Hole-transporting Organic Materials for Perovskite Solar Cells (PSCs)

M.Sc. Thesis

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Hole-transporting Organic Materials for Perovskite Solar Cells (PSCs)

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by ASHWINI MISHRA



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2022



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the thesis entitled Holetransporting Organic Materials for Perovskite Solar Cells (PSCs) in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from September 2021 to May 2022 of M.Sc. Thesis submission under the supervision of Prof. Rajneesh Misra, Professor, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree at this or any other institute.

19/05/2022 Signature of the student with date (Ashwini Mishra) This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.



Signature of the Supervisor of M.Sc. thesis

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DEDICATION

Every challenging work needs self-endeavour and the blessings of elders.

My modest effort I dedicate to my concern and supporting

FAMILY

Whose motivation, love, and encouragement make me able to complete my work efficiently.

Along with all inspiring and respected

TEACHERS

ABSTRACT

Researchers are currently interested in Phenothiazine (PTZ) based holetransporting materials (HTMs) because this can provide HTMs with high power conversion efficiency at a low cost. The main aim of the thesis is to design and synthesize PTZ-based hole-transporting materials (HTMs) for perovskite solar cells named PTZ-I and PTZ-II with the help of Buchwald–Hartwig crosscoupling reaction. Both the molecules are characterized by using different analytical techniques, such as mass spectrometry and ¹H and ¹³C NMR spectroscopy. We also investigate the photophysical properties and theoretical studies of PTZ-I and PTZ-II. We observed that PTZ-II shows a redshift in UVvis absorption spectroscopy because it has a more conjugated system than PTZ-I. Furthermore, Density Functional Theory (DFT) demonstrates that the HOMO and LUMO level of both HTMs are located on sidearms (An and TPA) groups and PTZ (core) respectively.

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ABBREVIATIONS

| mg | Milligram |
|-----|----------------|
| mol | Mole |
| g | Gram |
| °C | Degree Celsius |
| % | Percentage |
| h | Hours |
| min | Minutes |
| mL | Milliliter |
| π | Pi |
| λ | Wavelength |
| δ | Chemical shift |
| eV | Electron volt |
| V | Volt |

ACRONYMS

Abbreviations used here for substituents, reagents, etc. are largely in accordance with the recommendation of the IUPAC-IUC Commission on Biochemical Nomenclature, 1974, Pure and Applied Chemistry, 40, 315-331. Additional abbreviations used in this report are listed below:

| DMSO | Dimethyl sulfoxide |
|-------|-----------------------------------|
| DMF | Dimethylformamide |
| PCE | Power conversion efficiency |
| HTM | Hole transporting materials |
| PSC | Perovskite solar cell |
| DSSC | Dye-sensitized solar cells |
| D-A-D | Donor-acceptor-donor |
| TPA | Triphenylamine |
| DCM | Dichloromethane |
| DFT | Density functional theory |
| HRMS | High-resolution mass spectrometry |
| NMR | Nuclear magnetic resonance |
| PTZ | Phenothiazine |
| TMS | Tetramethylsilane |
| DAn | Di-anisole |
| An | Anisole |

Chapter 1

1.1. General Introduction

Energy consumption has risen dramatically in recent years as a result of the expansion of the social economy. As a result, we need efficient, clean, sustainable, and renewable energy sources to replace fossil fuels. The most suitable alternative is solar energy, which is unlimited and emits powerful radiation.¹ The use of solar energy to improve power conversion efficiency (PCE) is a hot topic among scientists right now. Photovoltaic is the process of converting light into energy using semiconducting materials, and the photovoltaic effect is the result. A photovoltaic system is a collection of solar cells that work together to generate electricity². Solar energy is a type of photovoltaic technology that can be used to provide affordable, long-term energy in order to prevent CO₂-induced global warming. This technology's main advantage is that it produces no pollutants or greenhouse gases.

Out of the numerous technologies based on photovoltaics, dye-sensitized solar cells (DSSCs) have gotten a lot of interest from researchers because of their cost-effectiveness, ease of manufacturing, eco-friendly, enhanced stability, more flexible, and high-power conversion efficiencies (PCEs).² The DSSC device has a stability difficulty due to the liquid electrolyte system, which makes commercialization impossible and drives the development of solid-state dye-sensitized solar cells (ssDSSCs).² Tennakone *et al.* reported first ssDSSCs having a heterojunction between CuSCN and TiO₂.^{3,4} However, these attempts resulted in reduced PCE; hence, other materials and techniques must be pursued.

