes. PEDOT: PSS layer is spun cast on ITO for 1 minute at 6000 rpm. Then heat treated for 15 minutes at 130 °C. After that, all substrates are transferred into glovebox.
5. Before spin coating of perovskite solution, substrate should be heated up to 85 °C, as well as perovskite solution.
6. Perovskite layer is spun cast at two step: first step at 1000 rpm for 15 seconds and second step at 5000 rpm, after 25 second of second step 0.6 mL toluene is dripped on the perovskite solution.
7. The perovskite layer is heat-treated at 100 °C for 15 minutes, since the perovskite layer converted to dark brown.

8. After cooling to room temperature, PCBM solution or another ETLs solution is spin cast at perovskite layer at 2200 rpm for 1 minute.
9. After heat treatment at 100 °C for 12 minutes, silver electrodes are thermally evaporated through mask with specific area 0.06 and 0.09 cm².
10. Then each cell measured illuminated J-V curves under solar simulator and with TRACER 2 software. ^[14]
11. For stability test, as-fabricated solar cells kept in dry box under controlled humidity 30 %.

3.4. Characterization of Organic transporting layer:

3.4.1 Fourier Transform Infrared Spectra (FTIR)

FTIR is very important technique for characterization of the structure of organic molecules and polymers. FTIR has the ability to identify the different functional groups of organic molecules and polymers. Before characterization, the sample should be mixed with KBr. Each functional group has its own position in the FTIR absorption or transmission curve. Each molecule has a specific frequency of its vibration mode. The vibration modes can be classified into three main groups: stretching vibration, in-plane bending and out-of plane bending. ^[15]

3.4.2 ¹H Nuclear Magnetic resonance (NMR) and ¹³C NMR

HNMR is a common characterization technique of organic materials, in contrast to FTIR, HNMR characterize the carbon-hydrogen bond. Each sample should be soluble in specific solvents such as chloroform, dimethyl sulfoxide and methanol. ¹³C NMR has the same principle of HNMR. ^[16]

3.4.3 Cyclic voltammetry (CV)

CV is one of electrochemical technique, which measures the electrochemical properties of organic molecules. In this experiment, the current is recorded versus applied voltage. The

typical CV cell consists of three electrodes: reference electrode, counter electrode and working electrode, as well as to electrolyte and solvent. This technique is useful to determine HOMO and LUMO of organic molecules. ^[17]

Figure 3.13 Typical cyclic voltammetry curve. ^[17]

3.4.4 Thermogravimetric analysis (TGA)

TGA technique is used to study the thermal analysis of the material. The typical experiment should be conducted under inert gas while measuring the mass of the material with increasing the temperature and time. It is a good indicator to study the thermal stability of the materials. ^[18]

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Chapter 4

NDI-based Small molecules as Electron Transporting Materials in Inverted Perovskite Solar Cells

NDI-based molecules have been investigated as electron transporting layers in inverted perovskite solar cells, due to their amazing properties including: low synthesis cost, high stability, high mobility and available commercial building block. In this chapter, novel six NDI-based molecules have been designed, synthesized and investigated as electron transporting layers in inverted perovskite solar cells. The function of nitrogen atoms and sulfur atoms in NDI-based molecules have been investigated, while nitrogen atoms and sulfur atoms have the ability to passivate surface traps on perovskite layer. Therefore, the effect of sulfur atoms and nitrogen atoms on the electron transporting properties and passivation properties have been investigated.

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***A. A. Said#**, S. M. Wagalgave#, J. Xie, A. L. Puyad, W.Q. Chen, Z.R. Wang, S. V. Bhosale, S.V. Bhosale, Q. Zhang, *J. Solid State Chem.*, **2019**, 270, 51–57.

*D. B. Shaikh#, **A. A. Said#**, Z. Wang, P. S. Rao, R. S. Bhosale, A. M. Mak, K. Zhao, Y. Zhou, W. Liu, W. Gao, J. Xie, S. V. Bhosale, S. V. Bhosale, Q. Zhang, *ACS Appl. Mater. Interfaces*, **2019**, 11, 47, 44487-44500.

4.1 Introduction

The (p-i-n) PSCs receive more scientists' attention since these cells don't have metal-oxide layers, which can allow the fabrication of (p-i-n) PSCs at low temperatures (maximum 100 °C). Such conditions are highly desirable to approach flexible solar cells as well as the large-scale fabrication^[1,2]. Furthermore, this type of solar cells can suppress the hysteresis, which is a vital obstacle in (n-i-p) PSCs^[3]. Since the selection of electron transporting layer (ETL) is a crucial step to achieve high performance PSCs, it is highly challenging to explore suitable ETLs for (p-i-n) PSCs. PCBM is a conventional electron transporting material in (p-i-n) PSCs^[4]. Although the efficiency of (p-i-n) PSCs with PCBM as ETLs can reach from 3.9%^[5] to ~ 15%^[6], the drawbacks of PCBM including poor morphology control and high cost^[7-9] have become an obstacle for its large-scale application. Thus, it is highly desirable to develop suitable alternatives to address these issues. Organic small molecules and n-type polymers are believed to be promising ETLs candidates to replace PCBM, because these materials are believed to overcome the limitations in PCBM^[10-16]. Moreover, organic small molecules are preferable comparing with n-type polymers due to their monodispersity as well as good molecular packing. The author's group has already developed many novel azaacene-based small molecules^[17-25] and some of them have been employed as ETLs in PSCs with the highest efficiency up to 18.2%^[26-28]. At the same time, Jen group also developed a crosslinking organic material and a hexaazatrinaphthylene-based organic molecule as the ETL in PSCs with an efficiency up to 17.6%^[29-30]. Chen group also demonstrated that mono-halogenated perylene diimides can be used as ETLs in PSCs^[31]. All these results clearly indicated that organic small molecules should be promising candidates to further push up the efficiency of solution-processing (p-i-n) PSCs. Continuing this research, naphthalenediimide (NDI) and its derivatives are believed to be a good system as ETLs in solution-processing (p-i-n) PSCs. In this chapter, different NDI-based molecules were investigated as ETLs in p-i-n PSCs. The properties of each NDI-based molecule have a crucial role to influence the as-fabricated p-i-n PSCs. These properties include: energy levels value (HOMO and LUMO), electron mobility, ability to passivate electron trap centers on perovskite layer and its morphology on the surface of perovskite layer. NDI-based molecules were divided into three groups, each group has two

slightly similar two molecules. First group includes PDPT and PMDPT, second group include DS1 and DS2, and finally, third group include NDI-BTH1 and NDI-BTH2. As mentioned before, all molecules are based on NDI building block. All molecules were investigated as ETLs. From structure point of view, in the same group, two molecules have slightly difference in structure. In group one, the difference between PDPT and PMDPT is the number of nitrogen atoms, while PMDPT has more nitrogen atoms than PDPT. It is worthy to note, the N-atoms in ETLs has ability to passivate the electron traps states on perovskite surface. Therefore, the ability of PDPT and PMDPT as ETLs in p-i-n PSCs was investigated. In fact, the PCE of PDPT-based device and PMDPT-based devices were poor, since PCE of PDPT-based device was 7.6 % and PCE of PMDPT slightly increased to 9.2 %. The higher PCE of PMDPT-based device was ascribed to additional N-atoms, which passivates trap centers. However, the performances of both molecules-based devices were very poor and doesn't satisfy the scientific community. Developing new ETLs was desirable to push the PCE of p-i-n PSCs. DS1 and DS2 were developed as ETLs in p-i-n, sulfur-atoms (S-atoms) were incorporated in DS1 and DS2. S atoms has strong ability to passivate electron trap centers on the surface of perovskite. The passivation process occurs by the interaction of S-atoms with positively charged under-coordinated Pb-atoms, which are considered as electron trap centers. The difference between DS1 and DS2 is the number of s atoms, since DS2 has excess number of S-atoms. DS2-based devices showed PCE (11.4 %) higher than DS1-based device (9.6%). The enhanced PCE was attributed to excess number of S atoms. However, the as-obtained PCEs of DS1-based device and DS2-based device still less than 15%, which is considered as satisfied for commercial applications. The poor performance was attributed to mismatching of frontier energy levels of DS1 and DS2 with valence band and conduction band of perovskite layer. Therefore, it is desirable to find novel NDI-based molecules, which have well matched frontier molecular orbitals with conduction band and valence band of perovskite layer, as well as having good electron mobility and good ability to passivate surface trap centers of perovskite layer. NDI-BTH1 and NDI-BTH2 were synthesized as novel ETLs in p-i-n PSCs, NDI-BTH2-based device showed decent PCE equaled to 15.4 %, which is higher than PCE of NDI-BTH1-based device (13.7 %). The higher performance was attributed to several factors: the electron mobility of NDI-BTH2 is higher than electron mobility of NDI-BTH1. Furthermore, the

LUMO of NDI-BTH2 is matched with conduction band of perovskite layer more than that of NDI-BTH1. Therefore, the loss in Voc of NDI-BTH2-based device is less than NDI-BTH1-based device. In addition, NDI-BTH2 as an ETL showed passivation power toward surface traps higher than that of NDI-BTH1. Finally, six NDI-based molecules were investigated as ETLs in p-i-n PSCs. The worse molecule was PDPT and the best molecule was NDI-BTH2.

4.2 PDPT and PMDPT as ETLs in Inverted perovskite solar cells.

As shown in **Figure 4.1**, NDI-based materials (4,4'-(piperazine-1,4-diyl) bis (2,7-dioctylbenzo[lmn]-[3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (PDPT) and 9,9'-(piperazine-1,4-diyl) bis (4-(4-methylpiperidin-1-yl)-2,7-dioctylbenzo [lmn] [3,8] phenanthroline-1, 3, 6, 8 (2H,7H)-tetraone) (PMDPT)) as the ETLs in PSCs. (p-i-n) PSCs were successfully fabricated with PEDOT:PSS as the hole transporting layer (HTL), CH₃NH₃PbI₃-xCl_x as the light absorber, and PDPT or PMDPT as ETLs. It is worth to note that the devices are fabricated under low temperature through solution processing spin-casting. All PSCs are completed by the evaporation of silver (Ag) electrodes. The as-fabricated PSCs with PMDPT and PDPT as ETLs show power conversion efficiencies (PCEs) up to 9.2% and 7.6%, respectively.

4.2.1 Synthesis and characterization of PDPT and PMDPT

The synthetic routes to obtain PDPT and PMDPT are shown in **Figure 4.1**. PDPT was synthesized in a yield of 57% by the addition of piperazine to the toluene suspension containing 4-bromo-2,7-dioctylbenzo[lmn]-[3,8]phenanthroline-1,3,6,8(2 H, 7 H)-tetraone^[32] at 70 °C. Characterizations including FT-IR, ¹H NMR, ¹³C NMR and TGA have been provided in appendix 1. The intermediate compound, 4-Bromo-9-(4-methylpiperidin-1-yl)-2,7-dioctylbenzo[lmn]-[3,8]phenanthroline -1, 3, 6, 8(2 H, 7 H)-tetraone, was synthesized according to the previous report^[33] and the characterizations are shown in appendix 1. PMDPT was obtained in 78% yield by the reaction between 4-Bromo-9-(4-methylpiperidin-1-yl)-2,7-dioctylbenzo[lmn]-[3,8]phenanthroline 1, 3, 6, 8(2 H, 7 H)-tetraone and piperazine in toluene at 70 °C. FT-IR, ¹H NMR, ¹³C NMR and TGA

characterizations of PMDPT are illustrated in appendix 1.

Figure 4.1. Synthetic routes to PDPT and PMDPT

4.2.2. Device fabrication and characterization

Device fabrication started with etching indium tin oxide (ITO) substrates with Zn powder and 2M HCl to form the desired patterns, followed by washing with dilute detergent, DI-water, acetone and isopropanol in ultrasonic bath, respectively. Before treating ITO with air plasma, ITO substrates were blown by nitrogen gas and stored in oven. Then, 30 nm PEDOT:PSS layer (Clevios pvp Al 4083) was spun cast at a speed of 6000 rpm for 60 s, followed by heat treatment at 130 °C for 15 min. All these steps were done after the filtration of PEDOT:PSS solution through a 0.45 μ m syringe filter. The perovskite solution was prepared by mixing 1.4 M PbI₂ (Sigma Aldrich 99.999%) and 0.28 M CH₃NH₃Cl (Sigma Aldrich) with 1.12M CH₃NH₃I (Dyesol) and stirring in the mixture of GBL: DMSO (7:3, v/v) overnight at 60 °C. A perovskite layer with a thickness of 350 nm was spun cast by two stages. The first stage was at 1000 rpm for 20 s and the second stage was at 4000 rpm. During the second stage after 20 s, 0.7 mL of toluene was dripped on the perovskite and then the formed film is directly transferred to a hot plate at 100 °C for 15 min^[34]. After

cooling the perovskite layer, PDPT solution and PMDPT solution (10, 15, 20, 25, 30 and 35 mg/ml of 1, 2- dichlorobenzene) were spun cast onto the surface of perovskite layer at 1800 rpm for 60 s. Then all the layers were heat-treated at 80 °C for 20 min. The final step was the evaporation of 100 nm of Ag electrode.

The perovskite film was characterized by powder XRD equipped with CuK α radiation (λ = 0.15418 nm operated at 40 kV and 30 mA). The surface morphology of perovskite film was investigated by SEM (JEOL, JSM 6360 at 5 kV). The thickness of each layer was measured by Alpha-Step D-600 Stylus Profiler (KLA-Tencor Corporation). The optical properties of perovskite layer were characterized by UV–visible spectroscopy (UV–Vis–NIR, Lambda 900, Perkin Elmer). The PL characteristics were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). The EQE measurement was carried out on Bentham PVE300, Photovoltaic EQE & IQE solution with 75W Xenon lamp. The current density-voltage (J-V) curves of solar cells were measured using Keithley 2400 source meter under a simulated AM1.5 illumination (100 mW/cm²) by a Xenon-lamp-based solar simulator (Abet Technologies, USA). The light intensity was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory.

4.2.3 Results and discussion

Figure 4.2 UV-visible spectroscopy of PDPT and PMDPT

Figure 4.3 SEM of perovskite layer surface

Thermal gravimetric analysis (TGA) shows excellent thermal stability of PDPT and PMDPT, since the onset decompositions are 353 °C and 409 °C as depicted in appendix 1. The optical absorption curves of each compound as the thin films are shown in **Figure 4.2**. The onsets of PDPT and PMDPT are 644 nm and 677 nm, respectively. The result indicates that the optical band gap (E_{optg}) of these two compounds are 1.92 eV and 1.83 eV, respectively. The lowest unoccupied molecular orbital (LUMO) of each compound could be estimated from the cyclic voltammogram as depicted in appendix 1. The E_{red} onset for PDPT and PMDPT are -0.9677 V and -1.0429 V, respectively. Hence, the LUMO of PDPT is estimated to be -3.73 eV and the LUMO of PMDPT is -3.65 eV. By applying the equation: $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{optg}}$, it was found that the highest occupied molecular orbitals (HOMOs) of PDPT and PMDPT are -5.65 eV and -5.48 eV, respectively.

The as-prepared perovskite layer doesn't show any pin holes. Furthermore, large grains can be observed from the SEM images as shown in **Figure 4.3**. If the number of pin holes is reduced, the shunt resistance will increase, leading to the increasing open-circuit voltage (V_{oc}) and PCE. From the investigation of the optical absorption of the perovskite layer (perovskite/PDPT bilayer, and perovskite/PMDPT bilayer), the onset of the perovskite absorption curve could be detected around 780–785 nm, which indicates that the band gap is 1.58 eV. Moreover, it can be noticed that the intensity of the absorption increases respectively as depicted in **Figure 4.4**. XRD patterns confirm the formation of pure $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer. The three strong peaks at 14.2° , 28.5° and 31.9° can be assigned to the (110), (220) and (310) crystal planes. No significant peak is observed at

12.6°, indicating the absence of any remnants of PbI_2 in the perovskite film as shown in **Figure 4.5 (a)**. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ exhibits strong photoluminescence (PL) at an excitation wavelength of 532 nm, which refers to the presence of a high-quality perovskite layer. PMDPT has more significant quenching effect comparing to PDPT as shown in **Figure 4.5 (b)**. These results strongly suggest the suitability of PMDPT and PDPT as ETLs for the extraction of electrons from the perovskite layer. To elucidate the appropriateness of PDPT and PMDPT as the ETLs, both compounds have been utilized in PSCs with the configuration of ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /ETL/Ag (**Figure 4.6 (a)**). 30 nm PEDOT:PSS layer was spun cast as HTL on the surface of ITO, followed by 350 nm $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layer. Different concentrations of PDPT and PMDPT solutions were spun cast onto the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layers. The energy level diagram of the utilized materials is illustrated in **Figure 4.6 (b)**. When the perovskite layer absorbs light, excitons are generated and separated as electrons and holes, which are transferred and collected by ETL/Ag and HTL/ITO, respectively.

Figure 4.4 UV-visible spectroscopy of perovskite layer, perovskite /PDPT bilayer and perovskite/PMDPT bilayer.

Figure 4.5 (a) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (b) PL characteristic of pure perovskite, perovskite/PDPT bilayer and perovskite/PMDPT bilayer.

Figure 4.6 (a) Device architecture of inverted PSCs fabricated in this work. (b) Energy levels diagram of each layer used in this work.

PDPT was exploited with different concentrations in 1, 2-dichlorobenzene as ETLs and applied in PSCs. After investigating the current density-voltage (J-V) curves and photovoltaic parameters of each PSC, It was found that the performance of PSCs is highly

dependent on the concentrations of ETL solutions. When the concentration is 5 mg/ml, the fill factor (FF) and V_{OC} are very low, leading to a poor PCE. This is due to the low coverage of ETL, which has increased charge carrier recombination; while at a high concentration of 35 mg/ml, the efficiency is low due to the high thickness of ETL, which can increase series resistance, resulting in low FF. It is found that the optimum concentration that could achieve the highest PCE, is 30 mg/ml, where the photovoltaic parameters have reasonable values. FF, V_{OC} , short circuit current density (J_{SC}) and PCE are 44%, 0.76 V, 22.9 mA/cm² and 7.6%, respectively as shown in **Figure 4.7 (a)** and **Table 4.1**. By using PDPT with concentration of 30 mg/ml, 36 devices were obtained with the same fabrication parameters. The efficiency distributions of PSCs are shown in **Figure 4.7 (b)**, although there are slight variations between the efficiencies of different PSCs, the author's devices are reproducible.