Perovskite solar cells' power conversion efficiency has grown from 3.81 to over 22% in just a few years.⁵ PSCs (perovskite solar cells) are a relatively new type of photovoltaic system that converts solar energy into electrical power and it provides a viable, clean, and hopeful solution to the energy crisis⁶. Perovskite cells have an electron transport layer and hole-transport layer and metallic counter electrode other than light-harvesting material.⁵ HTM is essential for hole transport from the perovskite layer to the back contact and the avoidance of charge recombination. Spiro-OMeTAD, a commonly used HTM has a few drawbacks, including a propensity to crystallize around 85 °C.⁷ Alternative HTMs must be developed with an appropriate level of energy, more soluble in organic solvents⁸, and forming a stable and smooth film, affordable manufacturing, and high hole mobility.

PSCs are undergoing extensive study to improve perovskite light-harvesting materials and fabrication procedures. The five components of the PSC device design are a transparent conductive oxide layer (FTO conductive substrate), an electron-transporting layer (n-type mesoporous semiconductor metal oxide), and light-harvesting material (perovskite), a hole-transporting layer (spiro-OMeTAD), and metal electrode (Au).⁹ Figure 1 shows the device design, several types of perovskite devices⁵ (Figure 1 a-d), an energy level diagram I, existing HTM energy levels (f), and crystal structure (g).



Figure 1. Device design, several types of perovskite devices (a-d), an energy level diagram (e), existing HTM energy levels (f), and crystal structure (g).

To increase the devices' performance, the quality of HTMs must be improved. To generate stable PSCs for commercialization, a very large number of research is going on to improve the quality of the active layer and hole-transport layer⁷. PSCs require HTMs to function properly, in order to increase PCE and stability.⁹ They must have increased photochemical and thermal stability, perfect alignment of the highest occupied molecular orbital (HOMO) for simple hole transfer, and better hole mobility to become champion HTMs. Currently, spiro-OMeTAD is the best hole-transporting material for solar cells, with a conversion efficiency of above 20%.¹⁰ Nonetheless, the synthesis of spiro-OMeTAD is time consuming and very expensive with the limited hole mobility (105 cm²V⁻¹s⁻¹), resulting in poor device performance and hence restricting commercialization.¹¹

In 2006, the first use of perovskite materials in the photovoltaic cells occurred, However, the conversion efficiency of CH₃NH₃PbBr₃ as a sensitizer in a liquid DSSC was just 2.2%. These researchers again observed increased PCE of 3.8% and 3.1%, respectively by utilizing CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ materials for perovskite as sensitizers with electrolyte liquid. Nevertheless, due to the breakdown of the perovskites in the liquid electrolyte, the gadgets were in a state of disarray, and only it was only for a few minutes. Park *et al.* adjusted the electrolyte solvent, perovskite deposition technique, and TiO₂ surface in 2011, reporting a 6.5% improvement in PCE in liquid-based devices using CH₃NH₃PbI₃⁴. The instability problems of the device were a big difficulty owing to perovskite dissolving in electrolytes having polar liquid remained, though. In 2012, a huge breakthrough was made when electrolytes with polar liquid were replaced with solid-state HTMs.⁷

Grätz and Parki utilized Spiro-OMeTAD as hole-transporting materials within solid-state perovskite solar cells based on CH₃NH₃PbBr₃ plated on the mesoporous oxide of Ti, & obtained 9.7% conversion efficiency in 500-hour stable PSC.⁴ Simultaneously, Snaith and colleagues used Al₂O₃ as a scaffold and achieved a PCE of over 10%. From 2012 onwards, the PSC research area exploded, with several groups concentrating on the designing & optimization of perovskite material, deposition processes, device architecture, and n-type & p-type charge-transporting materials to create solar cells.² In practically, all PSC topologies, the usage of a hole transporting materials to remove perovskites' holes and bring them to the electrode is still required. Spiro-OMeTAD, which was described approximately 20 years ago by Grätz *et al.*, is the most widely used classical HTM. For solid-state sensitized solar cells, Spiro-OMeTAD endures the most researched transporting materials.

The charge mobility of Spiro-OMeTAD was found to be less than ideal, and Grätz discovered methods of improving its semiconducting characteristics by utilizing ionic salts and dopants based on Co metal.¹¹ The dopants based on Co metal were developed as one-electron redox shuttles, and their oxidation potential was discovered to make better Spiro-OMeTAD characteristics. By utilizing an ionic salt to promote charge carrier mobility, on the other hand, is viewed as a compromise for stability.¹² Very few unique materials are currently being investigated as e⁻ selective layers for perovskite solar cells, with main focus being on developing very efficient and perfect HTMs. TiO₂ either similar common n-type materials are commonly used. The organic photovoltaic (OPV) community produces a wide range of materials, with the utilization of p-type materials receiving a lot of attention. The results of

OPV research on p-type organic semiconductors were significant in the construction and application of organic HTMs in PSCs.¹³

Few years ago, number of p-type materials have been used in PSCs, including organometallic complexes, inorganic semiconductors, organic small molecules (SMs)¹⁴, & conducting polymers with promising results.⁸ However, only a handful of these has been proven to be stable. In PSCs, polytriarylamine (PTAA)¹⁵, triazatruxene (TAT), & fluorene– dithiophene can only compete with traditional Spiro-OMeTAD.



Figure 2. Spiro-OMeTAD as Hole-transporting material.

Various small molecules, both inorganic and polymer HTMs, have been produced to replace spiro-OMeTAD, and several materials have arisen that come close to matching its performance, particularly in terms of PCE, cost, and stability.¹⁶ Small molecules have the benefit of being easier to purify and having less batch-to-batch variance. Among these, a phenothiazine-based HTMs have lately PSCs came into the picture, & have been demonstrated to be a promising choice for PSCs that have also performed well in dye-sensitized solar cells. Phenothiazine is nitrogen-containing e⁻-rich heterocyclic compound and sulfur as heteroatom. It has the ability to generate a stable radical cation with reversible oxidation and a low potential.¹

Furthermore, a phenothiazine (**PTZ**) is an affordable & cost-effective e⁻ rich aromatic unit with heteroatom that may be used to synthesize a large number of HTMs with very simple processes. Organic photovoltaics (OPVs) and organic transistors both have been reported as using PTZ-based materials for hole-transporting material.¹⁷ In PTZ based HTMs, the interaction between the perovskite and HTM is strengthened by S-heteroatom because Sulphur interacts with Pb+2 of perovskite layer and it increases the ability of good film-forming. The butterfly-like confirmation contains PTZ, which hinders the aggregation of molecules, and their capacity to transmit holes stimulated their identification in DSSCs, OLEDs, and OPVs. The level of disarray in the phenothiazine film, as well as aggregation of molecules, impact the optical characteristics.¹⁸



Figure 3. Phenothiazine based hole-transporting materials.

1.2. Aim and Strategy of our work

Herein, we have synthesized Di-Anisole (Dan) and Triphenylamine (TPA) substituted phenothiazine-based hole-transporting materials named **PTZ-I** and **PTZ-II**. Both **PTZ-I** and **PTZ-II** HTMs were characterized by HRMS, ¹H and ¹³C NMR techniques. Here our aim is to study the photophysical, structural, and theoretical studies of **PTZ-I** and **PTZ-II** molecules. DAn and TPA substituted **PTZ**-based symmetrical HTMs were synthesized by utilization of DAn and TPA as a donor with the help of Buchwald–Hartwig cross-coupling reaction.





Scheme 1. Overall Scheme.

Chapter 2

In 2019, J. Salunke *et al.* used simple, environmentally favorable, and affordable Schiff's base chemistry and affordable precursors to synthesize two phenothiazine (PTZ) based HTMs, AZO-I, and AZO-II. In these HTMs, the AZO-II produces highly promising results, with a 14% power conversion efficiency that was sustained at 90% after two months. We may use this AZO-II in industrial manufacturing because the production cost is low. In terms of cost and long-term performance, our findings show that AZO-II outperforms Spiro-OMeTAD.¹⁸



Figure 4. Structure of AZO-I and AZO-II as HTM.

In 2022, Mengde *et al.* synthesized two low-cost PTZ-based small molecules with symmetric (PTZT-FF) and asymmetric (PTZT-MPF) units as peripheral donors, finding that partially replacing the methoxybenzene unit in PTZT-MPF with the fluorene unit ensures an appropriate HOMO level, increased hole mobility, and better film-forming features.¹⁹



Figure 5. Structure of PTZT-MPF as HTM.

These research shows that phenothiazine-based affordable derivatives made using Schiff base chemistry have a lot of capability for environmentally acceptable HTMs with little environmental effect.

2.1. Chemicals, reagents, and methods

Chemicals utilized in synthesis and purification were in their pure form. These chemicals include phenothiazine (PTZ) (Sigma-Aldrich, 99.5%), bromine (Br₂) (Sigma-Aldrich, 99.5%), DCM (Spectrochem), DCE (Spectrochem), Hexane (Spectrochem), Sodium *tert*-butoxide (Sigma-Aldrich, \geq 99.5%), Pd(Oac)₂ (Sigma-Aldrich, 99%), NaOH (Sigma-Aldrich, \geq 99%), THF, DMF (Spectrochem, \geq 95%), Na₂SO₄ (Spectrochem, \geq 99.5%), NaOH, POCl₃ (Spectrochem, \geq 99%), AcOH (Sigma-Aldrich, 99.99%). Mainly we are dealing with C-N coupling reactions (Buchwald–Hartwig cross-coupling reaction). All these reactions are mostly moisture-sensitive reactions, so all the oxygen and wet sensitive reactions were performed in an inert (nitrogen/argon) atmospheric condition. ¹H and ¹³C NMR spectra of all compounds were recorded using a Bruker AV 500 and 125 MHz spectrometer respectively. Chemical shifts are described in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethyl silane (TMS) using left-over protonated able to make payment as an internal standard {CDCl₃ and DMSO-d₆}. The splitting patterns in ¹H-NMR spectra are explained by symbols as "s, singlet; d, doublet; t, triplet, and m, multiplet." Mass spectrometric analysis was done on Bruker-Daltonics, a microTOF-Q II mass spectrometer.