Figure 4.7 (a) J-V curves of PSCs with different concentration of PDPT as ETLs (b) Distribution of PSCs efficiency with optimum concentration of PDPT

Figure 4.8 (a) J-V curves of PSCs with different concentration of PMDPT as ETLs (b) Distribution of PSCs efficiency with optimum concentration of PMDPT

Table 4.1 Photovoltaic parameters of PSCs with different concentration of PDPT

Device no.	Conc. of ETL (mg/ mL)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	R _s (Ω cm ²)
1#	10	0.66	17.5	45	5.2	14.6
2#	15	0.68	18.2	52	6.4	N/A
3#	20	0.68	19.6	49	6.5	N/A
4#	25	0.67	19.7	50	6.6	N/A
5#	30	0.76	22.9	44	7.6	17
6#	35	0.77	22.9	36	6.35	24

PSCs with PMDPT as ETLs show better performance ETLs than PSCs with PDPT as ETLs. It is found that the highest PCE can be achieved by using a 30 mg/ml PMDPT solution. By exploiting the PMDPT solution with a concentration of 30 mg/ml, the photovoltaic parameters are 0.84 V, 22.4 mA/cm², 49% and 9.2% for V_{oc}, J_{sc}, FF and PCE, respectively. As shown in **Figure 4.8(a)** and **Table 4.2**, by increasing the concentration value exceeding 30 mg/ml, both the thickness and series resistance resulting in poor FF, thus low PCEs. Also, 36 cells were fabricated at the same parameter with 30 mg/ml of PMDPT solutions. Although there are slight variations in the PCEs of the PSCs, the values are reproducible as shown in **Figure 4.8 (b)**. External quantum efficiency (EQE) for devices with PDPT and PMDPT were investigated and shown in **Figure 4.9 (a, b)**, respectively. The corresponding calculated J_{sc} for best device with PDPT is 22.6 mA/cm², which is consistent with the measured J_{sc} for best device. Also, the corresponding calculated J_{sc} for best device with PMDPT is 22.1 mA/cm², which is coherent with the measured J_{sc} for best device. The thickness of ETL with different concentration were measured by Alpha-Step D-600 Stylus Profiler. The 30 mg/ml of PDPT ETL and PMDPT ETL showed 60 and 63 nm respectively, this is considered as an optimum concentration to form PDPT and PMDPT ETLs which covered the perovskite layer without undesired aggregation. However, the concentration of 10 mg/ml of PDPT and PMDPT delivered ETLs with thickness of 20 nm and 25 nm, which led to increase current leakage and deterioration of the device performance. Employing PDPT and PMDPT with the concentration of 35 mg/ml resulted in ETLs with the thickness of 75 nm and 79 nm, respectively, where the undesired aggregated particles can be clearly seen on the surface. To further explore the effect of the concentration on the performance

of devices. AFM investigation were carried out for 10 mg/ml and 30 mg/ml solution of PDPT as ETL on perovskite layer as shown in **Figure 4.10 (a and b)**, respectively. The 10 mg/ml PDPT as ETL showed less coverage and more pin holes than 30 mg/ml of PDPT. It is noteworthy that the same behavior of ETL coverage was followed by using 10 mg/ml of PMDPT and 30 mg/ml of PMDPT as depicted in **Figure (c and d)**, respectively. To investigate the capability of PDPT and PMDPT to block the current leakage, I-V dark current curves of PDPT-based devices and PMDPT based devices are shown in **Figure 4.11 (a, b)**, respectively.

Figure 4.9 a) EQE of best device with PDPT as ETL, b) EQE of best device with PMDPT as ETL.

Table 4.2 Photovoltaic parameters of PSCs with different concentration of PMDPT ETLs.

Device no.	Conc. of ETL (mg/ mL)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	R_s (Ω cm ²)
1#	10	0.69	15.4	55	5.9	13.6
2#	15	0.72	17.5	52	6.5	N/A
3#	20	0.73	17.6	56	7.0	N/A
4#	25	0.71	17.4	60	7.4	N/A
5#	30	0.84	22.4	49	9.2	14
6#	35	0.74	20.5	38	5.8	22

Figure 4.10 AFM figures of, a) 10 mg/ mL of PDPT solution as ETL layer on perovskite layer, b) 30 mg/ mL of PDPT solution as ETL layer on perovskite layer, c) 10 mg/ mL of PMDPT solution as ETL layer on perovskite layer, d) 30 mg/ mL of PMDPT solution as ETL layer on perovskite layer.

Figure 4.11 (a) I-V dark current curves of PDPT-based devices with different concentration, (b) I-V dark current curves of PMDPT-based devices with different concentration

Figure 4.12 Contact angle of (a) PDPT, (b) PMDPT and (c) PCBM

The reverse bias part of I-V dark current curve represents the leakage current. 30 mg/ml of PDPT solution as ETL showed the less current leakage than 10 mg/ml solution and 35 mg/ml solution. So, the optimum coverage is occurred by using 30 mg/ml solution. The forward bias part of I-V dark current curve is related to series resistance. By using 35 mg/ml of PDPT solution, the corresponding device showed higher series resistance. Also, by employing different concentration of PMDPT solution (10, 30 and 35 mg/ml) as ETL. The less current leakage was obtained by using 30 mg/ml PMDPT solution as ETL. The contact angle of each ETL is direct proportional with the stability of the device. The contact angles of PDPT, PMDPT and PCBM are shown in **Figure 4.12 (a, b and c, respectively)**. It is worthy to point that PDPT showed the highest contact angle (100.4 °C) and this value is higher than the contact angle of PMDPT (93.9 °C). Interestingly, the contact angle of PDPT and PMDPT are higher than contact angle of conventional ETL (here is PCBM). More importantly, PDPT and PMDPT-based devices retained approximately 80% of its stability after ten days. PMDPT ETL shows better performance than PDPT ETL. This phenomenon was attributed to the excess nitrogen atoms in PMDPT layer than PDPT layer. This passivation reduces the charge carrier recombination, thus delivering a higher VOC and PCE. It is believed that the PCE of the as-fabricated devices can be enhanced through the incorporation of more sulfur atoms into the framework of the original molecules because

sulfur atoms have more passivation effect than nitrogen atoms. Such passivation can enhance all photovoltaic parameters of the as-fabricated devices. Furthermore, embedding sulfur-atoms changes LUMO of PMDPT and PDPT to deeper value, which increases its matching with conduction band of perovskite layer and increases the electron mobility. Such results decline the charge carriers' recombination and enhance FF.

4.3 DS1 and DS2 as ETLs in Inverted perovskite solar cells.

In this contest, two new NDI derivatives such as 4-(5-((4,5-bis(octylthio)-1,3-dithiol-2-ylidene)methyl) thiophen-2-yl)-2,7-dioctylbenzo[Imn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (DS1) and 4,9-bis(5-((4,5-bis(octylthio)-1,3-dithiol-2-ylidene)methyl)thiophen-2-yl)-2,7-dioctylbenzo[Imn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (DS2) were synthesized and employed as ETL material in inverted p-i-n PSCs. PSC based on DS1 as ETL material delivered PCEs of 9.6% with a short-circuit current (J_{sc}) 23.41 mA/cm², an open-circuit voltage (V_{oc}) 0.74 V and a fill factor (FF) of 55. PSC based on DS2 as ETL exhibits PCE of 11.4% with J_{sc} =22.65 mA/cm², V_{oc} =0.80 V and FF=63. It was observed that the performance of PSCs based on DS2 (η =11.4%) as ETLs is higher than that of PSCs based on DS1 (η =9.6%).

4.3.1 Synthesis and characterization of DS1 and DS2

The synthetic route of new non-fullerene organic molecules DS1 and DS2 is depicted in the **Figure 4.13**. The synthesis of DS1 was achieved from ODT 1 and 5-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[Imn][3,8]phenanthroline-4-yl) thiophene-2-carbaldehyde 2 via phosphite-induced Horner-Wittig condensation reaction. Whereas, the target DS2 was synthesized via Horner-Wittig condensation reactions of two ODT 1 units and one 5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[Imn][3,8]phenanthroline-4,9-diyl)bis (thiophene-2-carbaldehyde) 3 unit.

Figure 4.13 Synthetic pathway of DS1 and DS2.

It was observed that DS1 and DS2 have 5% wt. loss at 296°C and 288°C, respectively under a nitrogen atmosphere. These results suggest that both DS1 and DS2 show good thermal stability. UV-vis absorption spectra of both DS1 and DS2 were recorded in dichloromethane solution (1×10^{-5} M) at room temperature and are displayed in **Figure 4.14 (a)**. The corresponding absorption values are summarized in **Table 4.3**. DS1 exhibits three absorption peaks at 364 nm, 382 nm and 683 nm. The absorption peaks at 364 nm and 382 nm can be assigned to π - π^* transitions independent dithiols ring and central NDI aromatic core units.

Figure 4.14. (a) UV-vis absorption spectra in dichloromethane (1×10^{-5} M) and (b) Cyclic voltammogram of DS1 and DS2 in dichloromethane (5×10^{-4} M).

The absorption peak appeared at 683 nm is due to charge transfer (CT) between electron donor dithiols ring and electron acceptor NDI aromatic moiety. Similar trend was observed in the absorption spectrum of DS2. The DS2 shows two absorption peaks at 391 nm and 733 nm. The peak at 391 nm belongs to $\pi-\pi^*$ transitions whereas the absorption peak at 733 nm, ascribed to charge transfer band. The absorption peak of DS2 appeared at 733 nm is 50 nm red-shifted compared to DS1 (683 nm). The 50 nm red-shifted CT band of DS2 than DS1 could be due to the presence of one extra dithiols ring system at NDI core which in turn extended π -conjugation.

To study the effect of electron donating dithiol rings on the electronic properties of electron acceptor NDI moiety of DS1 and DS2, cyclic voltammetry (CV) measurement was performed in dichloromethane (5×10^{-4} M). With respect to a silver (Ag/Ag^+) electrode the onset oxidation and reduction potential have been determined. As shown in **Figure 4.14 (b)** and in **Table 4.3**, the E_{ox} onset for DS1 and DS2 are 0.71 V and 0.6436 V, respectively. The difference in E_{ox} onset is due to the presence of dithiol ring (one in DS1 and two in DS2) on NDI core. The HOMO level values of DS1 and DS2 were calculated using the formula $E_{\text{HOMO}} (\text{eV}) = -q(E_{\text{ox}} \text{ onset} + 4.7)$. From these E_{ox} onset estimated highest occupied molecular orbital (HOMO) values of DS1 and DS2 are - 5.41 eV and - 5.3436 eV, respectively. The E_{red} onset of DS1 and DS2 are - 0.498 V and - 0.5038 V, respectively. The lowest unoccupied molecular orbital (LUMO) levels of DS1 and DS2 were calculated based on E_{red} onset values using an equation $E_{\text{LUMO}} (\text{eV}) = -q(E_{\text{ox}} \text{ onset} + 4.7)$ and are

Table 4.3. Optical and electrochemical properties of DS1 and DS2.

Molecule	UV-vis (nm)	E _{ox} , onset (V)	E _{red} , onset (V)	HOMO (eV)	LUMO (eV)
DS1	364, 382, 683	0.71	-0.498	-5.41	- 4.202
DS2	391, 733	0.6436	-0.5038	-5.3436	- 4.1962

found to be -4.202 eV and -4.1962 eV, respectively. The energy gap ($E_{g,cv}$) values are calculated from HOMO and LUMO values of DS1 and DS2 and found to be 1.208 eV and 1.1474 eV, respectively. These LUMO levels of DS1 (- 4.202 eV) and DS2 (- 4.1962 eV) are smaller than the conduction band of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (- 3.9 eV).^[35] It is presumed that the smaller energy barrier 0.302 eV and 0.2962 eV between the CB of perovskite and the LUMO level of DS1 and DS2, respectively, would allow the electron transfer from perovskite to the ETL, then followed to metal electrode easily. The generated gradient in the LUMO energy level of perovskite and ETL would reduce the charge recombination.

4.3.2 Results and discussion

On cleaned ITO substrate, PEDOT: PSS layer was spun cast and annealed at 130 °C for 15 minutes. Furthermore, perovskite solution of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ was spun cast at two stages with 350 nm thickness. Spun cast were performed at initial stage for 20 second (1000 rpm) and at second stage of 4000 rpm, respectively. After 20 s of second stage, 0.6 mL of toluene was dripped on the perovskite and then the resultant film is directly transferred to a hot plate at 100°C for 15 minutes. The perovskite layer was characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), UV-vis absorption and fluorescence emission spectroscopy. The SEM image of the perovskite layer revealed the presence of large grains with reduced pinholes (**Figure 4.15 a**). As the numbers of pinholes are reduced, the shunt resistance will increase. In turn, it is presumed that open-circuit voltage (V_{oc}) and PCE will also increase.

Figure 4.15. (a) SEM of perovskite layer; (b) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$; (c) UV-visible spectroscopy of perovskite layer; (d) PL characteristic of pure perovskite, perovskite/DS1 bilayer and perovskite/DS2 bilayer.

Figure 4.15 b exhibits XRD of pure $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer with three significant intense peaks at 14.2° , 28.5° and 31.9° . These three peaks can be assigned to the (110), (220) and (310) crystal planes, respectively. At 12.6° no significant peak was observed which suggests that the absence of any free PbI_2 in perovskite layer. UV-vis absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer shows absorption onset at ~ 782 nm as shown in **Figure 4.15 c**. Upon excitation at 532 nm, the perovskite layer exhibits strong emission peak at 780 nm (**Figure 4.15 d**, black dotted line). The ETL materials DS1 and DS2 were deposited on perovskite layer of varying concentration 4, 8, 12 mg/mL and annealed at 100°C for 10 min. The as-deposited DS1 and DS2 ETL materials on perovskite films show significant decrease in PL intensity of perovskite layer (**Figure 4.15 d**:

perovskite/DS1 bilayer-red dotted line and perovskite/DS2 bilayer-blue dotted line).

The overall PSCs device architecture ITO/PEDOT: PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /ETL/Ag is depicted in the **Figure 4.16 a**. The energy level diagram of the materials used in PSCs studies is shown in the **Figure 4.16 b**. Initially the perovskite layer absorbs light energy and generates excitons, which ultimately led to the dissociation and the formation of electrons and holes. The generated electron and holes channeled and collected by ETL/Ag and HTL/ITO electrodes, respectively.

Figure 4.16 (a) Device architecture of inverted PSCs fabricated in this work; (b) Energy levels diagram of each layer used in this work.

At first, the J-V curve of PSCs having DS1 as ETL material was investigated with varying concentrations such as 4 mg/mL, 8 mg/mL and 12 mg/mL (**Figure 4.17 a**). The photovoltaic (PV) parameters from J-V curve performance are reported in **Table 4.4**. When the DS1 concentration is 4 mg/mL, the PV parameters are recorded as $V_{oc}=0.72$ V, $J_{sc}=22.27$ mA/cm² and FF=49.4% which leads to PCE=7.9%. For 8 mg/mL of DS1 utilized as ETL, the obtained PV parameters from J-V curve are as $V_{oc}=0.74$ V, $J_{sc}=23.41$ mA/cm², FF=55.4% and PCE=9.6%. As for highest concentration of DS1 (12 mg/mL), the PSCs exhibited PV parameters are $V_{oc}=0.72$ V, $J_{sc}=22.6$ mA/cm², FF=44.5% and PCE=7.3%. When DS1 (8 mg/mL) was used as ETL, a higher value of PCE (~ 9.6%) was

Figure 4.17 (a) J-V curves of PSCs with different concentrations of DS1 ETLs, (b) Distribution of PSCs efficiency for perovskite solar cell with the optimum concentration of DS1 ETL, (c) J-V curves of PSCs with different concentrations of DS2 ETLs, (d) Distribution of PSCs efficiency for perovskite solar cell with the optimum concentration of DS2 ETL

obtained comparing to devices made up of 4 mg/mL ($\eta=7.9\%$) and 12 mg/mL ($\eta=7.3\%$). The lower PCE value of PSC device made from 4 mg/mL of DS1 is attributed to the discontinuous ETL film morphology formation, which ultimately leads to charge carrier recombination. Whereas ETL layer made from 12 mg/mL of DS1, the as-obtained PCE 7.3% is also lower than the ETL materials made from 8 mg/mL of DS1. This lower PCE could be due to the higher thickness of ETL, which in turn resulted into increased series resistance led to low FF. 27 devices were fabricated with optimum concentration of DS1, and all devices showed slightly variation in performance, which agrees with the reproducibility of new material DS1 as shown in **Figure 4.17 b**. The J-V curves of PSCs based on DS2 (4 mg/mL, 8 mg/mL and 12 mg/mL) as an ETL material are depicted in **Figure 4.17 c**.

Table 4.4 Photovoltaic parameters of PSCs with different concentrations of DS1 and DS2 ETLs.

Molecules	Conc. of ETL (mg/ ml)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
DS1	4	0.72	22.27	49.4	7.9
	8	0.74	23.4	55.4	9.6
	12	0.72	22.6	44.5	7.3
DS2	4	0.81	22.86	58.9	10.9
	8	0.80	22.65	63.0	11.4
	12	0.82	23.09	52.1	9.9

The PV parameters obtained from J-V curves are summarized in **Table 4.4**. For DS2 with 4 mg/mL, 8 mg/mL and 12 mg/mL utilized for ETL of PSCs, the PV parameters extracted from J-V curves are Voc=0.81 V, Jsc=22.86 mA/cm², FF=58.9% and PCE=10.9%; Voc=0.80 V, Jsc=22.65 mA/cm², FF=63% and PCE= 11.4%; and Voc=0.82 V, Jsc=23.09 mA/cm², FF=52% and PCE= 9.9%, respectively. The PCE values for DS2 used as 4 mg/mL (η =10.9%) and 12 mg/mL (η =9.9%) are lower than the DS2 of 8 mg/mL (η =11.4%). The difference in PCEs could be due to the two main causes such as (i) when 4 mg/mL of DS2 was used, the ETL coverage on perovskite is smaller, leading to increase charge carrier recombination; and (ii) while 12 mg/mL of DS2 was used, the thickness of ETL becomes higher, which yields an increase in series resistance and lower FF. As shown in **Figure 4.17 d**, DS2 showed reproducible results after the test of the as-fabricated 27 devices using 8 mg/ml of DS2 as ETL. The reason why all devices have low PCE and FF is because DS1 and DS2 don't possess holes blocking properties due to the HOMOs of DS1 (- 5.41 eV) and DS2 (- 5.34 eV) close to the valence band of perovskite layer. It is interesting to note that the PCEs values of DS2 (η = 11.4%) is higher than that of DS1 (η =9.6%). This difference in efficiency could be attributed to the low band gap and more binding between excess sulfur atoms of ETL and I and Pb of perovskite layer (S- I and S- Pb). The difference is due to the presence of two dithiol units at NDI core of DS2 and one dithiol unit in DS1. To further understand how the morphology affects the performance of the as-fabricated devices, AFM study has been conducted (**Figure 4.18 (a, b)**). The AFM

images could provide a strong evidence to explain DS2-based device have better efficiency. The film based on DS2 has a roughness of about 9.7 nm while DS1 exhibited a higher roughness (RMS=22.5 nm). The lower roughness and better morphology can enhance the contact between electrodes and ETLs, which facilitates the electrons transport, and then enhances the efficiency.

Figure 4.18 (a) AFM image of DS1 ETL on perovskite layer, (b) AFM image of DS2 ETL on perovskite layer.

4.4 NDI-BTH1 and NDI-BTH2 based ETLs in inverted perovskite solar cells

In this investigation, two naphthalenediimide (NDI) derivatives (NDI-BTH1 and NDI-BTH2) were designed and synthesized, and found that introduction of 2-(benzo[d]thiazol-2-yl) acetonitrile groups at NDI core position gave lowest unoccupied molecular orbital (LUMO, -4.326 eV) and displayed strong electron affinities, suggesting that NDI-BTH1 might be a promising electron transporting material (i.e. n-type semiconductor). Whereas, NDI-BTH2 bearing bis(benzo[d]thiazol-2-yl)methane at NDI core with LUMO of -4.243 eV was demonstrated to be ambipolar material. OFET-based on NDI-BTH1 and NDI-BTH2 have been fabricated and the charge carrier mobility of NDI-BTH1 and NDI-BTH2 are $14.00 \times 10^{-5} \text{ cm}^2/\text{Vs}$ (μe) and $8.64 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (μe)/ $1.68 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (μh) respectively. Moreover, a difference in NDI-core substituent moieties significantly alters the UV-vis absorption and cyclic voltammeter properties. NDI-BTH1 and NDI-BTH2 were further successfully employed as electron transport layer (ETL) materials in inverted

perovskite solar cells (PSCs). The PSC performance exhibits that NDI-BTH2 as ETL material gave power conversion efficiency (PCE) of 15.4%, while NDI-BTH1 as ETL material obtained PCE of 13.7%. The performance of PSCs is in agreement with the OFET results. It is presumed that improvement in solar cell efficiency of NDI-BTH2-based PSCs is due to increase in number of sulfur atoms in the molecular framework, which enhances the passivation power toward electron trap states on the perovskite layer surface and the binding between the lead of perovskite and the ETL, as well as the well-matched LUMO of NDI-BTH2 toward conduction band of perovskite layer, which in turn enhance electron extraction and transportation from the perovskite layer.

4.4.1 Synthesis and characterization of NDI-BTH1 NDI-BTH2

4.4.1.1 Synthesis of compound 2

In 50 mL clean oven dried round bottom flask, 2-aminothiophenol (1.0 g, 0.0079 mol) and malononitrile (0.63 g, 0.0095 mol) in 25 mL methanol solvent has taken and stirred at room temperature for 5 minutes followed by slow addition of catalytic acetic acid (1 mL). After the addition, reaction mixture was further stirred for 10 h at room temperature. The completion of reaction was monitored by TLC and then solvent was evaporated, the obtained crude solid was washed with methanol to afford orange solid in 92.51 % reaction yield (1.544 g). ^1H NMR (CDCl_3 , 400 MHz) δ ppm = 8.05 (d, 1H, J = 8.19 Hz), 7.90 (d, 1H, J = 8.55 Hz), 7.54 – 7.52 (m, 1H), 7.46 – 7.42 (m, 1H), 4.24 (s, 2H), ^{13}C NMR (CDCl_3 , 100 MHz) 158.18, 152.78, 135.40, 126.68, 125.93, 123.35, 121.69, 114.83, 23.18.

4.4.1.2 Synthetic procedure for compound 3

In 50 mL clean oven dried round bottom flask has charged with 2-aminothiophenol (2.66 g, 0.0212 mol) and malononitrile (0.26 g 0.0039 mol) in 25 mL methanol solvent and stirred at room temperature for 5 minutes, then the acetic acid being used as catalyst was added slowly (1mL). After the addition, reaction mixture was kept stirring for 15 h at refluxed temperature. The completion of reaction was monitored by TLC. Then, reaction mixture was cooled to room temperature; solvent evaporated and obtained solid was washed with methanol. This crude product was further purified by column chromatography by using hexane and ethyl acetate (8:2 v/v) eluent to afford greyish solid in 65 % reaction yield (3.89 g). ¹H NMR (CDCl₃, 400 MHz) δ ppm = 8.05 – 8.03 (d, 2H, J = 8.06 Hz), 7.85 – 7.82 (d, 2H, J = 8.06 Hz), 7.50 – 7.46 (m, 2H), 7.39 – 7.35 (m, 2H), 4.94 (s, 2H).; ¹³C NMR (CDCl₃, 100 MHz) δ ppm = 165.56, 153.00, 135.74, 128.28, 126.18, 125.29, 123.10, 121.58, 38.85.

4.4.1.3 Synthesis of (2E,2'E)-3,3'-(5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[lmn][3,8]phenanthroline-4,9-diyl)bis(thiophene-5,2-diyl))bis(2-(benzo[d]thiazol-2-yl)acrylonitrile) [NDI-BTH 1]

In 50 mL round bottom flask, 5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[lmn][3,8]phenanthroline-4,9-diyl)bis(thiophene-2-carbaldehyde) **1** (150 mg, 0.2113 mmol) 15 mL dry dichloromethane and acetonitrile (1:1), and 2-(benzo[d]thiazol-2-yl)acetonitrile **2** (80.98 mg, 0.4648 mmol) have taken. To this mixture, piperidine was added in catalytic amount and the reaction mixture was stirred at room temperature for 15 minutes followed by refluxing the mixture at 70 °C for 12 h as shown in **Figure 4.19**. Completion of reaction was monitored by TLC. Reaction mixture was cooled, solvent evaporated by rotary evaporator and the crude product was purified by column chromatography on silica gel (100–200 mesh) using dichloromethane and hexane

(1:1) as an eluent to afford black solid NDI-BTH 1 (140 mg, 64.76 %). M.P. 214-216 °C (open capillary, uncorrected); FT-IR (γ , cm⁻¹, KBr) 2921, 2851, 2213, 1705, 1665, 1572, 1428, 1376, 1310, 1251, 1185, 1086, 973, 935, 799, 756, 722, 586, 546.; ¹H NMR (CDCl₃, 500 MHz) δ ppm 8.77 (s, 2H), 8.45 (s, 2H), 8.08 – 8.06 (d, 2H, J = 8.08 Hz), 7.92 – 7.89 (m, 4H), 7.56 – 7.52 (t, 2H, J = 7.17 Hz), 7.46 – 7.42 (d, 2H, J = 7.17 Hz), 7.37 – 7.36 (d, 2H, J = 3.96 Hz), 4.13 – 4.10 (t, 4H, J = 7.47 Hz), 1.72 – 1.66 (m, 4H), 1.38 – 1.25 (m, 20H), 0.86 – 0.84 (t, 6H, J = 6.17 Hz).; ¹³C NMR (CDCl₃, 100 MHz) δ ppm = 161.61, 153.70, 148.17, 138.86, 138.24, 135.77, 135.09, 129.20, 127.68, 127.00, 125.92, 124.07, 123.42, 121.70, 116.61, 102.77, 41.37, 31.75, 29.68, 29.16, 27.97, 27.04, 22.59, 14.06.; MALDI-TOF calculated mass for C₅₈H₅₀N₆O₄S₄. 1023.32. Found: 1023.18 [M]⁺.

4.4.1.4 Synthesis of 4,9-bis(5-(2,2-bis(benzo[d]thiazol-2-yl)vinyl)thiophen-2-yl)-2,7-dioctylb enzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone [NDI-BTH 2]

Dry dichloromethane and acetonitrile solvents (1:1) was taken in 50 mL oven dried round bottom flask, to this solvent mixture compound 5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[lmn][3,8]phenanthro line-4,9-diyl)bis- (thiophene-2-carbaldehyde) 127 (150 mg, 0.2113 mmol and bis(benzo[d]thiazol-2-yl)methane 3 (282.38 mg, 0.4648 mmol) were added. Piperidine was added in a catalytic amount and the resulting mixture was stirred at room temperature for 15 minutes followed by refluxed at 70 °C for 12 h. as shown in **Figure 4.19**. After completion of reaction, mixture was cooled to room temperature and solvent was evaporated by rotary evaporator. The crude product was purified by column chromatography on silica gel (100–200 mesh) dichloromethane: hexane (1:1) as an eluent to afford green solid NDI-BTH 2 (190 mg, 72.57 %). M.P. 240-242 °C (open capillary, uncorrected); FT-IR (γ , cm⁻¹, KBr) 3447, 3056, 2921, 2851, 1703, 1664, 1566, 1435, 1376, 1311, 1246, 1184, 1093, 1046, 919, 868, 792, 755, 723, 546, 429.; ¹H NMR (CDCl₃, 400 MHz) δ ppm = 8.54 (s, 2H), 8.22 (s, 2H), 8.16 – 8.14 (d, 2H, J = 8.07 Hz), 8.02 – 8.00 (d, 2H, J = 8.19 Hz), 7.95 – 7.93 (d, 2H, J = 7.82 Hz), 7.82 – 7.80 (d, 2H, J = 7.94 Hz), 7.49 – 7.34 (m, 10H), 7.13 – 7.12 (d, 2H, J = 3.79 Hz), 3.98 – 3.94 (t, 4H, J = 7.21 Hz), 1.60 – 1.54 (m, 4H), 1.30 – 1.25 (m, 20H), 0.88 – 0.84 (t, 6H, J = 6.48 Hz).; ¹³C NMR (CDCl₃, 100 MHz) δ ppm = 167.31, 162.63, 162.06, 161.82, 154.04,

153.43, 146.47, 140.39, 139.51, 137.25, 136.24, 135.51, 135.21, 131.45, 128.50, 127.64, 126.81, 126.10, 125.69, 125.54, 125.35, 124.26, 123.58, 122.15, 121.69, 41.41, 32.07, 29.99, 29.49, 28.19, 27.35, 22.92, 14.39.; MALDI-TOF calculated mass for C₇₀H₅₈N₆O₄S₆. 1239.64. Found: 1239.19 [M]⁺.

Figure 4.19 Synthetic pathway of NDI-BTH1 and NDI-BTH2

4.4.2 OFET Device Fabrication Method

The charge transport property of NDI-BTH 1 and NDI-BTH 2 were investigated by the bottom-gate top-contact (BGTC) organic thin-film field effect transistors (OTFTs) with the n-octadecyltrimethoxysilane (OTS) modified SiO₂ (300nm, C_i = 11 nF/cm²) as dielectric layer, the highly n-doped silicon wafer as gate electrode and the thermally evaporated gold as source/drain electrodes. The thin film was obtained by spin-coating

4.4.3 Results and Discussion

Thermal gravimetric analysis (TGA) was employed to investigate the thermal stability of NDI-BTH1 and NDI-BTH2 at the heating rate of 10 °C/min under a nitrogen atmosphere. TGA exhibited good thermal stabilities of NDI-BTH1 and NDI-BTH2 with the 5% weight loss temperatures (T_d) over 396 °C and 318 °C. Compound NDI-BTH2 exhibited two weight loss temperatures at 318 °C and 435 °C, suggesting that this compound undergoes two decomposition processes. The good thermal stability of NDI-BTH1 and NDI-BTH2 provided a base for wide range of thermal annealing for the device optimization of OFETs and PSCs. The as-obtained NDI-BTH1 and NDI-BTH2 show the melting points at 214-216 °C and 240-242 °C, respectively, indicating both chromophores are stable enough for device fabrications.

The UV-vis absorption spectra of NDI-BTH1 and NDI-BTH2 in solution state as well as thin-film state were depicted in **Figure 4.20 a**. The UV-vis spectra of NDI-BTH1 exhibited two maxima absorption peaks at 395 nm and 510 nm, whereas the optical absorption of their thin-film showed peaks at 415 nm and 580 nm.

Figure 4.20 (a) UV-vis absorption spectra in dichloromethane (1×10^{-5} M); (b) cyclic voltammogram of NDI-BTH1 (red line) and NDI-BTH2 (violet line) in dichloromethane (5×10^{-4} M)

Table 4.5 The optical and electrochemical properties of NDI-BTH 1 and NDI-BTH 2

Compound	λ_{onset} (nm)	$E_{\text{onset red}}$ (V)	HOMO (eV)	LUMO (eV)	E_g
NDI-BTH 1	750	-0.374	-5.979	-4.326	1.653
NDI-BTH 2	806	-0.457	-5.781	-4.243	1.538

The absorption of NDI-BTH1 in thin-film exhibited 20 nm and 70 nm bathochromic-shifts while NDI-BTH2 showed two maximum absorption band wavelengths at 384 nm and 540 nm in solution state as shown in **Figure 4.20 a**. The thin-film state of NDI-BTH2 displayed absorption maxima wavelengths at 426 nm and 625 nm with red-shift of 42 nm and 85 nm. NDI-BTH2 thin-film state exhibited greater bathochromic shifts compared to those of NDI-BTH1, which suggests that the flanked benzothiazole facilitates stronger π - π interaction. The higher energy absorption peak at 300-500 nm can be attributed to the π - π^* transitions whereas the lower energy absorption band at 500-800 nm should be ascribed to the intramolecular charge transfer (ICT) effect. The bathochromic absorption spectral shifts are attributed to strong intermolecular interactions and should be instrumental for charge mobilities. The optical absorption onset wavelength (λ_{onset}) based on thin-film absorption of NDI-BTH1 and NDI-BTH2 were employed to calculate the optical band gap ($E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$) and were summarized in **Table 4.5**. The onset absorption of NDI-BTH1 and NDI-BTH2 are 750 nm and 806 nm, respectively. The estimated E_g^{opt} of NDI-BTH1 and NDI-BTH2 were found to be 1.653 eV and 1.538 eV, respectively. To determine LUMO energy level, cyclic voltammetry (CV) measurements of NDI-BTH1 and NDI-BTH2 were conducted in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate and are depicted in **Figure 4.20 b** and are listed in **Table 4.5**. The onset reduction potentials ($E_{\text{red}}^{\text{onset}}$) for NDI-BTH1 and NDI-BTH2 were determined and found to be -0.374 V and -0.457 V, respectively. Therefore, by employing the equation: $E_{\text{LUMO}} = -q (E_{\text{red}}^{\text{onset}} + 4.7)$, the corresponding LUMO energies of NDI-BTH1 and NDI-BTH2 were estimated to be -4.326 eV and -4.243 eV, respectively (**Table 4.5**). The LUMO energy levels of NDI-BTH1

and NDI-BTH2 are lower compared to unsubstituted NDIs.^[36] This may be attributed to the elongation of π -conjugation and induction of electron due to the incorporation of functional subunits. The low LUMO energies of NDI-BTH1 and NDI-BTH2 indicate that both compounds may have good electron-transporting abilities and could exhibit better performance in OFETs. By applying the equation: $E_{\text{HOMO}} = E_{\text{g}}^{\text{opt}} + E_{\text{LUMO}}$, the highest occupied molecular orbital (HOMO) energies of NDI-BTH1 and NDI-BTH2 were determined to be -5.979 eV and -5.781 eV, respectively, as shown in **Table 4.5**. The perovskite $\text{FAyMA}_{1-y}\text{PbI}_{3-x}\text{Cl}_x$ layer was deposited onto the cleaned ITO substrate, pre-coated with the PEDOT: PSS layer using two steps spin cast coating method. Spin-coating were performed at first stage for 15 seconds with 1000 rpm, followed by second step at 5000 rpm for 25 seconds.

Figure 4.21 (a) SEM of the perovskite layer surface; (b) XRD pattern of prepared perovskite layer; (c) UV-vis absorption spectrum of perovskite layer; (d) band gap of perovskite layer from Tauc plot curve.

Then 0.6 mL of toluene was dripped onto perovskite layer and the film were thermally treated at 100 °C for 20 min. The perovskite layer was examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis as depicted in **Figure 4.21 a** and **Figure 4.21b**, respectively. As shown in **Figure 4.21 a**, SEM image showed the well-developed grain morphology with crystalline platelets of pristine perovskite layer. These platelets were appeared to be hundreds of nanometer in length scale and without any pin holes. Furthermore, the XRD patterns of the deposited perovskite layer was examined, which exhibits five significant characteristic peaks at 43.2°, 41.2°, 31.9°, 28.5° and 14.2°. These peaks can be attributed to the (330), (213), (220) and (110) crystal planes of FAyMA1-yPbI3-xClx, respectively. In XRD analysis no significant peak was observed at 12.6°, indicating absence of free PbI₂ in the perovskite layer. **Figure 4.21 c** depicts the UV-vis absorption spectra of pristine perovskite film. The corresponding absorption onset value for FAyMA1-yPbI3-xClx was observed at ~785 nm. The calculated optical band gap from onset absorption value is ~1.58 eV. The calculated band gap was supported by recording the band gap of perovskite layer using Tauc plot as shown **Figure 4.21 d**.

Figure 4.22 (a) Inverted perovskite solar cell device architecture fabricated in this work; (b) Energy level diagram of each layer used in this work.

The schematic structure of inverted p-i-n structured PSCs used in this study with NDI-BTH1 and NDI-BTH2 as ETL is illustrated in **Figure 4.22a**. The PSCs device architecture is fabricated as ITO/PEDOT: PSS/ FA_yMA_{1-y}PbI_{3-x}Cl_x/ETLs/Ag, where a perovskite light harvester is sandwiched between the bottom poly (3, 4-ethylenedioxythiophene): poly (styrene sulphonate) i.e. PEDOT: PSS hole transport layer (HTL), which is deposited on indium tin-oxide (ITO), and the upper n-type semiconductor ETLs. The HTL material extracting the holes from the perovskite layer and collected to the anode (ITO). Whereas, the ETL materials facilitating the efficient electron extraction from perovskite layer and transport to the cathode, silver (Ag) electrode, at the top. **Figure 4.22 b** provides a schematic illustration of the corresponding energy level diagram for the layers used in this PSCs study. As shown in **Figure 4.22 b**, LUMO level of NDI-BTH1 and NDI-BTH2 are -4.32 eV and -4.24 eV, respectively, which are close to the conduction band of the perovskite layer. The well-matched energy levels facilitate the favorable electron transfer from the perovskite layer to the Ag electrode *via* ETL layers based on NDI-BTH1 and NDI-BTH2. The HOMO energy levels of NDI-BTH1 (-5.979 eV) and NDI-BTH2 (-5.781 eV) are lower than the valence band of the FA_yMA_{1-y}PbI_{3-x}Cl_x layer, which supports their hole blocking ability towards the Ag electrode. These results imply that NDI-BTH1 and NDI-BTH2 are the promising ETL materials in inverted PSCs.