2.2. General procedure for the preparation of the precursors

The following procedure was used to synthesize compounds 1-7.

2.2.1. Synthetic pathway for Compound 1

A mixture of 4-bromoanisole (1.496 g, 8.00 mmol), *p*-anisidine (0.985 g, 8.00 mmol), Pd(OAc)₂ (0.036 g, 0.16 mmol), dppf (0.177 g, 0.32 mmol) and sodium tert-butoxide (1.153 g, 12.00 mmol) in toluene (40 mL) was stirred at 110 °C for 48 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. The column chromatography was used to purify the crude product. (Hexane/CH₂Cl₂ = 1/1 vol/vol) to obtain Compound **1** (1.291 g, 70.3% yield) as an off-white solid. ¹H-NMR (500 MHz, CDCl₃): δ 7.01-6.97 (m, 4H); 6.86-6.82 (m, 4H); 6.77 (s, br, 1H); 3.76 (s, 6H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 55.7, 114.7, 119.6, 137.9, 154.3 ppm. HRMS (ESI): Calculated for C₁₄H₁₅O₂N [M+H]⁺: 230.1176, found: 230.1176.

2.2.2. Synthetic pathway for Compound 2

mixture of 1-bromo-4-methoxybenzene (1.100)2.86 Α g, mmol), bis(pinacolato)diborane (1.089 g, 4.29 mmol), Pd(OAc)₂ (0.033 g, 0.14 mmol), 1,1'ferrocenediylbis (diphenyl phosphine) (0.161 g, 0.29 mmol) and potassium acetate (0.571 g, 5.72 mmol) in 1,4-dioxane (10 mL) was stirred at 60 °C for 16 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. Column chromatography was used to purify the crude product (SiO₂, Hexane/CH₂Cl₂ = 1/1 vol/vol) to obtain compound 2 (1.053 g, 74.6% yield) as a white solid. ¹H-NMR (500 MHz, CDCl₃): δ 1.33 (s, 12 H) 3.82 (s, 3 H) 6.89 (m, J = 8.55 Hz, 2 H) 7.75 (m, J = 8.54 Hz, 2 H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 24.8, 25.0, 55.5, 83.4, 83.5, 113.3, 114.1, 127.7, 136.5, 162.1, ppm. HRMS (ESI): Calculated for C₁₃H₁₉BO₃ [M+H]⁺: 235.1502, found: 235.1502.

2.2.3. Synthetic pathway for Compound 3

A mixture of bis(4-methoxyphenyl) amine (1.355 g, 5.91 mmol), 1-Bromo-4iodobenzene (1.671 g, 5.91 mmol), Pd(OAc)₂ (0.066 g, 0.29 mmol), 1,1'-ferrocenediylbis(diphenylphosphine) (0.323 g, 0.58 mmol) and sodium *tert*-butoxide (0.852 g, 8.87 mmol) in toluene (30 mL) was stirred at 110 °C for 24 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. Column chromatography was used to purify the crude product (SiO₂, Hexane/CH₂Cl₂ = 9/1 vol/vol) to obtain compound **3** (1.723 g, 75.9% yield) as a white solid. ¹H-NMR (500 MHz, CDCl₃): δ 7.26 (d, *J* = 8.8 Hz, 2H); 7.05 (d, *J* = 8.9 Hz, 4H); 6.85 (d, *J* = 8.9 Hz, 4H); 6.81 (d, *J* = 8.8 Hz, 2H); 3.82 (s, 6H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 55.5, 112.4, 114.8, 122.0, 126.6, 131.8, 140.6, 147.9, 156.1 ppm. HRMS (ESI): Calculated for C₂₀H₁₈BrO₂N [M]⁺: 383.0515, found: 383.0528.

2.2.4. Synthetic pathway for Compound 4

A mixture of **3** (1.100 g, 2.86 mmol), bis(pinacolato)diborane (1.089 g, 4.29 mmol), $Pd(OAc)_2$ (0.033 g, 0.14 mmol), 1,1'-ferrocenediylbis (diphenyl phosphine) (0.161 g, 0.29 mmol) and potassium acetate (0.571 g, 5.72 mmol) in 1,4-dioxane (10 mL) was stirred at 60 °C for 16 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying

with Na₂SO₄. Column chromatography was used to purify the crude product (SiO₂, Hexane/CH₂Cl₂ = 1/1 vol/vol) to obtain compound **4** (1.003 g, 73.3% yield) as a white solid. ¹H-NMR (500 MHz, CDCl₃): δ 7.57-7.54 (m, 2H); 7.11-7.08 (m, 4H); 6.96-6.93 (m, 4H); 6.81-6.78 (m, 2H); 3.82 (s, 6H); 1.32 (s, 12H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 156.8, 151.6, 140.1, 135.7, 127.4, 117.6, 114.8, 83.1, 54.8, 24.3 ppm. HRMS (ESI): Calculated for C₂₆H₃₀BO₂N [M]⁺: 431.2267, found: 431.2391.