The passivation power toward electron trap centres of NDI-BTH2 is higher than that of NDI-BTH1, which was confirmed by steady-state photoluminescence (PL). Time-resolved photoluminescence (TRPL) of FA_yMA_{1-y}PbI_{3-x}Cl_x layer, NDI-BTH1-perovskite bilayer and NDI-BTH2-perovskite bilayer were performed to gain detail insight into the charge extraction process. These results are depicted in **Figure 4.23 a** and **Figure 4.23 b**. Upon excitation at 532 nm, pristine perovskite film without ETL exhibits strong photoluminescence at 775 nm. The FA_yMA_{1-y}PbI_{3-x}Cl_x film with the NDI-BTH1 and NDI-BTH2 as the ETL, displayed the quantitative quenching of photoluminescence with blue shift of maximum peak. Interestingly, NDI-BTH1 and NDI-BTH2 showed passivation of electron trap centres. However, NDI-BTH2 has stronger passivation property. Regarding to the maximum peak of bare perovskite layer PL emission, the maximum peak of NDI-BTH2/ perovskite bilayer PL emission showed more blue-shifting than maximum peak of

Figure 4.23 (a) Steady-state photoluminescence characteristic of perovskite layer, perovskite /NDI-BTH1 bilayer and perovskite/NDI-BTH2 bilayer; (b) Time-resolved TRPL of perovskite/NDI-BTH 1 bilayer as well as perovskite/NDI-BTH2 bilayer.

NDI-BTH1/ perovskite bilayer PL emission. [37, 38] Thus, it is confirmed that the NDI-BTH1 and NDI-BTH2 are the strong electron acceptors. Passivation properties were further confirmed by Time-resolved photoluminescence (TRPL) decay experiments of perovskite/ NDI-BTH1 and perovskite/NDI-BTH2 bilayer (**Figure 4.23 b** and **Table 4.6**). The PL lifetimes of perovskite/NDI-BTH1 and perovskite/NDI-BTH2 bilayers were calculated by using an exponential decay with double exponential function 1.

$$Y = Y_0 + A_1e^{-x/\tau_1} + A_2e^{-x/\tau_2} \quad (1)$$

Where τ_1 can be ascribed to possible mechanism; non-radiative recombination of charge carriers in perovskite layer and transfer of electrons from perovskite layer to ETL. τ_2 represents the radiative recombination of charge carriers inside perovskite layer.

Table 4.6 TRPL calculated amplitudes A1, A2 and lifetimes τ_1 , τ_2 from **Figure 4.23b**

	τ_1 (ns)	A1	τ_2 (ns)	A2
NDI-BTH1	8.86	32668.80	41.35	10385.07
NDI-BTH2	8.62	28188.18	48.15	10615.22

By investigation of τ_1 of each molecule on perovskite layer, it is noted that, the extraction of electrons from perovskite layer by NDI-BTH2 is little faster than NDI-BTH1. The longer

lifetime τ_2 of NDI-BTH2/perovskite bilayer than τ_2 of NDI-BTH1/perovskite bilayer indicated that NDI-BTH2 has stronger passivation property toward electron trap centres than NDI-BTH1. ^[39, 40] In perovskite/NDI-BTH1 and perovskite/NDI-BTH2 bilayers, the life-time τ_1 are 8.86 ns and 8.62 ns, respectively. The PL life-time for these ETL on $\text{FA}_{1-y}\text{MA}_y\text{PbI}_{3-x}\text{Cl}_x$ layer were found to significantly decrease comparing that of bare perovskite layer (**Table 4.6**). These results revealed faster charge transport and more efficient electron extraction from the perovskite films to NDI-BTH1 and NDI-BTH2 layers. These properties could lead to suppress electron/hole recombination and in turn increases the short-circuit current density (J_{sc}) and fill-factor (FF). These results clearly demonstrate that NDI-BTH1 and NDI-BTH2 are promising ETL entities comparable with conventional fullerene acceptors such as PC_{61}BM in inverted p-i-n PSCs.

The detailed experiments for fabrication procedure of inverted PSCs are well demonstrated in the experimental section. Under stimulated solar irradiation (AM 1.5, 100 mW cm^{-2}), the current density-voltage (J - V) characteristic curves were measured for the inverted PSCs incorporated with NDI-BTH1 and NDI-BTH2 as ETLs. **Figure 4.24 a** presents the optimal J - V curves of the inverted p-i-n PSC device with increasing concentration of the NDI-BTH1 ETLs of 6 mg/mL, 8 mg/mL and 10 mg/mL. The detailed PSCs photovoltaic parameter values are summarized in **Table 4.7**. The optimal inverted PSC device with NDI-BTH1 (6 mg/mL) ETL materials yields a power conversion efficiency (PCE) of 11.3%. By applying NDI-BTH1 with concentration of 6 mg/mL, the lower PCE can be associated with the discontinuous ETL thin-film morphology formation over perovskite layer and might lead to charge recombination. As depicted in **Figure 4.24 a and Table 4.7**, the PCE of 13.7% is obtained when the PSCs device fabricated with NDI-BTH1 as ETL (8 mg/mL). As shown in **Table 4.7**, the other parameters such as an open circuit voltage (V_{oc}) of 0.94 V, a short circuit current (J_{sc}) 21.30 mA/cm^2 and a fill factor (FF) of 60% are obtained from the NDI-BTH1 based devices. The higher J_{sc} , V_{oc} and FF values for PSC device based on NDI-BTH1 ETL are attributed to the higher electron mobility of NDI-BTH1. When the concentration of NDI-BTH1 as ETL reaches 10 mg/mL, each photovoltaic parameter shows considerable decrease with PCE of 10.6%. The decrease in parameters might be due to the higher thickness of aggregated ETL with increase in concentration. The device based on higher thickness of ETL exhibits increased series resistance (R_s) which may lead to

lower the FF. The statistical histograms of inverted p-i-n PSCs for 27 individual devices with optimum concentration of NDI-BTH1 are depicted in **Figure 4.24 b**. The PSCs devices displayed slight variations in PCE. Though photovoltaic performance slightly varied, the devices are reproducible. Furthermore, the solar cells were fabricated with NDI-BTH2 as ETLs. The current density-voltage (J - V) curves of the inverted p-i-n PSC devices based on NDI-BTH2 as an ETL thin film is depicted in **Figure 4.24 c**. The PSC devices were fabricated an optimized with various concentration of NDI-BTH2 such as 6 mg/mL, 8 mg/mL, 10 mg/mL and 12 mg/mL. The resulted photovoltaic parameters of these PSCs are compared with photovoltaic parametrs of PCBM-based PSC and summarized in **Table 4.7**. As shown in **Figure 4.24 c and Table 4.7**, the PSC device based on NDI-BTH2 ETL with 6 mg/mL concentration exhibited 11.9% efficiency. When NDI-BTH2 ETL with 8 mg/mL concentration was employed for PSC device fabrication, the highest efficiency of 15.4% with short circuit current (J_{sc}) 22.13 mA/cm², open circuit voltage (V_{oc}) of 0.98 V, and a fill factor (FF) of 71% was obtained. The higher PCE is associated with the higher electron mobility shown by NDI-BTH2 ETL. Beyond the optimum concentration such as for 10 mg/mL and 12 mg/mL, all of the parameters start to decrease. When the concentration reaches to 12 mg/mL, considerable decrease in each parameter was observed (**Table 4.7**, entry 4). The explanation for photovoltaic parameters decrease is attributed to the rough thin film formation due to higher concentration, which might lead to the aggregation of the ETL on perovskite thin-film, which in turn results into increase in series resistance and decrease in FF. **Figure 4.24 d** shows the statistical efficiency parameters were obtained by fabrication of 27 identical PSC devices employing 8 mg/mL of NDI-BTH2 as ETL. The obtained results suggest though there are small variation in PCEs and the device architecture is an efficient one. The photovoltaic parameters of the optimized PCE device for NDI-BTH2 ETL (8 mg/mL) shows higher PCE of 15.4% compared to 13.7% PCE of PSCs device fabricated using NDI-BTH1 as ETL. The increase in efficiency of PSC with NDI-BTH2 ETL is attributed to (i) its excellent J_{sc} value (22.13 mA/cm²), (ii) higher electron mobility as shown by OFETs, (iii) lower band gap, and (iv) well matched LUMO of NDI-BTH2 with conduction band of perovskite layer. The increase in sulphur atoms leads to more interaction between ETL and I or Pb of perovskite through S-I and S-Pb bonding, which helps in passivation of under-coordinated Pb-atoms

Figure 4.24 (a) J - V curves of PSCs with different concentrations of NDI-BTH1 and (b) distribution of PSCs efficiency for perovskite solar cell with the optimum concentration of NDI-BTH1 as ETL, (c) J - V curves of PSCs with different concentrations of NDI-BTH2 and (d) distribution of PSCs efficiency for perovskite solar cell with the optimum concentration of NDI-BTH2 as ETL.

Positive charges under coordinated Pb-atoms act as electron trap centres, which resulted from anti-solvent dripping during the fabrication of perovskite layer. In NDI-BTH2 four benzothiazole moieties and in NDI-BTH1 two benzothiazole subunits are present. The increase in sulphur-atoms yields lower the LUMO level of NDI-BTH2 and matches with the conduction band of $\text{FA}_y\text{MA}_{1-y}\text{PbI}_{3-x}\text{Cl}_x$. This might lead to enhance charge extraction efficiency from perovskite layer and transportation to the Ag cathode is higher. It is presumed that these parameters are involved to enhance the PCE of PSCs devices with NDI-BTH2 ETL. The I- V curves of the inverted PSCs devices with the NDI-BTH1 and NDI-BTH2 ETLs in the dark was also investigated as depicted in **Figure 4.25**. The dark current curves clearly display that the leakage current of the NDI-BTH2 based device is slightly lower than that of the NDI-BTH1 PSC device. In addition, the rectifying behaviour significantly appeared stronger in NDI-BTH2 based devices than NDI-BTH1 based devices.

It is presumed that the NDI-BTH2 ETL has higher coverage on the perovskite thin-film compared with the NDI-BTH1 ETL, which ultimately prevent the leakage of current.

Figure 4.25 Dark I-V curves of NDI-BTH1 and NDI-BTH 2 based devices

Table 4.7 Photovoltaic parameters of fabricated PSCs with different concentration of NDI-BTH 1 NDI-BTH 2 optimum concentration of PCBM.

	Conc. (mg/mL)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
NDI-BTH 1	6	19.95	0.94	60	11.3
	8	21.30	0.96	67	13.7
	10	19.65	0.96	56	10.6
NDI-BTH 2	6	21.17	0.94	60	11.9
	8	22.13	0.98	71	15.4
	10	19.96	0.96	64	12.3
	12	17.85	0.91	58	9.4
PCBM	22	22.7	0.99	69	15.6

To better understand the behaviour of the NDI-BTH1 and NDI-BTH2 ETLs materials on the interfacial recombination at the interface between the ETL and the $FA_yMA_{1-y}PbI_{3-x}Cl_x$ in the performance of PSCs devices, the electrochemical impedance spectroscopy (EIS) method was applied. The EIS is the effective techniques to get an in-depth idea about

interfacial behaviour in PSCs. The EIS properties are investigated in the dark under forward biases. The characteristic Nyquist plots of PSCs device with NDI-BTH1 and NDI-BTH2 ETLs are depicted in Figure 10, which gives the information about the photogenerated hole/electron pairs and the charge transfer resistance.^[41] As shown in **Figure 4.26**, for PSCs with NDI-BTH1 and NDI-BTH2 ETLs exhibits two semicircles with higher and lower frequency regions. These semicircles are related to the two different charge transfer properties. At higher frequency in both spectra an arc is observed, which represents the charge transfer resistance. In fact, the charge transfer resistance of NDI-BTH2-based devices is slightly lower than that of NDI-BTH1-based devices. By fitting Nyquist plot of NDI-BTH1-based device, we got $R_1 = 14.1 \, \Omega$, $R_2 = 2270 \, \Omega$, $R_3 = 2.4 \times 10^5 \, \Omega$, $CPE_1 = 2.04 \times 10^{-8} \, F$ and $CPE_2 = 4.47 \times 10^{-6} \, F$. For NDI-BTH 2-based device, we got $R_1 = 10.94 \, \Omega$, $R_2 = 1637 \, \Omega$, $R_3 = 2.1 \times 10^5 \, \Omega$, $CPE_1 = 1.97 \times 10^{-8} \, F$ and $CPE_2 = 5.28 \times 10^{-6} \, F$.

Figure 4.26 Electrochemical impedance spectroscopy characterization of PSCs devices with optimum concentration of NDI-BTH1 and NDI-BTH2 ETLs.

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Chapter 5

Novel Pyrene-Based Small Molecules as Electron Transporting Material in Inverted Perovskite Solar Cells

*In this study, two novel small organic molecules (PTTI-1 and PTTI-2, the difference between them is the position of sulfur atom in thieno[3,4-*b*]thiophene(TT)) are designed and synthesized through introduction of the pyrene unit as the central building block and TT as the conjugated linking units. The as-prepared compound have been demonstrated as electron transport layers (ETLs) for perovskite solar cells (PSCs), and PTTI-1 shows a better power conversation efficiency (PCE) value of 15.37%, higher than that of PTTI-2 (11.07%), which may be due to the suitable energy level, strong passivation behavior, and higher electron mobility of PTTI-1. Our study clearly indicates that the sulfur position in this type of electron-transport materials plays an important role in influencing the performance of PSCs. More importantly, the devices show decent stability, where PTTI-1-based devices retain about 83% of its initial stability after 10 days of testing.*

5.1 Introduction

To push up the power conversation efficiency (PCE) in inverted PSCs, discovering appropriate organic HTL and ETL materials plays a vital role.^[1] There has been vast research focusing on exploring novel HTL materials.^[2-4] As the counterpart, the progress on ETL materials is slower. To ensure that n-type materials have better performance in PSCs, they should have good solubility, high electron mobility, and suitable energy levels aligned with perovskite materials.^[5] Currently, most of the present electron-transport materials are based on n-type organic semiconductors, especially those with large planar π -conjugated structures. Some of the representative small molecules include imine compounds (hexaazatrinaphtho [2,3-c] [1,2,5] thiadiazole (HATNT) and hexaazatrinaphthylene (HATNA)^[6,7]), which can exhibit best PCE result higher than 18%, and imide compounds (e.g. perylenediimide (PDI)^[8-10], naphthalene imide (NDI)^[11-15] and even coronene diimide (CDIN)^[16]), which can also displayed promising photovoltaic performance up to 20%. The rigid planar structures of the above-mentioned materials as well as the low-lying LUMO energy level were proven to be favourable for electron transport. Recently, non-fullerene acceptors in organic solar cells (OSCs) constructed from indacenodithiophene (IDT), indacenodithieno[3,2-b]thiophene (IDTT) and their analogues have attracted wide attention due to their tuneable energy levels and good charge transport, resulting from the rigid multi-fused ring. With these intrinsic advantages, they were also utilized as ETL materials for PSCs and excellent PCE results up to 19% were obtained, which encouraged researchers to discover more novel efficient ETL materials.^[5, 17-20] With a perfect planar structure and ten possible functional positions, pyrene has been widely used as a building core to prepare various active components for organic electronics including organic light-emitting diodes (OLEDs),^[21-22] organic field-effect transistors (OFETs),^[23-25] organic solar cells (OSCs)^[26] and even batteries^[27]. In addition, pyrene is also employed as an important building block to construct the polycyclic aromatic hydrocarbons (PAH) in the author's groups.^[28-33] Nevertheless, despite of possessing outstanding photoelectrochemical properties,^[21] pyrene was rarely introduced as a donor unit to construct n-type materials as ETLs for PSCs. In this work, for the first time, the central building block of the former ETL molecules based on the indacenodithiophene (IDT)

and its analogues was replaced with pyrene as the donor building block and two novel small molecules 2,2'-((2Z,2'Z)-(((5,5,11,11-tetrakis(4-(octyloxy)phenyl)pyreno[4,5-d:9,10-d']bis([1,3]dioxole)-2,8-diyl)bis(2-(2-ethylhexyl carboxylate)thieno[3,4-b]thiophene-6,4-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (PTTI-1) and 2,2'-((2Z,2'Z)-(((5,5,11,11-tetrakis(4-(octyloxy)phenyl)pyreno[4,5-d:9,10-d']bis([1,3]dioxole)-2,8-diyl)bis(2-(2-ethylhexyl carboxylate)thieno[3,4-b]thiophene-4,6-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (PTTI-2) as ETL materials were synthesized. It is worth to note that a large number of previous researches have demonstrated that the perpendicular tetraphenyl substituents on the IDT and their analogue units could effectively increase the steric hindrance, reduce the intermolecular interaction, and thus prevent the over self-aggregation and large phase separation in the film, which will facilitate the transport and the separation of electrons.^[34] Therefore, in this work, to increase the solubility, enhance the electron density of the donor pyrene part and facilitate the molecular packing of these two ETL compounds, four alkoxy groups, which are perpendicular to the pyrene plane, were intentionally introduced on the 4,5,9,10- positions through one step diazo reaction with pyrene-4,5,9,10-tetraone. Meanwhile, there have been reported that the sulfur atom could form interfacial S-I or S-Pb interaction to passivate the crystal surfaces of the perovskite and was beneficial for enhancing the performance of PSCs.^[12] Hence, the thieno[3,4-b]thiophene unit was brought into as a bridge in the two novel molecules and the influence of the different position of sulfur atoms on the photovoltaic performance were also systematically investigated. The performance of these two molecules were evaluated and a maximum PCE of 15.37% was obtained for PTTI-1, which was higher than that of PTTI-2 (11.07%). The reasons accounting for their different PSCs performances were also studied.

Figure 5.1 Synthetic route to PTTI-1 and PTTI-2

5.2 Synthesis of PTTI1 and PTTI2

As shown in **Figure 5.1**, compounds 1^[35, 36] and 2^[37, 38] were synthesized from the commercially-available chemicals pyrene and 4,4'-dihydroxybenzophenone according to the reported literatures through a two-step reaction, respectively. Following a similar procedure,^[39] compound 3 was obtained by injecting the solution of 2 into the anhydrous THF solution of 1 at 0 degree under argon protection, and further reacted with bis(pinacolato)diboron to form the key intermediate 4 containing boron ester group in high yield (92%).^[40] Afterwards, compound 4 reacted with the 2-ethylhexyl 6-bromo-4-formylthieno[3,4-b]thiophene-2-carboxylate to form the aldehyde intermediate, which could be further transformed into the designed target molecule via reacting with the excessive building block 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile.^[41]

Figure 5.2 **a)** UV/Vis absorption (10^{-5} M solution) and thin film of PTI-1 and PTI-2; **b)** CV of PTI-1 and PTI-2; **c)** Structure of p-i-n PSC device in this work; **d)** Energy levels diagram of each material used in this work.

The combined yield for these two-step reactions is around 50% for PTI-1. However, when the position of sulfur atom changed from isomer 5 to isomer 6, the yield of the coupling reaction decreased sharply to $\sim 22\%$. In the final step, PTI-2 could be successfully obtained by adopting the same procedure to prepare PTI-1. All the compounds were confirmed by NMR and MS spectra as shown in appendix 2

5.3 Results and discussion

The UV-Vis absorption spectra of PTTI-1 and PTTI-2 were measured in CH₂Cl₂. As shown in **Figure 5.2 a**, both PTTI-1 and PTTI-2 displayed an apparent broad absorption between 500 and 700 nm with the $\lambda_{\max}$ at 638 nm and 612 nm, respectively. Meanwhile, the λ_{onset} was blue-shifted from 694 nm (for PTTI-1) to 668 nm (for PTTI-2). By using the equation of $E_g^{\text{opt}} = 1240 \text{ nm} / \lambda_{\text{onset}}$, the band gaps of PTTI-1 and PTTI-2 are calculated to be 1.79 eV and 1.86 eV, respectively. For the thin films of PTTI-1 and PTTI-2, λ_{onset} was red-shifted to 756 nm and 735 nm, respectively. Thus, the band gaps of PTTI-1 and PTTI-2 decreased to 1.64 eV and 1.69 eV, accordingly. Electrochemical properties of PTTI-1 and PTTI-2 were tested through cyclic voltammetry (CV) in a dry CH₂Cl₂ solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as electrolyte and the corresponding data were provided in **Figure 5.2 b**. The $E_{\text{red}}^{\text{onset}}$ of PTTI-1 and PTTI-2 were recorded to be −0.88 V and −0.98 V with ferrocene as a standard. Thus, their LUMO energy levels were calculated to be −3.92 eV and −3.82 eV respectively by using the empirical equation of $\text{LUMO} = -(4.80 + E_{\text{red}}^{\text{onset}})$. Consequently, their HOMOs were calculated to be −5.56 eV and −5.51 eV accordingly by the equation of $\text{LUMO} = \text{HOMO} + E_g^{\text{opt}}$. The corresponding data are summarized in **Table 5.1**

Table 5.1 Physicochemical properties of PTTI-1 and PTTI-2.

Molecule (thin film)	λ_{onset} [nm]	E_g^{opt} [eV]	$E_{\text{red}}^{\text{onset}}$ [V]	LUMO [eV]	HOMO [eV]
PTTI-1	756	1.64	−0.88	−3.92	−5.56
PTTI-2	735	1.69	−0.98	−3.82	−5.51

Device Performance. To evaluate the appropriateness of PTTI-1 and PTTI-2 as ETLs, PTTI-1 and PTTI-2 have been employed as ETLs materials in p-i-n PSC with the following structure: ITO/PEDOT: PSS/Perovskite layer/ETLs/Ag as shown in **Figure 5.2 c**. PEDOT: PSS is utilized as a hole transport layer, which can block the electrons moving to anode and extracts holes from perovskite layer. The light photons can be absorbed by perovskite

layer, wherein excitons originate and dissociate to electrons and holes that can be extracted by ETLs and PEDOT: PSS, respectively

Figure 5.3 XRD pattern of the as-prepared perovskite layer.

Figure 5.4 a) SEM of the perovskite layer surface and b) cross-section SEM of perovskite layer, sandwiched between ITO/PEDOT: PSS and ETL.

Finally, Ag electrode and ITO have been used to collect the electrons and the holes, respectively. **Figure 5.2 d** shows the energy levels of materials used in this work. It is noteworthy that, the LUMO of PTTI-1 matches well with the conduction band of perovskite layer, generating the driving force that enhances the electron extraction and intuitive electrons transfer from perovskite layer to Ag electrode.

Figure 5.5 a) UV-vis absorption spectrum of perovskite layer, b) Band gap of perovskite layer from Tauc plot curve.

More importantly, its HOMO is deeper than valence band of perovskite layer, which supports the holes blocking property of PTTI-. Such merits decrease the leakage current and enhance V_{OC} and FF. Undesirably, PTTI-2 shows higher LUMO compared with the conduction band of perovskite layer, which produces electrons accumulation and charges recombination, leading to V_{OC} loss and the deteriorated FF.

Figure 5.3 shows the X-ray diffraction pattern of perovskite layer, where three characteristic peaks significantly appeared at 14.2° , 28.5° , and 31.9° that be assigned to the (110), (220), and (310) planes of the perovskite crystal. Scanning electron microscope (SEM) has been utilized to further investigate the quality and the morphology of the as-prepared perovskite layers. As shown in **Figure 5.4 a** and **b**, the as-prepared perovskite layer surface showed large grains with pin holes free surface. More importantly, cross

section SEM of perovskite layer indicated that the perovskite layer consisted of giant grains in vertical dimension, respectively. **Figure 5.5 a** shows the UV-vis absorption spectrum of perovskite layer. The absorption onset approximately equals to 785 nm, which indicates a band gap of 1.58 eV. The value corresponds with the band gap confirmed by Tauc plot as depicted in **Figure 5.5 b**. To fully evaluate PTTI-1 and PTTI-2 as ETL materials, their PSCs were fabricated. The optimized thickness of each ETL was achieved by utilizing different concentration of PTTI-1 solution in dichlorobenzene (DCB) (6, 8, 10, 12 and 14 mg/ml), as well as, PTTI-2 with different concentration (6, 8, 10, 12 and 14 mg/ml).

Figure 5.6. **a)** *J-V* curves of PSCs with different concentrations of PTTI-1 as ETLs; **b)** *J-V* curves of PSCs with different concentrations of PTTI-2 as ETLs

Table 5.2 Photovoltaic parameters of the as-fabricated PSCs with different concentrations of PTTI-1 and PTTI-2.

Molecule	Concentration [mg/ml]	Jsc (mA/cm ²)	Voc (V)	FF [%]	PCE[%]
PTTI-1	6	18.16	0.981	59.3	10.56
	8	20.20	1.025	68.5	14.20
	10	21.26	1.027	70.4	15.37
	12	19.26	1.027	65.9	13.03
	14	16.02	0.995	58.8	9.40
PTTI-2	6	18.3	0.76	33.0	4.59
	8	20.11	0.905	53.8	9.80
	10	21.15	0.915	57.2	11.07
	12	18.55	0.880	49.0	8.00
	14	14.6	0.73	31.6	3.37

As shown in **Figure 5.6 a**, the as-fabricated devices based on PTTI-1 showed various PCEs with different concentrations of PTTI-1 solutions as an ETL material, whereas the highest PCE of 15.37 % was obtained with 10 mg/ml of PTTI-1 solution with J_{SC} of 21.26 mA/cm², V_{OC} of 1.027 V and FF of 70.4%. The lower concentrations (8 mg/ml and 6 mg/ml) showed a decreased PCE from 14.2 % to 10.56%, which resulted from the decline of J_{SC} and FF. This deterioration was attributed to the low coverage of ETL on perovskite layer, therefore charge recombination increased but FF and J_{SC} decreased. On the contrary, when increasing ETL concentration to 12 mg/ml, the corresponding PCE of the as-fabricated PSC achieved 13.03%. This decreased PCE resulted from the increased thickness of ETL, which resulted in the increased series resistance. Therefore, the declined FF and J_{SC} were observed. Additional increasing to 14 mg/ml deteriorated PCE to 9.4 %. Regrettably, PTTI-2 showed lower PCEs compared with that of PTTI. The highest PCE of 11.07% was obtained for PTTI-2-based PSC with J_{SC} of 21.15 mA/cm², V_{OC} of 0.915 V and FF of 57.2 % in 10 mg/ml as shown in **Figure 5.6 b**. When the concentration of PTTI-2 solution increased gradually to 14 mg/ml or decreased gradually to 8 mg/ml, PCE declined due to the high series resistance and low coverage, respectively, as it was mentioned above. All the

corresponding photovoltaic data are summarized in **Table 5.2**. To compare the as-synthesized molecules in this research with conventional electron transporting materials, PCBM-based devices as control experiments have been fabricated and tested.

To further investigate the effect of ETL concentrations on the performance of devices, electrochemical impedance spectroscopy (EIS) measurements have been conducted in the range of 10^6 Hz to 1 Hz. The results are in agreement with the illuminated *J-V* curves. Nyquist plots showed two significant semi-circles: 1) at low frequency which is related to charge recombination resistance, and 2) at high frequency, which is related to charge transfer resistance. For both molecules at 10 mg/ml, the charge recombination resistance was the highest compared with other concentrations. By increasing the concentration, the charge recombination resistance decreases due to charge accumulation that leads to charge recombination. Decreasing the concentration (less than 10 mg/ml) leads to the low coverage, which also decreases charge recombination resistance. By increasing the concentration of both molecules (more than 10 mg/ml), the charge transfer resistance increased due to the increased thickness as shown in Figure 5.7. By fitting Nyquist plot of PTTI 1-based device and PTTI 2-based device with optimum concentrations of PTTI 1 and PTTI 2 as ETLs. For PTTI 1-based device we got $R_1 = 14.25 \Omega$, $R_2 = 1041 \Omega$, $R_3 = 2.3 \times 10^5 \Omega$, $CPE_1 = 2.4 \times 10^{-8} F$ and $CPE_2 = 4.2 \times 10^{-6} F$. For PTTI 2-based device we got, $R_1 = 14.98 \Omega$, $R_2 = 1124 \Omega$, $R_3 = 1.42 \times 10^5 \Omega$, $CPE_1 = 4.02 \times 10^{-8} F$ and $CPE_2 = 6.45 \times 10^{-6} F$.

Figure 5.7 a) Nyquist plot of PTTI-1-based devices with different concentrations, b) Nyquist plot of PTTI-1-based devices shows charge transfer resistance, c) Nyquist plot of PTTI-2-based devices with different concentrations, d) Nyquist plot of PTTI-2-based devices shows charge transfer resistance.

As shown in **Figure 5.8 a**, strong photoluminescence (PL) was obtained by the excitation of perovskite layer with 532 nm light. The maximum peak of the corresponding PL was 769.02 nm. The as-obtained PL, which was produced by the excitation of PTTI-1/perovskite bilayer and PTTI-2/perovskite bilayer, quenched with a blue-shifted peak at 760.96 nm and 761.94 nm, respectively. Regarding to these results, it is believed that the passivation property of surface trap states by PTTI-1 is higher than that of PTTI-2, since the surface traps and grain boundaries produce band bending, which decreases the band gap of the surface compared with the band gap of the bulk of perovskite layer as reported by Huang et al. [42, 43]

Figure 5.8 **a)** Steady-state PL of bare perovskite layer, PTTI-1/perovskite bilayer and PTTI-2/perovskite bilayer; **b)** TRPL of PTTI-1/perovskite bilayer and PTTI-2/perovskite bilayer with fitted curves.

Table 5.3 TRPL calculated amplitudes A1, A2 and lifetimes τ_1 , τ_2 from **Figure 5.8 b**.

	A1	τ_1 (ns)	A2	τ_2 (ns)
PTTI-1/Perovskite	1.64379	7.66	0.47534	57.63
PTTI-2/Perovskite	1.28667	15.43	0.33323	46.80

To further investigate the passivation properties of PTTI-1 and PTTI-2, as depicted in **Figure 5.8 b**, time-resolved photoluminescence (TRPL) measurements were carried out and the nascent spectra were fitted regarding to exponential decay equation, $Y = Y_0 + A1e^{-x/\tau_1} + A2e^{-x/\tau_2}$ where A is the amplitude and τ in nano-second (ns) is lifetime of charge carriers. All calculated data are summarized in **Table 5.3**. By resolving the equation (1), two transport processes involved in electron transfer processes, termed as τ_1 and τ_2 were discovered. It is known that τ_1 referred to two possible mechanisms: non-radiative recombination of the charges in perovskite layer and charges transfer to ETL from perovskite layer. The lifetime τ_2 is attributed to charge-radiative recombination inside perovskite layer. [44-46] TRPL confirmed the higher passivation property of PTTI-1 than that of PTTI-2. It is worthy to note that PTTI-1 has higher electron extraction power than that of PTTI-2, whereas τ_1 of PTTI-1/perovskite bilayer is shorter than τ_1 of PTTI-2/perovskite bilayer. This result is ascribed to stronger electron extraction power of PTTI-1 from perovskite layer higher than that of PTTI-2. The longer τ_2 of PTTI-1/perovskite

bilayer than τ_2 of PTTI-2/perovskite bilayer is attributed to stronger trap states passivation of PTTI-1 than PTTI-2. These results were in agreement with these which reported by Bazan and Huang et al. [47]

Figure 5.9. AFM measurements of (10 mg/ mL.) PTTI-1/perovskite and (10 mg/ mL.)PTTI-2/perovskite.

We measured the OFET properties for these two molecules and found out that the electron mobility of PTTI-1 ($\sim 9.0 \times 10^{-4} \text{ m}^2/\text{V.s}$) is much higher than that of PTTI-2 ($\sim 1.5 \times 10^{-4} \text{ m}^2/\text{V.s}$). Hence, the higher PCE of PTTI-1, compared with PCE of PTTI-2-based devices, may be partially ascribed to the high performance of PTTI-1based devices. Furthermore, the well-matched LUMO and HOMO of PTTI-1 to the energy levels of perovskite layer plays a crucial role in enhancing photovoltaic parameters of PTTI-1-based PSCs. Moreover, the strong passivation power of PTTI-1, which is confirmed by steady-state and TRPL, also contributes to its better performance. The surface morphology of PTTI-1 and PTTI-2 on perovskite layer were investigated by AFM as shown in **Figure 5.9**, where the roughness of PTTI-1 (11.2 nm) was lower than roughness of PTTI-2 (12.38 nm). It is believed that the lower roughness of ETL declines the leakage current of the as-fabricated devices. Finally, the I - V curves under dark condition of PTTI-1-based and PTTI-2-based PSCs are in consistent with all previous measurements. **Figure 5.10** shows that the leakage current of PTTI-1-based PSCs is lower than that of PTTI-2-based device. To evaluate the reliability of the as-fabricated devices, 27 devices were prepared with 10 mg/mL of ETL.

The distribution of photovoltaic parameters has been shown in **Figure 5.11**. PTI-1 based PSCs showed neglectable hysteresis as shown in **Figure 5.12**, whereas, the PCE obtained

Figure 5.10 I–V curves of **PTI-1** and **PTI-2**-based devices under dark conditions.

Figure 5.11. Distributions of photovoltaic parameters of PTI-1-based devices and PTI-2-based devices each ETL with 10 mg/mL, a) PCE, b) FF, c) Voc and d) Jsc.

Figure 5.12 . J - V hysteresis curves of PTTI-1-based device.

by scan in reverse direction was 15.37 % and in forward direction was 14.5 %. The surface trap passivation by PTTI-1 could be attributed to the decline of hysteresis of PTTI-1-based PSCs. Stability is another important factor, which can hinder PSCs technology toward their commercialization. Therefore, the stability of PTTI-1-based PSCs was investigated and compared with that of PCBM-based devices. PTTI-1-based device retained 83% of its initial stability after 10 days while PCBM-based devices lost 27 % of its initial stability after 10 days of testing. PTTI-2-based devices showed the worst case. Since the devices lost 33 % of its initial efficiency as depicted in **Figure 5.13**, the high stability of PTTI-1 based devices was attributed to the strong electron traps passivation power of PTTI-1, which decreases the electron recombination and increases operational stability. Our assumption is in agreement with the research done by Naveen et. al. ^[48] Also the reason behind the decent stability of PTTI-1-based PSCs was ascribed to the hydrophobicity nature of PTTI-1 (compared with PCBM based devices), whereas PTTI-1 showed the larger contact angle (100.4°) while PCBM only has 90° as exposed in **Figure 5.14**. All devices were kept in air with the controlled humidity environment (30%) during the period of stability measurement.

Figure 5.13 Stability test diagram of PTTI-1-based device, PTTI-2-based device and PCBM-based device.

Figure 5.14 Contact angles of PTTI-1 and PCBM.

Finally, two new organic compounds (PTTI-1 and PTTI-2) as ETL materials in PSCs were synthesized by first introducing four-alkoxy-substituted pyrene as the donor unit. The best PCE result is 15.37% for PTTI-1, higher than that of PTTI-2 (11.07%), due to the different position of sulfur atom in thieno[3,4-b]thiophene (TT) which may account for a different LUMO energy level, surface passivation, and electron mobility behavior between these two molecules. This study clearly indicates that the sulfur position in the ETLs materials plays an important role in influencing the performance of the as-fabricated PSCs. Moreover,

much stronger donating groups might be necessary to introduce when adopting pyrene as the donor unit in the future.

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Chapter 6

N-type conjugated Polymers-based Electron Transporting Materials in Inverted Perovskite Solar Cells

It is highly desirable to employ n-type polymers as electron transporting layers (ETLs) in inverted perovskite solar cells (PSCs) due to their good electron mobility, high hydrophobicity, and simplicity of film forming. In this research, the capability of three n-type donor-acceptor₁-donor-acceptor₂ (D-A₁-D-A₂) conjugated polymers (pBTT, pBTTz and pSNT) is firstly explored as electron transporting layers because these polymers possess electron mobility as high as 0.92, 0.46 and 4.87 cm²/Vs in n-channel organic transistors, respectively. The main structural difference among pBTT, pBTTz and pSNT is the position of sp²-nitrogen atoms (sp²-N) in the polymer main chains. Therefore, the effect of different substitution positions on the PSC performances was comprehensively studied. The as-fabricated p-i-n PSCs with pBTT, pBTTz and pSNT as ETLs showed the maximum photoconversion efficiencies (PCEs) of 12.8%, 14.4%, and 12.0%, respectively. To be highlighted, pBTTz-based device could maintain 80% of its stability after ten days due to its good hydrophobicity, which was further confirmed by a contact angle technique. More importantly, pBTTz-based device showed a neglected hysteresis.