2.2.5. Synthetic pathway for Compound 5

A mixture of 10*H*-phenothiazine (1.355 g, 5.91 mmol), 1, 4 iodobromobenzene (1.671 g, 5.91 mmol), Pd(OAc)₂ (0.066 g, 0.29 mmol), tributylphosphaniumtetrafluoroborate (0.323 g, 0.58 mmol) and sodium *tert*-butoxide (0.852 g, 8.87 mmol) in toluene (30 mL) was stirred at 100 °C for 24 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. The crude product was purified by column chromatography (SiO₂, Hexane/CH₂Cl₂ = 9/1 vol/vol) to obtain compound **5** (1.843 g, 82.9% yield) as a white solid. ¹H-NMR (500 MHz, CDCl₃) δ 6.18 (m, *J* = 8.09 Hz, 2 H) 6.75 – 6.83 (m, 4 H) 6.97 (dd, *J* = 7.32, 1.53 Hz, 2 H) 7.18 – 7.21 (m, 2 H) 7.63 (m, *J* = 8.54 Hz, 2 H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 116.5, 121.1, 121.6, 122.9, 126.9, 126.9, 131.9, 133.9, 140.3, 143.8 ppm. HRMS (ESI): Calculated for C₁₈H₁₂BrNS [M]⁺: 354.9849, found: 354.9846.

2.2.6. Synthetic pathway for Compound 6

A mixture of 10-(4-bromophenyl)-10*H*-phenothiazine (1.485 g, 5.71 mmol), (4-((4methoxyphenyl) amino) phenoxy) methylium (1.741 g, 5.91 mmol), Pd(OAc)₂ (0.066 g, 0.29 mmol), tributylphosphaniumtetrafluoroborate (0.323 g, 0.58 mmol) and sodium *tert*-butoxide (0.852 g, 8.87 mmol) in toluene (30 mL) was stirred at 100 °C for 24 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. The crude product was purified by column chromatography (SiO₂, Hexane/CH₂Cl₂ = 9/1 vol/vol) to obtain compound **6** (1.967 g, 78.9% yield) as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 3.81 (s, 6 H) 6.30 (d, *J* = 8.24 Hz, 2 H) 6.75 – 6.81 (m, 2 H) 6.83 – 6.92 (m, 6 H) 6.94 – 7.01 (m, 2 H) 7.06 (d, *J* = 8.85 Hz, 2 H) 7.13 (d, *J* = 8.85 Hz, 2 H) 7.14 – 7.18 (m, 4 H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 55.5, 114.8, 115.7, 119.6, 120.7, 122.1, 126.5, 126.8, 127.2, 131.4, 132.1, 140.3, 144.7, 156.3 ppm. HRMS (ESI): Calculated for C₃₂H₂₆N₂O₂S [M]⁺: 502.1710, found: 502.1710.

2.2.7. Synthetic pathway for Compound 7

After this the Compound **6** was employed bromination reaction, N-(4-(10Hphenothiazine-10-yl) phenyl)-4-methoxy-N-(4-methoxyphenyl) aniline (2 g, 8.28 mmol) was dissolved in 13 ml CHCl₃ and a solution of NaOH (0.496 g, 12.42 mmol) in 50 ml glacial acetic acid was added to the above mixture. Then at last bromine (0.42 ml, 8.28 mmol, in 10 mL glacial acetic acid) was added dropwise at 0 °C. The mix was stirred at 0 °C for 30 minutes till the complete addition of bromine took place. After this mix was removed and workup with water and DCM, and the organic layer was dried over MgSO₄. At last, we got a light-yellow liquid of mono-bromo TPA substituted PTZ Bromo-phenothiazine-bis(4-methoxyphenyl) aniline with a yield of 69%. HRMS (ESI): Calculated for $C_{32}H_{25}BrN_2O_2S$ [M]⁺: 580.0815, found: 580.0846.

2.3. Synthetic pathway for Final Compounds

The Buchwald–Hartwig cross-coupling reaction of Compound 7 with DAn and TPA resulted in mono substituted DAn and TPA substituted PTZ (**PTZ-I** and **PTZ-II**).