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6.1 Introduction

Nowadays, inverted perovskite solar cells (p-i-n PSCs) have received more researchers' attentions, attributing to their several promising factors compared with regular perovskite solar cells (n-i-p) PSCs:^[1] (1) The p-i-n PSCs with metal oxide-free charge transporting layers (e.g. organic charge transporting layers) would simplify the fabrication of p-i-n PSCs at low temperature; (2) Organic layers provide more opportunities to fabricate flexible solar cells as well as integrate other devices into flexible substrates; and (3) The replacement of traditional TiO₂ inorganic compounds with organic electron-transporting materials in inverted p-i-n PSCs makes solution-processing large-area fabrication possible. All these advantages of p-i-n PSCs have opened a novel route toward the future commercialization and marketing of p-i-n PSCs.^[2, 3]

From the architecture point of view, PSCs can be classified into two groups according to the arrangement of charge transporting layers: One is the n-i-p PSC, where the electron-transport layer (ETL) is deposited on indium tin oxide (ITO) prior to the perovskite layer,^[4] and the other is the p-i-n PSC, where the ETL is deposited after the perovskite layer.^[5] Although, hole transporting layers were well studied and decent efficiencies could be achieved by HTL (hole-transport layer)-free PSCs,^[6-8] ETL has been considered as a performance-dependent layer in PSCs.^[9] The first p-i-n PSC was fabricated by employing PCBM as an ETL and the power conversion efficiency (PCE) could reach up to 3.9 %.^[10] Few years later, the PCE has been pushed to 21%.^[11] However, the high cost of PCBM as well as its poor film-morphology stability under thermal treatment has become stumbling blocks toward its large scale fabrication.^[12-14] Later on, modified-PCBM compounds have been developed as alternatives of PCBM to enhance the PCE and the stability of p-i-n PSCs.^[15] However, the cost to synthesize these compounds still frustrates scientists for practical applications. Thus, searching for new organic materials to replace PCBM or its derivatives is very important and highly desirable.

Currently, several types of n-type organic small molecules (e.g. azaacenes,^[16, 17] naphthalene diimide (NDI),^[18, 19] perylene diimide (PDI),^[20-23] hexaazatrinaphthylene derivatives (HATNA),^[24] coronene diimide (CDIN),^[25] benzobis(thiadiazole) (B2F)^[26] and

copper phthalocyanine derivatives ($F_{16}CuPc$)^[27] have been developed and employed as ETLs in p-i-n PSCs, and the PCEs based on these molecules as ETLs range from 2% to 19%. In this research, a series of novel n-type organic small molecules was also developed^[28-36] and some of them have been applied as promising ETLs in p-i-n PSCs with the PCE up to 18.2%.^[37-40] However, organic small molecules still face several issues during device fabrication, including poor morphology control (conjugated small molecules are easy to aggregate and crystallize), uneven surface coverage while using dilute solutions, and crack formation. Thus, in order to address these issues, more and more efforts have been made to develop high-performance n-type conjugated polymers.^[41-43] In fact, some of n-type conjugated polymers have shown better electron mobility, higher hydrophobicity, and the simplicity of film forming compared to the n-type small molecules.^[44] Even in this case, the number of the reported PSCs using n-type polymers as ETLs is still much smaller,^[45-47] and the highest reported PCE based on n-type conjugated polymers is about 17 %.^[44] Thus, it is believed that there is still plenty of room left for scientists to search new n-type conjugated polymers as ETLs for enhancing the performance of PSCs. In this study, the authors are interested in some recently reported n-type donor-acceptor₁-donor acceptor₂ (D-A₁-D-A₂) conjugated polymers (namely, pBTT, pBTTz and pSNT).^[48] pBTT, pBTTz and pSNT were employed as ETLs in PSCs and investigated the effect of substitution position of sp^2 -N atoms on the PSC performances. There are two reasons to choose these polymers: (1) These polymers are naphthalene-diimide (NDI)-based n-type polymers (pBTT, pBTTz and pSNT) with field-effect electron mobilities up to 0.92, 0.46 and 4.87 cm^2/Vs , respectively, which should be promising candidates as ETLs in PSCs; and (2) NDI-based polymers have been demonstrated to show a great record of high photovoltaic performances in the field of organic solar cells.^[43,45] p-i-n PSCs were successfully fabricated with pBTT, pBTTz and pSNT as ETLs and the maximum PCEs delivered by these polymers were 12.8%, 14.4%, and 12.0 %, respectively. Although introducing sp^2 -N atoms into the donor thiophene units of pBTT produced pBTTz with a slightly declined electron mobility, the PCE of PSCs was still significantly improved. On the other hand, pSNT with two additional sp^2 -N atoms and very high electron mobility showed a poorer PSC performance. In addition, it was found that the electron-rich sulfur atoms have a strong impact on the passivating of the under-coordinated Pb-atoms, as reflected by the current

density-voltage (J-V) hysteresis curves of the pBTTz-based devices. More importantly, due to the hydrophobic nature of polymers, pBTTz-based devices retained 80% of its stability after ten days. It is worthy to point that, to the best of authors' knowledge, this study is the first demonstration of the effect of sp^2 -N position in polymer main chain (pBTT) on the properties of (D-A₁-D-A₂) n-type polymers as ETLs in PSCs.

6.2 Synthesis and characterization

Three n-type polymers (pBTT, pBTTz and pSNT) were synthesized and characterized according to the reported methods.^[48]

Device fabrication: After etching ITO glass slides to the desired patterns, all slides were cleaned by DI-water, acetone and isopropanol in an ultrasonic bath. The device fabrication was started by spin-cast of PEDOT:PSS as the HTL on ITO at 6000 rpm for 60 s, followed by heat treatment at 140 °C for 15 minutes. Immediately, all slides were transferred to a glovebox for spin coating of perovskite solution. The perovskite solution was prepared by mixing of 1.26 M PbI₂, 0.14 M PbCl₂ and 1.35 M CH₃NH₃I in a mixed solvent of DMSO:GBL (3:7 v,v) at 70 °C for 12 hr. The spin coating technique was processed at two steps. The first step was at 1000 rpm for 20 s, and the second step was at 4000 rpm, after 40 s of starting, 0.65 mL of toluene dripped on the substrate. Then, the perovskite substrate was transferred onto a hot plate and thermally treated by a mixed solvent vapor annealing at 100 °C for 20 min.^[49, 50] The ETL polymers were dissolved in *o*-dichlorobenzene (DCB) with different concentrations (3, 5 and 8 mg/ml). Each polymer solution was spin-casted at 2000 rpm for 60 s and immediately heat-treated at 100 °C for 10 minutes. The final step of fabrication was completed by evaporation of 100 nm of Ag electrode.

6.3 Results and discussion

Three n-type polymers (pBTT, pBTTz and pSNT, **Figure 6.1**) were synthesized according to the reported methods.^[23] It is well-known that inserting electron-withdrawing groups (EWG, such as F, Cl and CN) into the main chains of conjugated polymer strengthens n-type characters, which is beneficial for the efficient electron injection and transport.

Figure 6.1 Structures of the three n-type polymers: pBTT, pBTTz and pSNT.

In this study, sp^2 -N atoms were introduced to the n-type polymers since it is seldom studied in the field of PSCs. Starting from pBTT composed of the NDI and thiophene-benzothiadiazole-thiophene moiety, the replacement of the electron-donating thiophene rings with the thiazole units gave pBTTz, while the incorporation of the diazole unit into the electron-accepting benzothiadiazole moiety produced pSNT (**Figure 6.1**). As a result, these three polymers are a class of n-type polymers suitable for the investigation of the sp^2 -N effect on the PSC performances. **Figure 6.2 (a)** shows the structures of pBTT, pBTTz and pSNT-based p-i-n PSCs. The configuration of the as-fabricated PSCs is built as ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /ETLs/Ag, where poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) acts as an HTL for extracting the holes from the perovskite layer and blocking electron transfer to the anode, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer functions as a light absorbing material, and n-type polymers are employed as ETLs for facilitating the electron transfer to the cathode and blocking the hole transport to the anode. The corresponding energy level diagram is depicted in **Figure 6.2 b**, in which the

lowest unoccupied molecular orbital (LUMO) of pBTTz matched well with the conduction band of the perovskite layer compared to pBTT.

Figure 6.2 (a) Device architecture of inverted PSCs fabricated in this work. (b) Energy levels diagram of each layer used in this work.

Thus, electrons can readily transfer from the perovskite layer to the cathode through the pBTTz layer. In addition, the highest occupied molecular orbital (HOMO) of pBTTz is deeper than the valence band of the perovskite layer, which supports the efficient blocking of holes toward the cathode. Compared with pBTTz, the HOMO and LUMO of pBTT suggest the less efficient electron transfer and hole blocking from the perovskite layer to the cathode. Regrettably, the HOMO of pSNT is approximately similar to the valence band of the perovskite layer, which could result in a negligible hole blocking effect and thus deteriorate the photovoltaic parameters of the as-fabricated PSCs. The light photons can be absorbed by the perovskite active materials, where excitons are generated and dissociated to electrons and holes that can further diffuse through the perovskite material to the carrier-transport layers. Eventually, holes pass through PEDOT:PSS and are collected by the ITO electrode, while electrons pass through the ETL and are collected by the Ag electrode. The as-prepared perovskite films have been characterized by several tools. As shown in **Figure 6.3 (a)**, the crystallinity of the perovskite layer was investigated by XRD. Three characteristic peaks could be found at 14.2° , 28.5° and 31.9° , which can be assigned to the (110), (220) and (310) planes of the perovskite crystal. Scanning electron micrograph

(SEM) (**Figure 6.3 (b)**) indicated that the as-prepared perovskite layer consists of large grains without any pin holes.

Figure 6.3 (a) XRD of the perovskite layer, (b) SEM of the perovskite layer.

Figure 6.4. a) UV-visible spectroscopy of the perovskite layer, b) Tauc plot of perovskite layer and extracted band gap.

UV-visible absorption spectroscopy indicated that the optical band gap of the as-prepared perovskite layer is ~1.58 eV because the optical absorption onset of this layer was observed at 785 nm as shown in **Figure 6.4 (a)** and to further verify the band gap value, Tauc plot has been drawn with extracted band gap as shown in **Figure 6.4 (b)**. The as-prepared perovskite layer also displayed strong photoluminescence under excitation at 532 nm, indicating the high purity of the as-prepared perovskite layer.

Figure 6.5 (a) PL characteristic of bare perovskite, perovskite/PCBM bilayer, perovskite/pBTT bilayer, perovskite/pBTTz bilayer and perovskite/pSNT bilayer. (b) TRPL of bare perovskite, perovskite/pBTTz bilayer and perovskite/PCBM bilayer.

However, this photoluminescence was gradually quenched when the ETLs were deposited on it. The order of quenching was pSNT < pBTT < PCBM < pBTTz (**Figure 6.5 (a)**). Surprisingly, pBTTz has a more efficient quenching effect than the common ETL material PCBM. To further investigate the lifetime of the perovskite/pBTTz and perovskite/PCBM referenced to the bare perovskite, time-resolved photoluminescence (TRPL) measurements were carried out as shown in **Figure 6.5 (b)**. After fitting the resultant TRPL curves and employing the exponential decay equation (1) for the bare perovskite layer, exponential decay equation (2) was applied to the perovskite/pBTTz bilayer and perovskite/PCBM bilayer, as showing below.

$$Y = Y_0 + A_1 e^{-x/\tau_1} \quad (1)$$

$$Y = Y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} \quad (2)$$

Table 6.1 TRPL calculated amplitudes A_1 , A_2 and lifetimes τ_1 , τ_2 from **Figure 6.5 (b)**

	A_1	τ_1 (ns)	A_2	τ_2 (ns)
Bare perovskite	9590	220.98	-----	----
Perovskite/pBTTz	10446	1.77	6798	22.61
Perovskite/PCBM	16904	3.96	42219	40.04
Perovskite/pSNT	13466	3.82	33946	42.8

where A is the amplitude and τ in nano second (ns) is the lifetime of the exciton. All calculated data from **Figure 6.5 (b)** are summarized in **Table 6.1**. The results confirm that the electron transfer from the perovskite layer to pBTTz was more efficient than that from the perovskite to PCBM. All these results indicate that these n-type polymers are promising candidates as ETLs in p-i-n PSCs. The surfaces of pBTT, pBTTz, and pSNT on the perovskite layers were studied through atomic force microscopy (AFM). As shown in **Figure 6.6**, the AFM images of pBTT, pBTTz and pSNT suggested that the roughness parameters (RMS) of the grains are 18.0, 18.8 and 17.8 nm, respectively. As shown in **Figure 6.7**, the dark current-voltage (I-V) curves of pBTT, pBTTz, pSNT and PCBM-based devices were consistent with the previous results, in which the pBTTz-based device showed smaller dark currents. This result implies that the pBTTz-based devices have less current leakage.

Figure 6.6 AFM images of (a) pBTT, (b) pBTTz and (c) pSNT.

To fully elucidate the potential of pBTT, pBTTz and pSNT, PSCs with pBTT, pBTTz and pSNT as the ETLs were fabricated. In order to optimize the film thickness of the ETLs,

different concentrations of the polymers (3, 5 and 8 mg/ml in *o*-dichlorobenzene (DCB)) were applied. For example, it was revealed that the concentration of the pBTT solution played a critical role in the PSC performances. Among the current density-voltage (J-V) curves of the as-fabricated devices based on pBTT (3, 5 and 8 mg/ml in DCB) as ETLs, the highest PCE of 12.8% with the V_{oc} of 0.88 V, J_{sc} of 22.51 mA/cm² and FF of 64.4 % was achieved if the concentration of 5 mg/ml was used. When the concentration of pBTT decreased to 3 mg/ml, the corresponding PCE declined to 10.7%. This declination was ascribed to the uncoverage of the surface, which led to the decrease in the J_{sc} and FF. In contrast, increasing the concentration of pBTT to 8 mg/ml dramatically dropped the PCE to 8.9% associated with the decrease in the J_{sc} and FF due to the increase in the series resistance as shown in **Figure 6.8 (a)**. Embedding the sp²-N into the donor (thiophene) unit of pBTT resulted in a new polymer pBTTz with a significantly modified energy levels (deeper HOMO and LUMO). The corresponding HOMO and LUMO levels are shown in **Figure 6.2 (b)**. The highest PCE of the device based on pBTTz was 14.4 % with the V_{oc} of 0.91 V, J_{sc} of 21.95 mA/cm² and FF of 72.3%. This improvement was induced by the HOMO and LUMO of pBTTz well-matched with the valence and conduction bands of the perovskite layer, respectively, leading to an enhancement of both V_{oc} and FF, and accordingly, a higher PCE resulted.

Figure 6.7 I-V curves of pBTT, pBTTz, pSNT and PCBM-based devices under dark conditions.

Figure 6.8 (a) J-V curves of PSCs with different concentrations of pBTT as ETLs. (b) Distribution of PSCs efficiency with the optimum concentration of pBTT.

Figure 6.9 (a) J-V curves of PSCs with different concentrations of pBTTz as ETLs and PCBM. (b) Distribution of PSCs efficiency with the optimum concentration of pBTTz.

The optimum concentration of pBTTz in DCB was 5 mg/ml. By decreasing or increasing the concentration, the PCEs decreased as shown in **Figure 6.9 (b)**. For further verification of measured J_{sc} of champion pBTTz-based PSC, external quantum efficiency (EQE) plot was investigated as shown in **Figure 6.10** and the calculated J_{sc} was 21.5 mA/cm² which is well matched with measured J_{sc} .

Figure 6.10 EQE of champion pBTTz-based perovskite solar cell

Figure 6.11 (a) J-V curves of PSCs with different concentrations of pSNT as ETLs. (b) Distribution of PSCs efficiency with the optimum concentration of pSNT.

Table 6.2 Effect of polymer concentrations and PCBM on photovoltaic parameters of devices

Polymer-based devices	Concentration (mg/1 mL DCB)	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
pBTT	3	0.88	21.2	57.4	10.7
	5	0.88	22.5	64.4	12.8
	8	0.89	18.5	54	8.9
pBTTz	3	0.90	20.60	60.4	11.2
	5	0.91	21.95	72.3	14.4
	8	0.90	20.75	54.6	10.2
pSNT	3	0.88	18.1	56.2	9
	5	0.88	20.5	66.5	12
	8	0.90	18.6	53.1	8.9
PCBM	22	0.99	22.7	69.1	15.6

Embedding sp^2 -N atoms into the electron-accepting benzothiadiazole of pBTT through the addition of a fused ring with two sp^2 -N atoms produced another new polymer pSNT. The electron mobility of this polymer significantly increased, and the LUMO became slightly deeper and much closer to the conduction band of the perovskite layer. However, the HOMO also became shallower and it is very close to the valence band of the perovskite layer.

Figure 6.12 J-V curves of pBTTz-based devices with different heat treatment temperature. (b) J-V hysteresis curves of pBTTz-based devices.

Table 6.3 Effect of heat treatment on the photovoltaic parameters of pBTTz- based devices.

Polymer-based devices	Heat treatment temperature (°C)	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
pBTTz	80	0.93	20.6	66.8	12.8
	90	0.93	21.1	69.3	13.6
	100	0.91	21.95	72.3	14.4

Figure 6.13 Contact angle of the surface of (a) PCBM, (B) pBTT, (c) pBTTz and (d) pSNT.

This change resulted in a decrease of FF, then a deterioration of the PCE. The highest PCE achieved was 12% with the concentration of 5 mg/ml. By changing the concentration of pSNT to 3 or 8 mg/ml in DCB, the PCEs became poorer as shown in **Figure 6.11 (a)**. To explore the reliability of as-fabricated solar cells, 36 devices based on each polymer as ETLs have been prepared and tested. The distributions of the PCEs are shown in **Figure 6.8 (b)**, **Figure 6.9 (b)** and **Figure 6.11 (b)** for pBTT, pBTTz and pSNT, respectively.

All photovoltaic parameters of the experiments are summarized in **Table 6.2**. The thermal annealing effect on the performances of the pBTTz-based devices was investigated by heat treatment of the devices at 80, 90 and 100 °C after spin-coating of pBTTz. The PCEs gradually increased from 12.8% to 14.4% by increasing the temperature from 80 °C to 100 °C as shown in **Figure 6.12 (a)** and **Table 6.3**. In addition, the pBTTz-based devices showed negligible hysteresis effects as shown in **Figure 6.12 (b)**. This result was attributed

to the well-matched HOMO and LUMO of pBTTz with the conduction and valence bands of the perovskite, respectively. Moreover, the sulfur atoms have successfully passivated the under-coordinated Pb atoms. This passivation reduced the charge accumulation, therefore reducing the hysteresis.

Furthermore, the dewettability of each polymer was measured and compared with that of PCBM. Interestingly, the contact angles of these polymers were higher than that of PCBM as shown in **Figure 6.13**. This result reflects the hydrophobic nature of these n-type polymers. Finally, the stability of the PSCs based on both pBTTz and PCBM was evaluated. After ten days of testing, the pBTTz-based device still retained 80% of its original PCE, which is higher than that of the PCBM-based device with a stability retention of 73 % as shown in **Figure 6.14**. Each cell was tested in ambient air and then kept in controlled humidity condition in dry box. All these results strongly suggest that employed polymers are suitable candidates to replace PCBM as effective ETLs in future p-i-n PSCs.

In conclusion for the first time, the effect of the sp^2 -N substitution position in the main chains of polymers on the photovoltaic properties of PSCs has been investigated. Inverted perovskite solar cells based on pBTT, pBTTz or pSNT as ETLs have been successfully fabricated. The research indicates that PSCs based on pBTTz (possessing the sp^2 -N atoms at the thiophene units) delivered the highest PCE of 14.4% with a negligible hysteresis. Moreover, the device based on pBTTz retained 80% of its original PCE even after ten days. On the other hand, pSNT with two additional sp^2 -N atoms at the electron-accepting benzothiadiazole unit showed a poor efficiency due to its inappropriate HOMO level that was very close to the valence band of the perovskite layer.