2.3.1. Synthetic pathway for Compound PTZ-I

A mixture of 4-(3-bromo-10H-phenothiazin-10-yl)-N,N-bis(4-methoxyphenyl)aniline (1.485 g, 5.71 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.741 g, 5.91 mmol), Palladium acetate (0.066 g, 0.29 mmol), tributylphosphaniumtetrafluoroborate (0.323 g, 0.58 mmol) and Pd(OAc)₂ (0.852 g, 8.87 mmol) in THF : H₂O (4:1) (5 mL) was stirred at 80 °C for 24 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. Column chromatography was used to purify the crude product (SiO₂, Hexane/CH₂Cl₂ = 9/1 vol/vol) to obtain compound **PTZ-I** (1.877 g, 82.9% yield) as a yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 3.80 – 3.84 (m, 9 H) 6.32 (t, *J* = 9.84 Hz, 2 H) 6.76 – 6.81 (m, 1 H) 6.89 (d, *J* = 8.39 Hz, 5 H) 6.92 (d, *J* = 8.39 Hz, 2 H) 6.99 (d, *J* = 7.32 Hz, 1 H) 7.03 – 7.08 (m, 3 H) 7.13 – 7.19 (m, 7 H) 7.40 (d, *J* = 8.09 Hz, 2 H) ppm. ¹³C-NMR (125 MHz, CDCl₃): δ 55.3, 55.5, 114.1, 114.9, 115.7, 115.9, 119.3, 120.0, 120.7, 122.1, 124.6, 124.9, 126.6, 126.8, 127.2, 127.3, 131.3, 132.0, 132.5, 134.9, 140.3, 143.4, 144.5, 148.6, 156.3, 158.8 ppm. HRMS (ESI): Calculated for C₃₉H₃₂N₂O₃S [M]⁺: 608.2128, found: 608.2173.

2.3.2. Synthetic pathway for Compound PTZ-II

A mixture of 4-(3-bromo-10H-phenothiazin-10-yl)-N,N-bis(4-methoxyphenyl)aniline (1.565 g, 5.71 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)phenyl)aniline (1.921 g, 5.91 mmol), Pd(OAc)₂ (0.066 g, 0.29 mmol), tributylphosphaniumtetrafluoroborate (0.323 g, 0.58 mmol) and Potassium acetate (0.852 g, 8.87 mmol) in THF : H₂O (4:1) (5 mL) was stirred at 80 °C for 24 h. The mixture was diluted with dichloromethane (DCM) and rinsed with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na₂SO₄. Column chromatography was used to purify the crude product (SiO₂, Hexane/CH₂Cl₂ = 9/1 vol/vol) to obtain compound PTZ-II (1.557 g, 71.8% yield) as a yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 3.81 (d, J = 9.16 Hz, 12 H) 6.32 (t, J = 8.01 Hz, 2 H) 6.77 - 6.81 (m, 1 H) 6.82 -6.86 (m, 5 H) 6.89 (d, J = 8.70 Hz, 5 H) 6.94 (d, J = 8.39 Hz, 2 H) 6.99 (d, J = 7.93 Hz, 1 H) 7.07 (d, J = 8.70 Hz, 7 H) 7.14 – 7.19 (m, 6 H) 7.29 (d, J = 8.39 Hz, 2 H) ppm. ¹³C-NMR (125) MHz, CDCl₃): δ 55.5, 114.6, 114.7, 114.9, 115.7, 115.9, 119.3, 119.9, 120.7, 120.8, 121.1, 122.1, 124.3, 124.7, 126.4, 126.5, 126.6, 126.7, 126.8, 126.9, 127.1, 127.2, 131.4, 131.9, 132.1, 134.9, 140.3, 140.9, 141.1, 143.3, 144.5, 147.7, 148.6, 155.7, 155.8, 156.3 ppm. HRMS (ESI): Calculated for C₅₂H₄₃N₃O₄S [M]⁺: 805.2969, found: 805.2995.

Chapter 4

3.1. Synthetic pathway and characterization

The synthesis of DAn and TPA substituted PTZ compounds from 1 to **PTZ-II** are shown in different schemes one by one. Compound 1 was synthesized by performing a Buchwald–Hartwig C-N cross-coupling reaction between 4-methoxyphenylamine and 1-bromo-4-methoxybenzene in toluene solvent with ^{*t*}BuONa as the base and Pd(OAc)₂ as the catalyst at 110 °C, according to following earlier reports. The compound 1 was obtained with 68.5% yield. (Scheme 2)



Scheme 2. Synthetic pathway for Compound 1.

Compound 2 was synthesized by performing Suzuki Miyaura borylation reaction between Bis(pinacolato)diboron and 1-Bromo-4-methoxybenzene in toluene solvent with AcOK as the base and Pd(OAc)₂ as the catalyst at 60 °C, according to following earlier reports. Compound 2 was obtained with 78.6% yield. (Scheme 3)



Scheme 3. Synthetic pathway for Compound 2.

Compound **3** was synthesized by performing a Buchwald–Hartwig C-N cross-coupling reaction between Compound **1** and 1-bromo-4-iodobenzene in toluene solvent with ^{*t*}BuONa as the base and Pd(OAc)₂ as the catalyst at 110 °C, according to following earlier reports. Compound **3** was obtained with 76.9% yield. (Scheme **4**)



Scheme 4. Synthetic pathway for Compound 3.