Figure 6.14 Stability test diagram of pBTTz-based device and PCBM-based device.

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Chapter 7

Current and Future Work

This chapter includes general summary of whole project. The summary is presented by discussing the hypothesis, then followed by the achieved outcomes in overall thesis. Generally, this thesis focuses on design, synthesis and characterization of organic non-fullerene acceptors, which include organic N-type conjugated polymers and N-type small molecules. Then these organic materials were utilized as electron transporting materials in inverted perovskite solar cells. Current works, which hasn't been completed, are discussed in current work section. Since tellurium tetraiodide is utilized as an absorbing material in photovoltaic application. Proposed future work to discover all mysterious properties of tellurium tetra iodide as absorbing material in solar cell. General future work focuses on two projects: in first project, developing novel stable and ecofriendly lead-free perovskite solar cell, discovering new material beyond perovskite structure for photovoltaic application and develop bilayer heterojunction (polymer/perovskite) solar cell. In second project, I will develop novel organic non- fullerene acceptors with high stability and low cost through adjusting the LUMO and HOMO of organic ETLs to reduce Voc loss in perovskite solar cells.

7.1 General discussion

This thesis focuses on two projects: 1) To design, synthesize, and characterize organic non-fullerene acceptors and utilize them as ETLs in p-i-n PSCs.; and 2) to develop lead-free solar cells with ecofriendly and stable absorbing material. The trails to achieve the objective are discussed in each chapter. The conclusion of each chapter is summarized in the following sub-section.

7.1.1 NDI-based Molecules as Electron Transporting Materials in p-i-n PSCs.

In chapter 4, six novel NDI-based small molecules were designed, synthesized, characterized and utilized as ETLs in p-i-n PSCs (PDPT, PMDPT, DS1, DS2, NDI-BTH1 and NDI-BTH2). NDI-based molecules have significant merits such as easy of solution synthesis, easy of purification, high thermal and air stability, high charge carriers mobility and commercial available building blocks. Reported NDI-based molecules exhibited different performance as ETLs in p-i-n PSCs. The difference performance resulted from the different properties of each molecules. The lowest PCE of p-i-n PSC was achieved by PDPT, since PCE= 7.6 %, J_{sc} = 22.9 mA cm⁻², V_{oc} =0.76 V and FF=44%. The poor performance was due to the mismatching energy level of PDPT with valence and conduction band of perovskite layer. By embedding sulfur atoms and adjusting ending group in NDI-based small molecules, NDI-BTH2 has decent electron mobility and well matched LUMO and HOMO with conduction band and valence band of perovskite layer, respectively. These properties delivered decent performance. NDI-BTH2-based device exhibited decent PCE equaled to 15.4 %, J_{sc} =22.13 mA cm⁻², V_{oc} =0.98 V and FF=71%.

Figure 7.1 NDI-based molecules used as ETLs in p-i-n PSCs in chapter 4.

7.1.2 Pyrene-Based Small Molecules as Electron Transporting Material in p-i-n PSCs

In chapter 5, for the first time, two novel pyrene-based molecules (PTTI 1 and PTTI 2 as shown in **Figure 7.2**) were designed, synthesized, characterized and investigated as ETLs in pi-n PSCs. Pyrene is distinguished by planar structure with ten functional positions. Furthermore, good photoelectrochemical properties. The difference between PTTI 1 and PTTI 2 is the position of sulfur atom in thieno[3,4-b]thiophene. Interestingly, the sulfur position has a key rule on the properties of each molecule, which reflected on the performance of PTTI 1 and PTTI 2. The highest PCE was achieved by PTTI 1-based device, since PCE=15.37%, J_{sc} = 21.26, V_{oc} = 1.027 V and FF= 70.4%. To further investigate the origin of higher performance of PTTI 1 than PTTI 2 as ETLs. Steady-state PL. And TRPL confirmed that, PTTI 1 as ETL has passivation ability toward surface traps of perovskite layer stronger than PTTI 2. It is worthy note that, sulfur position play crucial role to determine, electron mobility, energy levels and passivation power toward electron trap centers.

Figure 7.2 Structures of PTTI 1 and PTTI 2

7.1.3 Conjugated Polymers-based Electron Transporting Materials in p-i-n PSCs.

In chapter 6, three different conjugate polymers (D-A₁-D-A₂) was investigated as ETLs in p-i-n PSCs (pBTT, pBTTz and pSNT (**Figure 7.3**)). N-type conjugated polymers have the advantages of n-type organic small molecules, moreover, the simplicity of film is formed without cracks and high hydrophobicity. The main difference between each polymer is the position of sp²-N. The maximum PCE was achieved by pBTTz-based device. PCE equaled 14.4 %, J_{sc} (21.95 mA/cm²), V_{oc} (0.91 V) and FF (72.3%). sp²-N has an important role to influence the properties of each polymer. In pSNT, sp²-N is located in acceptor group, which enhanced the electron mobility to 4.87 cm² (Vs)⁻¹. sp²-N is located in donor group in pBTTz, therefore, LUMO and HOMO have well matched value with conduction band and valence band of perovskite layer, respectively.

Figure 7.3 Structures of pBTT, pBTTz and pSNT polymers

7.2 Current work

7.2.1 Tellurium tetraiodide (TeI₄)-based solar cell.

As mentioned before in chapter 1 that MAPbI₃ has intrinsic instability toward (oxygen, water vapor and heat). PbI₂ is the most dangerous degradation product. Therefore, various researches are devoted to find stable and ecofriendly materials for solar cell application. Different materials were investigated to replace Pb²⁺, such as Sn²⁺, Ge²⁺, Bi³⁺ and Sb³⁺.^[1]

In this work, TeI₄ is used for the first time as an absorbing material. TeI₄ obtained this interest due to its theoretical band gap (1.78-1.8 eV), which is suitable for photovoltaic application^[2] and Te⁴⁺ has the same electronic structure of Sb³⁺ and Bi³⁺, which has active lone pair of active s orbital.^[3]

The preliminary results demonstrate the potential of TeI₄ as an absorbing material and its potential in photovoltaic application. The highest PCE was obtained by TeI₄-based device was 3.6 %.

7.2.1.1 Experimental section

ITO slides are cleaned and treated with air plasma cleaner. Then, PEDOT:PSS as HTL is spun cast at 6000 rpm for 1 minute. After heat treatment of PEDOT: PSS AT 130 °C for 15 minutes, TeI₄ solution (DMF: DMSO (4:1, v/v) is spun cast on the PEDOT:PSS layer at 3500 rpm for 1 minute. Then 22 mg/ml of PCBM solution is spun cast on TeI₄ layer at 2200 rpm for 1 minute. Finally, 60 nm of Ag electrode is evaporated on PCBM layer. The device architecture used in this work is ITO/PEDOT: PSS/TeI₄/PCBM/Ag, as shown in **Figure 7.4**.

Figure 7.4 Device architecture of TeI₄-based solar cell.

7.2.1.2 Results and discussion

TeI₄-based solar cell was fabricated with 0.8 M TeI₄ in different solvents (DMF, acetonitrile (ACN), cosolvent DMF+DMSO (4:4, v,v) and , cosolvent ACN+DMSO (4:4, v,v)). However, the solubility of TeI₄ in DMF or ACN was very poor. Therefore, the as-deposited film from each solvent was also very poor, which reflected on the poor performance of solar cell. Finally, solar cells fabricated with DMF or ACN alone don't have photovoltaic performance. It is worthy to note that, TeI₄ is soluble in cosolvent DMF+DMSO (4:1, v/v) and, cosolvent ACN+DMSO (4:1, v,v). As shown in **Figure 7.5** and **Table 7.1**, the solar cells fabricated by using DMF+DMSO (4:4, v/v) exhibited higher current density than that of solar cell fabricated using ACN+DMSO (4:4, v, v). Interestingly, Voc and FF of solar cells, which fabricated using ACN+DMSO, are higher than that fabricated by DMF+DMSO. The highest PCE was obtained from devices fabricated with DMF+DMSO.

To further improve the performance of TeI₄-based solar cells, different concentration (0.6, 0.7, 0.8, 0.9 and 1 M) of TeI₄ in DMF: DMSO (4:1 v, v) as a solvent were investigated as absorbing materials.

Device which was fabricated by 0.6 M TeI₄ exhibited very poor results, since PCE is less than 0.02 %. Then PCE could be enhanced gradually by increasing the concentration of TeI₄. The highest PCE (3.6 %) was obtained by 0.9 M TeI₄. When the concentration of

TeI₄ increased more than 0.9 M, the declining PCE was observed as shown in **Figure 7.6** and **Table 7.2**.

Figure 7.5 J-V of TeI₄-based solar cells using cosolvent ACN+DMSO (4:1, v/v) and DMF+DMSO (4:1, v/v)

Table 7.1 Photovoltaic parameters of TeI₄-based solar cells fabricated by different solvent

	Jsc (mA/cm ²)	Voc (V)	FF (%)	PCE (%)
DMF+DMSO	4.82	0.66	43.1	1.4
ACN+DMSO	1.87	0.70	50	0.7

Figure 7.6 J-V curves of TeI₄-based solar cell with different concentration of TeI₄

Table 7.2 Effect of TeI₄ concentration on the photovoltaic parameters of TeI₄-based solar cells.

	Conc. (M)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
TeI ₄	0.7	3.53	0.582	41.7	0.9
	0.8	4.82	0.66	43.1	1.4
	0.9	11.56	0.604	50.9	3.6
	1	7.45	0.579	42.3	1.8

The optimum concentration is 0.9 M, which showed the highest PCE. The concentration of TeI₄ has significant effect on J_{sc}, which reflects on PCEs. This observation can be ascribed to that, the increasing the concentration of TeI₄ enhances J_{sc} since the light absorption, therefore J_{sc} enhanced. However, at concentration of 1M, J_{sc} decreased again, which might be ascribed to increased thickness of TeI₄ and increased series resistance.

To further enhance the performance of TeI₄-based solar cell, anti-solvent strategy was applied. The antisolvent strategy enhanced the performance of lead-based perovskite solar cell. Unexpectedly, the performance decreased after applying ant-solvent strategy. 0.6 mL of toluene was dripped on TeI₄ during the spin coating.

The performance of solar cells fabricated with different dripping times (8, 10, 12, 15 and 18 s) are shown in **Figure 7.7** and **Table 7.3**.

Figure 7.7 J-V curves of TeI₄-based devices fabricated with different dripping time

Table 7.3 Effect of anti-solvent dripping time on the performance of as-fabricated solar cells

Dripping time (s)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
8	0.60	0.439	35.5	0.1
10	6.70	0.576	52.3	2.01
12	10.20	0.548	32.1	1.79
15	9.84	0.545	44.6	2.4
18	6.67	0.609	55	2.2

7.3 Future work

The future work can be divided into three approaches:

- Future work of TeI₄ as an absorber in solar cell.
- Future work of lead-free perovskite solar cell.
- Future work of organic non- fullerene acceptors.

7.3.1 Future work of TeI₄ as an absorber in solar cell.

The promising PCE of TeI₄-based solar cells encourages to investigate the optoelectronic properties of TeI₄. Furthermore, the origin of photovoltaic performance of TeI₄-based solar cells should be discovered. The previous study on TeI₄ in photovoltaic application lack various information about the optoelectronic properties of TeI₄. Numerous questions should be addressed to demonstrate TeI₄ as a novel light absorber in photovoltaic application. These questions can be summarized in the following points:

- 1-Designing new fabrication technique to obtain pin holes free and high quality TeI₄ film.
- 2-TeI₄ thin film should be characterized by SEM and XRD.
- 3-UV-vis absorption spectroscopy to determine the wavelength of excitation light and optical band gap
- 4-Lifetime of charge carriers should be measured using TRPL.
- 5-Electrical measurements such as series resistance should be measured.

7.3.2 Future work of lead-free perovskite solar cells.

As mention in chapter 1, lead-based perovskite solar cell achieved high PCE. However, its intrinsic stability and toxicity hinder its application in marketing. Therefore, it is highly desired to choose another element, which can replace Pb²⁺. Various reports related to lead-free perovskite solar cells were published. These reports demonstrate the famous four

elements (Sn, Ge, Bi and Sb), which replaced Pb^{2+} . However, all these elements couldn't achieve the better performance than that of lead-based perovskite. Sn-based perovskites is most investigated element beyond Pb^{2+} -based perovskite because they has narrow band gap, which can be considered optimum band gap for photovoltaic application. Although ASnI_3 -based solar cells achieved decent PCE, its stability is very poor. Sn^{2+} is easily oxidized to Sn^{4+} , which deteriorates the performance of ASnI_3 -based solar cell. Other structure of Sn-based perovskite, A_2SnI_6 , has decent stability. However, its performance as absorbing material is very low. Bi-based perovskites are intensively investigated. Contrary to Sn-based perovskite, Bi-based perovskite has long term stability.

The challenges are how to increase the long-term stability of Sn-based perovskite and how to increase the performance of Bi-based perovskite. ^[4]

It is desirable to develop efficient and stable lead-free perovskite solar cell with high performance and long term stability. To achieve this aim, the following objective should be followed:

- 1- Develop new perovskite materials by choosing stable element and checking the tolerance and octahedron factor. Tolerance and octahedron factors confirm if perovskite structure will form or will not.
- 2- Try to enhance the performance of Bi-based perovskite by doping or finding new structure beyond perovskite structures.
- 3- Benefitting from high optical absorption of conjugated polymers. Heterojunction bilayer solar cells can be developed. This bilayer consists of polymer and lead-free perovskite materials.

7.3.3 Future work of novel non-fullerene acceptors.

As mentioned in this thesis, organic non-fullerenes including conjugated polymers and small molecules exhibited high performance as ETLs in p-i-n PSCs. To push PCE of p-i-n PSCs with organic ETLs, some challenges should be addressed. Some of organic non-fullerene acceptors have been synthesized with more than one route with one or two building blocks, so decreasing the cost of organic ETLs is challenge. Voc is related to band

gap energy, however, part loss of Voc occurs due to the mismatch of LUMO and HOMO of ETLs with conduction band and valence band of perovskite layer, respectively. In p-i-n PSCs, ETL is the last deposited layer, therefore ETLs has a great contribution to the stability of p-i-n PSCs. The grain boundaries of perovskite layer have a negative effect on the performance of solar cells. ^[5] Therefore, the treatment, filling and passivation of these boundaries are required to enhance the performance of PSCs.

To address all these challenges, following objectives should be achieved:

- 1- Developing novel synthesis routes for scalable production of organic ETLs, which decrease the price of overall solar cells.
- 2- Developing novel organic ETLs with well matched energy levels to the conduction and valence band of perovskite layer is required to decrease Voc loss.
- 3- Developing stable organic ETLs enhances the overall stability of p-i-n PSCs.
- 4- Developing novel organic ETLs with the ability to passivate grain boundaries and antisite (PbI_3^-) is required to enhance the shunt resistance.

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Appendix 1

Experimental procedure

Materials and Methods

All chemicals and solvents were purchased from commercial suppliers such as Sigma Aldrich, Alfa Aesar and Finar Company, India. Reagents are used without further purification unless stated. The solvents are used dried and purified by standard method. FT-IR spectra were obtained on a Thermo Nicolet Nexus 670 FT-IR spectrometer in the form of KBr pellets and are reported in frequency of absorption (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance as a 500 MHz, 400 MHz for ^1H also for ^{13}C in 125 MHz, 100 MHz spectrometer chloroform- d_6 as solvent, respectively. Spectra were recorded at 298 K. ESI-MS data were taken on Shimadzu lab solutions. MALDI-TOF measurements on a Shimadzu Biotech Axima performance spectroscopic instrument are used. UV-vis absorption spectra were recorded in a Shimadzu UV-1800 spectrophotometer and 10^{-5} molar of the sample were analyzed in 3 mL quartz cuvette in chloroform. *Differential Scanning Calorimetry* (DSC) experiments were measured by using Q-100. DSC instrument with nitrogen as a purging gas. Samples were heated to 250-350 $^{\circ}\text{C}$ at a heating rate 10 $^{\circ}\text{C}/\text{min}$. The *thermal gravimetric analysis* (TGA) experiment were recorded on a Q-500 TGA instrument with using dynamic scans under nitrogen gas, sample were heated to 600-800 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. The cyclic voltammetry (CV) was recorded in the solution of tetrabutyl ammonium hexafluorophosphate (0.1 M in dichloromethane as supporting electrolyte) were purchased from Sigma Aldrich and used without purification. The solutions were deoxygenated by bubbling of nitrogen gas and the experiment was performed by working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire.

Synthesis of PDPT

Scheme A 1. 1. Synthetic route of **PDPT**.

To a suspension of 4-bromo-2,7-dioctylbenzo[lmn]-[3,8]phenanthroline-1,3,6,8 (2H,7H)-tetraone **1** (555 mg, 0.975mmol),¹ piperazine (28 mg, 0.325 mmol) in toluene (10 mL) was stirred at 70 °C for 12 h under the N₂ atmosphere. The reactions were monitored by TLC. After completion, the excess toluene was removed by evaporation to afford a dark red solid. The product was purified by column chromatography on silica gel 100-200 mesh, eluting with CH₂Cl₂ in hexane (90:10%), yields **PDPT** (196 mg, 57%). FT-IR (KBr, cm⁻¹): ν 2917, 2850, 1691-1652 (C-CO-N), 1428, 1341, 1428, 1179, 1016; ¹H NMR (400 MHz, CDCl₃) δ: 8.73 (d, *J* = 7.82 Hz, 2H), 7.56 (s, 2H), 8.51 (d, *J* = 7.82Hz, 2H), 4.20 (q, *J* = 7.54 Hz, 8H), 3.90 (s, 8H), 1.73 (m, 8H), 1.45-1.27 (m, 40H), 0.86 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.18, 162.90, 161.80, 153.80, 131.21, 130.31, 126.79, 126.59, 126.05, 125.26, 125.00, 121.47, 108.44, 51.76, 41.06, 40.95, 31.79, 29.35, 29.16, 29.26, 28.27, 28.05, 27.21, 27.06, 22.62, 14.06; MS (MALDI-TOF) *m/z* for C₆₄H₈₂N₆O₈: 1064.06 [M+H]⁺ and 1086.13 [M+Na]⁺. Elemental analysis calculated for C₆₄H₈₂N₆O₈(%): C 72.29, H 7.77, N 7.90; found C 72.34, H 7.93, N 7.87.

Synthesis of Compound 4 ⁽²⁾

Scheme A1. 2. Synthetic route to compound 4.

Synthesis of 4-bromo-9-(4-methylpiperidin-1-yl)-2,7-dioctylbenzo[1,2-m:3,8-b']phenanthroline-1,3,6,8(2H,7H)-tetraone (**4**): To a suspension of *N,N'*-dioctyl-2,6-dibromo-1,4,5,8-naphthalenediimide¹ **2** (200 mg, 0.30 mmol), 4-methyl piperidine **3** (0.040 mL, 0.33 mmol), *N*-methyl pyrrolidine-2-one (NMP, 1 mL), Et₃N (1 mL) was mixed together in 5 mL round bottom flask (observation: the reaction mixture turned colorless to pinkish color immediately at room temperature). then the stirring continued for additional 2 h under the N₂ atmosphere. The dark purple solution was poured in cold water and extracted with CH₂Cl₂ and solvent evaporated under vacuum. The residue was purified with a column chromatography on silica gel 60-120 mesh, eluting with 50% CH₂Cl₂ in hexane to give a purple solid **4** (120 mg, 59%). FT-IR (KBr, cm⁻¹): ν 2924, 2858, 1654 (C-CO-N), 1516, 1434, 1314, 1240, 1173, 783; ¹H NMR (500 MHz, CDCl₃) δ : 8.80 (s, 1H), 8.50 (s, 1H), 4.15 (m, 4H), 3.68 (d, J = 13.24 Hz, 2H), 3.38 (t, J = 12.32 Hz, 2H), 1.85 (d, J = 13.24 Hz, 2H), 1.80-1.66 (m, 5H), 1.54-1.27 (m, 22H), 1.05 (d, J = 6.25 Hz, 3H), 0.87 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ : 162.19, 161.98, 161.45, 153.28, 137.60, 129.75, 127.00, 125.63, 124.59, 122.88, 121.37, 106.39, 52.86, 41.35, 40.98, 34.55, 31.77, 30.38, 29.30, 29.25, 29.19, 28.17, 27.93, 27.11, 22.61, 21.66, 14.07; ES-MS (m/z %) for C₃₆H₄₈BrN₃O₄: 666.35 [M+H]⁺(⁷⁹Br), 668.40 [M]²⁺(⁸¹Br). Elemental analysis calculated for

C₃₆H₄₈BrN₃O₄(%): C 64.86, H 7.26, N 6.30; found C 64.84, H 7.26, N 6.32.

Synthesis of Compound PMDPT

Scheme A1. 3. Synthetic route to **PMDPT**.

4-Bromo-9-(4-methylpiperidin-1-yl)-2,7-dioctylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone **4** (150 mg, 0.224 mmol) was mixed with piperazine (7.7 mg, 0.089 mmol) in toluene (5 mL). The reaction mixture was stirred at 70 °C for 12 h under the N₂ atmosphere. The progress of the reaction was monitored by TLC. After completion, reaction mixture was cooled to room temperature. Then toluene was removed under reduced pressure on rotary evaporator. The residue was purified with column chromatography on silica gel 60-120 mesh, eluting with 50-70% CH₂Cl₂ in hexane to give a blue solid of **PMDPT** (80 mg, 78%). FT-IR (KBr, cm⁻¹): ν 2923, 2852, 1690-1651 (C-CO-N), 1569, 1449, 1183; ¹H NMR (500 MHz, CDCl₃): δ 8.53 (s, 2H), 8.50 (s, 2H), 4.19 (t, J = 7.06 Hz, 8H), 3.72 (s, 8H), 3.64 (d, J = 12.81 Hz, 4H), 3.26 (t, J = 12.05 Hz, 4H), 1.82 (d, J = 12.05 Hz, 4H), 1.72 (m, 10H), 1.55-1.25 (m, 44H), 1.05 (d, J = 6.40 Hz, 6H), 0.87 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ : 163.03, 161.93, 161.88, 152.28, 151.66, 126.10, 125.76, 125.64, 125.25, 124.27, 123.98, 111.37, 108.61, 52.92, 52.29, 41.00, 40.89, 34.50, 31.80, 30.54, 29.36, 29.33, 29.26, 29.22, 28.23, 27.22, 27.15, 22.64, 21.79, 14.08;

MS (MALDI-TOF) m/z for $C_7H_{10}N_8O_8$: 1258.05 $[M+H]^+$ and 1260.16 $[M+2H]^+$.
 Elemental analysis calculated for $C_7H_{10}N_8O_8$ (%): C 72.58, H 8.34, N 8.91; found C 72.61, H 8.36, N 8.93.

Figure A1.1. FT-IR of compound PDPT.

Figure A1.2. 1H NMR of compound PDPT.

Figure A1. 3. ¹³C NMR of compound PDPT.

Figure A1.4. TGA of compound PDPT.

Figure A1.5. FT-IR of compound 4.

Figure A1.6. ^1H NMR of compound 4.

Figure A1.7. ^{13}C NMR of compound 4.

Figure A1.8. FT-IR of compound PMDPT.

Figure A1.9. ¹H NMR of compound PMDPT.

Figure A1.10. ¹³C NMR of compound PMDPT.

Figure A1.11. TGA of compound **PMDPT**.

Figure A1.12 Cyclic voltammogram of **PDPT**.

Figure A1.13. Cyclic voltammogram of **PMDPT**.

Appendix 2

Experimental Section

General information: All reactions were performed under Argon protection. The solvents were purified and dried according to standard procedures. The chemicals were purchased from Alfa Aesar, Sigma-Aldrich, Acros Ltd and used as received.

NMR spectra were recorded with a Bruker AV 300 Spectrometer at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR). High Resolution Mass Spectra (HRMS) were recorded on Waters ACQUITY UPLC® System or a Varian ProMALDI instrument. UV–Vis absorption spectra were taken on a SHIMADZU UV-2501PC. Fluorescence emission spectra were taken on a Shimadzu RF-5301-PC Fluorescence Spectrophotometer and the excitation wavelength was set at 350 nm. FTIR were taken on a FTIR Perkin Elmer Frontier. Electrochemical Cyclic Voltammetry (CV) was analysed on a CHI 660C Electrochemical Workstation. In the CV measurement, a Pt disk was used as the working electrode, one Pt wire as the counter electrode and another Pt wire as the reference electrode were used in dried solution of methylene chloride with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at 100 mV s^{-1} . Meanwhile, CV of ferrocene was also taken for comparison.

Device Fabrication: Device fabrication was started by spin coating of PEDOT: PSS on ITO at 6000 rpm for 60 S, followed by heat treatment at 135°C for 15 minutes. Perovskite solution was prepared by mixing 1.26 M of PbI_2 , 0.14 M PbCl_2 , 1.08 M MAI and 0.27 M FAI in (3: 7 v,v) DMSO: GBL solvents.¹ The deposition step of perovskite solution was proceeded by two step, starting by spin casting at 1000 rpm for 20 s, then 5000 rpm. After 20 s of the second step, 0.6 mL of toluene dripped on perovskite layer. Then, the perovskite layer was heat-treated at 100°C for 15 minutes. ETL solution was spun cast at 2000 rpm for 60 s and then heat-treated at 100°C for 12 minutes. Finally, 100 nm of Ag was evaporated as the electrode.

Device Characterization: The perovskite layer was investigated by powder XRD equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$ operated at 40 kV and 30 mA). The surface morphology and cross section of perovskite film were investigated by SEM (JEOL, JSM 6360 at 5 KV). The optical properties of the perovskite layer were characterized by UV–

vis spectroscopy (UV–vis–NIR, Lambda 900, Perkin Elmer). The PL characteristics were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). TRPL was measured by PicoHarp 300, PicoQuant. Contact angle of each ETL was measured by contact angle equipment, DataPhysics, OCA 15 Pro. Electrochemical Impedance Spectroscopy (EIS) was analysed on a CHI 660C Electrochemical Workstation. The current density–voltage (J – V) curves of solar cells were measured using Keithley 2400 source meter under a simulated AM1.5 illumination (100 mW cm^{-2}) by a Xenon-lamp-based solar simulator (Abet Technologies, USA). The light intensity was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory.

Synthesis

Compound 3: A 40 mL anhydrous THF solution containing compound 2 (2.7 g, 6.0 mmol) was injected slowly into another 50 mL anhydrous THF solution containing compound 1 (1.0 g, 2.4 mmol) at 0 °C. After the injection, the reaction was kept running overnight until 1 was completely consumed. The solvent was removed under the reduced pressure and purified through column chromatography (Hexane: Methylene Chloride = 1: 1 as eluent) to give the desired product as yellow solid (1.95 g, 64%). ^1H NMR (300 MHz, CDCl_3): δ 8.35 (s, 4H), 7.62 (d, $J = 9.0 \text{ Hz}$, 8H), 6.90 (d, $J = 9.0 \text{ Hz}$, 8H), 3.94 (t, $J = 7.5 \text{ Hz}$, 8H), 1.80–1.71 (m, 8H), 1.42–1.27 (m, 40H), 0.89–0.85 (m, 12H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 160.0, 138.4, 131.8, 128.1, 121.9, 120.8, 129.7, 129.2, 115.8, 114.1, 68.1, 31.8, 29.3, 29.2, 29.2, 26.0, 22.6, 14.1; HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{74}\text{H}_{89}\text{Br}_2\text{O}_8$ 1265.4904; found 1265.4851.

Compound 4

A 2-neck dry flask was charged with compound 3 (1.26 g, 1.0 mmol), bis(pinacolato)diboron (760mg, 3.0 mmol), anhydrous potassium acetate (392 mg, 4.0 mmol), and [1,1'- bis(diphenylphosphino)ferrocene]dichloropalladium(II) (73 mg, 0.1 mmol). Then, the flask was flushed three times with a vacuum/argon cycle. Anhydrous 1,4-dioxane (30 mL) was added and purged with argon gas for 20 mins, and the reaction was heated to 110 °C overnight. After the mixture was cooled, MeOH (100 mL) was added, and the resulted crude product was filtrated and purified through column chromatography

(Hexane: Methylene Chloride = 1: 1 as eluent) to give the desired product 4 as a yellow solid (1.25 g, 92%). ^1H NMR (300 MHz, CDCl_3): δ 8.69 (s, 4H), 7.67 (d, J = 9.0 Hz, 8H), 6.88 (d, J = 9.0 Hz, 8H), 3.93 (t, J = 6.0 Hz, 8H), 1.77–1.70 (m, 8H), 1.45–1.27 (m, 64H), 0.88–0.85 (m, 12H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.8, 138.5, 132.6, 128.3, 122.2, 120.6, 119.1, 118.8, 114.1, 84.2, 68.1, 31.8, 29.3, 29.2, 26.0, 25.0, 22.7, 14.1; HRMS (ESI/Q-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{86}\text{H}_{113}\text{B}_2\text{O}_{12}$ 1359.8418; found 1359.8413.

Compound 7

Compounds 4 (136 mg, 0.1 mmol) and 5 (129 mg, 0.3 mmol, 3 equiv.) were added into 9 mL of a mixture of aqueous K_2CO_3 (2.0 M) and dioxane (1:2 v/v) under argon. The reaction mixture was purged with argon for 20 minutes and then $\text{Pd}(\text{PPh}_3)_4$ catalyst (11.5 mg, 0.01 mmol, 0.1 equiv.) was added. The reaction solution was stirred at 95 °C overnight under argon atmosphere. After reaction finished, the resulted mixture was poured into 100 mL of ethyl acetate. The organic layer was washed with water and brine and was dried over Na_2SO_4 . The solvent was filtrated and removed under reduced pressure. The resulted orange solid was purified on a silica-gel column chromatography using hexanes and dichloromethane (1:2) as the eluent to give the desired product as an orange solid (122 mg, 66%). ^1H NMR (300 MHz, CDCl_3): 10.10 (s, 2H), 8.53 (s, 4H), 8.19 (s, 2H), 7.75 (d, J = 9.0 Hz, 8H), 6.95 (d, J = 9.0 Hz, 2H), 4.35–4.32 (m, 4H), 3.94 (t, J = 6.0 Hz, 8H), 1.80–1.71 (m, 10H), 1.45–1.26 (m, 56H), 1.02–0.84 (m, 24H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 179.7, 162.5, 160.1, 149.6, 145.1, 140.9, 139.4, 138.2, 132.2, 131.8, 130.3, 130.0, 128.3, 121.7, 120.1, 116.9, 114.2, 68.6, 68.1, 38.9, 31.8, 30.4, 29.3, 29.2, 28.9, 26.0, 24.0, 23.0, 22.6, 14.0, 11.1; MALDI-TOF m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{106}\text{H}_{127}\text{O}_{14}\text{S}_4$ 1752.8064; found 1752.7360.

PTTI-1

2-(5,6-diFluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (92 mg, 0.40 mmol) and compound 7 (116 mg, 0.066 mmol) were added into a Schlenk flask and flushed three times with a vacuum/argon cycle. 10 mL of chloroform and 2 drops of pyridine were injected through syringe consequently. The reaction was placed in an oil bath at 65 °C and was stirred for 12 hours. After the solvent was removed under reduced press, methanol was

added to dissolve the excessive 2-(5,6-diFluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile and filtrated to obtain rough blue solid, which was directly purified through column chromatography using chloroform as eluent to give the desired product as blue solid (110 mg, 77%). ¹H NMR (300 MHz, CDCl₃): 9.21 (s, 2H), 8.56 (s, 4H), 8.31–8.26 (m, 2H), 8.13 (s, 2H), 7.84 (d, *J* = 9.0 Hz, 8H), 7.42–7.37 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.43–4.30 (m, 4H), 3.94 (t, *J* = 6.0 Hz, 8H), 1.80–1.73 (m, 10H), 1.59–1.25 (m, 56H), 1.06–0.83 (m, 24H); ¹³C NMR (CDCl₃, 75 MHz): δ 185.9, 161.9, 160.1, 157.9, 157.1, 155.9, 147.7, 145.9, 139.7, 137.8, 136.3, 134.2, 132.6, 131.8, 130.0, 128.2, 127.3, 122.6, 121.8, 120.7, 116.9, 116.9, 114.6, 114.3, 113.9, 112.7, 112.4, 69.9, 68.7, 68.1, 38.9, 31.8, 30.5, 29.2, 29.0, 26.0, 24.0, 23.0, 22.6, 14.1, 14.0, 11.1; MALDI-TOF *m/z*: [M+H]⁺ calcd for C₁₃₀H₁₃₁F₄N₄O₁₄S₄ 2176.8436; found 2176.3338.

Compound 8

Compounds 4 (136 mg, 0.1 mmol) and 5 (129 mg, 0.3 mmol, 3 equiv.) were added into 9 mL of a mixture of aqueous K₂CO₃ (2.0 M) and dioxane (1:2 v/v) under argon. The reaction mixture was purged with argon for 20 minutes and then Pd(PPh₃)₄ catalyst (11.5 mg, 0.01 mmol, 0.1 equiv.) was added. The reaction solution was stirred at 95 °C overnight under argon atmosphere and then was poured into 100 mL of ethyl acetate. The organic layer was washed with water and brine, and was dried over Na₂SO₄. The solvent was filtrated and removed under reduced pressure. The resulted orange solid was purified on a silica-gel column chromatography using hexanes and dichloromethane (1:2) as the eluent to give the desired product as an orange solid (40 mg, 22%). ¹H NMR (300 MHz, CDCl₃): 9.97 (s, 2H), 8.54 (s, 4H), 8.26 (s, 2H), 7.70 (d, *J* = 9.0 Hz, 8H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.32–4.25 (m, 4H), 3.93 (t, *J* = 6.0 Hz, 8H), 1.77–1.66 (m, 10H), 1.45–1.26 (m, 56H), 0.97–0.84 (m, 24H); ¹³C NMR (CDCl₃, 75 MHz): δ 179.4, 162.5, 160.2, 146.5, 142.8, 141.9, 139.5, 132.3, 131.7, 130.9, 130.6, 128.3, 121.8, 120.3, 115.6, 114.2, 114.0, 68.4, 68.1, 38.9, 31.8, 30.4, 29.4, 29.2, 29.0, 26.0, 24.0, 23.0, 22.7, 14.1, 11.1; MALDI-TOF *m/z*: [M+H]⁺ calcd for C₁₀₆H₁₂₇O₁₄S₄ 1752.8064; found: 1752.7132.

PTTI-2

2-(5,6-diFluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (28 mg, 0.12 mmol) and compound 8 (35 mg, 0.002 mmol) were added into a Schlenk flask and flushed three times with a vacuum/argon cycle. 4 mL of chloroform and 2 drops of pyridine were injected through syringe consequently. The reaction was placed in an oil bath at 65 °C and was stirred for 12 hours. After the solvent was removed under reduced press, methanol was added to dissolve the excessive 2-(5,6-diFluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile and filtrated to obtain rough blue solid, which was directly purified through column chromatography using chloroform as eluent to give the desired product as blue solid (25 mg, 57%). ¹H NMR (300 MHz, CDCl₃): 8.94 (s, 2H), 8.66 (s, 4H), 8.38–8.30 (m, 4H), 7.76 (d, *J* = 9.0 Hz, 8H), 7.47–7.44 (m, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.33–4.31 (m, 4H), 3.94 (t, *J* = 6.0 Hz, 8H), 1.78–1.71 (m, 10H), 1.59–1.25 (m, 56H), 0.99–0.83 (m, 24H); ¹³C NMR (CDCl₃, 75 MHz): δ 186.4, 162.0, 160.2, 158.8, 158.0, 157.1, 153.2, 142.1, 141.3, 139.7, 136.4, 134.2, 133.0, 131.7, 130.8, 128.3, 124.2, 121.9, 120.7, 117.3, 115.9, 114.3, 114.0, 112.8, 112.5, 70.0, 68.8, 68.1, 38.8, 31.8, 30.5, 29.7, 29.4, 29.2, 29.0, 26.1, 24.1, 23.0, 22.7, 14.1, 14.0, 11.1; MALDI-TOF *m/z*: [M+H]⁺ calcd for C₁₃₀H₁₃₁F₄N₄O₁₄S₄ 2176.8436; found: 2176.6594.

Figure A2.1 ^1H and ^{13}C NMR of compound 3.

Figure A2.2. ^1H and ^{13}C NMR of compound 4.

Figure A2.3. ¹H and ¹³C NMR of compound 7.

Figure A2.4. ^1H and ^{13}C NMR of compound PTTI-1.

Figure A2.5 ^1H and ^{13}C NMR of compound 8

Figure A2.6. ^1H and ^{13}C NMR of compound PTTI-2

Compound 3 **Compound 4** **Figure A 2.7 . MS Spectra of compounds 3 and 4.**

Compound 7 **Compound 8**

Figure A 2.8. MS Spectra of compounds 7 and 8.

PTTI1 **PTTI2** **Figure A 2.9** MS Spectra of PTTI-1 and PTTI-2