Compound **4** was synthesized by performing a Suzuki Miyaura borylation reaction between Compound **3** and Bis(pinacolato)diboron in toluene solvent with AcOK as the base and Pd(OAc)₂ as the catalyst at 60 °C, according to following earlier reports. The compound **4** was obtained with 89.9% yield. (Scheme **5**)



Scheme 5. Synthetic pathway for Compound 4.

Compound **5** was synthesized by performing a Buchwald–Hartwig C-N cross-coupling reaction between 10*H*-phenothiazine and 5-bromo-2-iodobenzene-1,3-diylium in toluene solvent with NaO^tBu as the base and Pd(OAc)₂ as the catalyst at 100 °C, according to following earlier reports. Compound **5** was obtained with 81.5% yield. (Scheme **6**)



Scheme 6. Synthetic pathway for Compound 5.

Compound **6** was synthesized by performing a Buchwald–Hartwig C-N cross-coupling reaction between 10-(4-bromophenyl)-10*H*-phenothiazine and (4-((4-methoxyphenyl) amino) phenoxy) methylium in toluene solvent with NaO^tBu as the base and Pd(OAc)₂ as the catalyst at 100 °C, according to following earlier reports. Compound **6** was obtained with 91.5% yield. (Scheme **7**)



Scheme 7. Synthetic pathway for Compound 6.

Compound 7 was further brominated using liquid bromine in chloroform and glacial acetic acid at 0 °C to give brominated product compound 7. Compound 7 was obtained with 69.9% yield. (Scheme 8)



Scheme 8. Synthetic pathway for Compound 7.

PTZ-I was synthesized by performing a Suzuki cross-coupling catalyzed reaction between Compound 7 and Compound 2 in THF and water solvent with K_2CO_3 as the base and $Pd(PPh_3)_4$ as the catalyst at 80 °C. The **PTZ-I** was obtained with 76.5% yield. (Scheme 9)



Scheme 9. Synthetic pathway for Compound PTZ-I.

PTZ-II was synthesized by performing a Suzuki cross-coupling catalyzed reaction between Compound 7 and Compound 4 in THF and water solvent with K_2CO_3 as the base and $Pd(PPh_3)_4$ as the catalyst at 80 °C. The **PTZ-I** was obtained with 74.8% yield. (Scheme 10)



Scheme 10. Synthetic pathway for Compound PTZ-II.

The purification of all PTZ compounds was carried out by column chromatography, and ¹H NMR, ¹³C NMR, and mass spectra were used to characterize all of the compounds.

3.2. Photophysical properties

The photophysical properties of DAn and TPA substituted **PTZ**-based HTMs (**PTZ-I** and **PTZ-II**) were studied using electronic absorption spectroscopy. A solution of **PTZ-I** and **PTZ-II** in 10⁻⁵ M DCM solution was used to study the photophysical properties. The UV-vis spectra (Figure 6) of **PTZ-I** and **PTZ-II** displayed absorption bands between 250-350 nm. The **PTZ-I** and **PTZ-II** exhibit an intense absorption band at 279 nm and 306 nm respectively. Furthermore, we discovered that **PTZ-II** has a redshift in UV-vis absorption spectroscopy because it has a more conjugated system than **PTZ-I**. The addition of DAn substitute in **PTZ-II** increases the donor strength which further shifts the transitions of **PTZ** derivatives to a longer wavelength.



Figure 6. Absorption spectra of PTZ-I and PTZ-II in 1×10^{-5} M DCM solution.

3.3. Theoretical calculations

The molecular orbital distribution of **PTZ-I** and **PTZ-II** were measured through Density Functional Theory study. The frontier molecular orbitals of **PTZ-I** and **PTZ-II** were investigated with DFT calculations by using Gaussian 09W program (Figure 7, at the B3LYP/6-31G(d) and structure optimization was carried out in the gas phase to better understand their structural properties and electronic properties. The E_{HOMO} levels of PTZ-I and **PTZ-II** are located on the **An** and **TPA** groups, while the E_{LUMO} levels were mainly located on the (**PTZ**) phenothiazine (core) (Figure 7). The E_{HOMO} values of **PTZ-I** and **PTZ-II** determined from the theoretical studies are -4.27 and -4.24 eV, respectively, while the E_{LUMO} levels of **PTZ-I** are -0.75 eV and -0.54 eV, respectively.



Figure 7. Energy level diagram showing the HOMO and LUMO levels of PTZ-I and PTZII determined at the B3LYP/6-31G(d) level.

4.1. Conclusion

Solar energy is the application of photovoltaics, and it is the most efficient, clean, sustainable, and renewable energy resource that can be used to replace non-renewable energy sources such as fossil fuels. We can transform light into electricity with this technique by employing semiconductors or biological molecules. Perovskite solar cells are a form of solar cell that converts light into electricity using perovskite materials. Over the previous ten years, the power conversion efficiency has skyrocketed from 3.8% to 25.2%. PSCs have certain unique photophysical qualities, such as a customizable bandgap and a high absorption coefficient, which make it an ideal technology for addressing today's energy issue. We can achieve the high-performing perovskite solar cells by just selecting suitable perovskite material.

Solar cells consisting of organic-inorganic hybrid materials are highly promising in terms of conversion efficiency, however, they have considerable limits in terms of stability. Spiro-OMeTAD was a game-changing finding for scientists since it can provide PCE of up to 22.8 %, but the synthesis procedure is time-consuming and very expensive. A lot of study is now underway on phenothiazine (**PTZ**) based organic compounds as HTM, with promising results. They employed **PTZ** derivatives as donor moieties and coupled them to appropriate acceptor moieties to control the photophysical parameters of solar cells. Scientists are currently interested in D-A-D-based HTMs because they offer promising outcomes in terms of high-power conversion efficiency and relatively low costs.

For perovskite solar cells, we have synthesized two **PTZ**-based hole-transporting materials named **PTZ-I** and **PTZ-II** by Pd-catalyzed C-N coupling reaction. Each and every molecule was well characterized by various spectroscopic techniques like ¹H and ¹³C NMR, and HRMS. We also studied the optical, electrochemical, and theoretical properties of both **PTZ-I** and **PTZ-II** molecules. The **PTZ-I** and **PTZ-II** have a strong absorption band at 279 nm and 306 nm, respectively. **PTZ-II** shows a redshift in UV-vis absorption spectroscopy because it has a more conjugated system than **PTZ-I**. Furthermore, Density Functional Theory (DFT) demonstrates that the HOMO level of both HTMs is located on **An** and **TPA** groups and LUMO level of both HTMs is located on **PTZ** (unit) respectively.

Today's world is facing a major energy dilemma, necessitating the development of more efficient, sustainable, and long-lasting energy sources. We can say that solar energy is the best answer for this situation, and I am hopeful that it will meet all of our hopes and provide the world with clean, green energy for a very long time. Organic perovskite was a game-changing discovery for scientists, and it's yielding very good results for us, since its power conversion efficiency has grown by 25%, and I expect it to continue to rise in the future.

APPENDIX-A

Characterization of Compound 1

1.1 ¹H NMR spectrum of Compound 1



Figure 8. ¹H NMR spectrum of Compound 1.

1.2 ¹³C NMR spectrum of Compound 1



Figure 9. ¹³C NMR spectrum of Compound 1.

1.3 HRMS of Compound 1



Figure 10. HRMS of Compound 1.

Characterization of Compound 2

2.1 ¹H NMR spectrum of Compound 2



Figure 11. ¹H NMR spectrum of Compound 2.

2.2 ¹³C NMR spectrum of Compound 2



Figure 12. ¹³C NMR spectrum of Compound 2.





Figure 13. HRMS of Compound 2.

Characterization of Compound 3

3.1 ¹H NMR spectrum of Compound 3



Figure 14. ¹H NMR spectrum of Compound 3.

3.2 ¹³C NMR spectrum of Compound 3





3.3 HRMS of Compound 3



Figure 16. HRMS of Compound 3.

Characterization of Compound 4

4.1 ¹H NMR spectrum of Compound 4



Figure 17. ¹H NMR spectrum of Compound 4.

4.2 ¹³C NMR spectrum of Compound 4



Figure 18. ¹³C NMR spectrum of Compound 4.

4.3 HRMS of Compound 4



Figure 19. HRMS of Compound 4.

Characterization of Compound 5

5.1 ¹H NMR spectrum of Compound 5



Figure 20. ¹H NMR spectrum of Compound 5.

5.2¹³C NMR spectrum of Compound 5



Figure 21. ¹³C NMR spectrum of Compound 5.

5.3 HRMS of Compound 5



Figure 22. HRMS of Compound 5.

Characterization of Compound 6

6.1 ¹H NMR spectrum of Compound 6



Figure 23. ¹H NMR spectrum of Compound 6.

6.2¹³C NMR spectrum of Compound 6









Figure 25. HRMS of Compound 6.

Characterization of Compound 7

7.1 HRMS of Compound 7



Figure 26. HRMS of Compound 7.

Characterization of PTZ-I

8.1 ¹H NMR spectrum of PTZ-I



Figure 27. ¹H NMR spectrum of PTZ-I.

8.2 ¹³C NMR spectrum of PTZ-I









Figure 29. HRMS of PTZ-I.

Characterization of PTZ-II

9.1 ¹H NMR spectrum of PTZ-II





9.2 ¹³C NMR spectrum of PTZ-II



Figure 31. ¹³C NMR spectrum of PTZ-II.

9.3 HRMS of PTZ-II



Figure 32. HRMS of PTZ-II.

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