Synthesis of Phenothiazine Incorporated Phenanthroimidazole Derivatives

M.Sc. thesis

by

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DEPARTMENT OF CHEMISTRY

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Synthesis of Phenothiazine Incorporated Phenanthroimidazole Derivatives

A THESIS

submitted in the partial fulfilment of the requirements

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of

Master of Science

By

Garima Singh

DEPARTMENT OF CHEMISTRY

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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis titled "**Synthesis of Phenothiazine Incorporated Phenanthroimidazole Derivatives"** in the partial fulfilment 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 as during the time period from August, 2020 to May, 2021 under the supervision of Prof. Rajneesh Misra, Professor, Department of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

GARIMA SINGH

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

PROF. RAJNEESH MISRA

Garima Singh has successfully given her M.Sc. Oral Examination held on 08.06.2021.

Signature of Supervisor of M.Sc. thesis

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Date: 09.06.21

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Signature of PSPC Member

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Date: 09.06.2021

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Dedicated to

My Family

Abstract

Stimuli-responsive small conjugated organic molecules have gained significant interest for utility in smart materials like OLEDs, memory devices, sensors, rewritable papers that are reshaping the ways in which security should function in today's cyberworld. It is a prerequisite for a molecule to show intense solid-state emission to be employed in various applications. One of the preferred ways to synthesize such molecules with high fluorescence efficiency is to upgrade the D-A (donor-acceptor) molecules by introducing π-linkers between multiple donor and acceptor moieties. Herein, we have followed elementary D-A approach to synthesize phenothiazine incorporated phenanthroimidazole molecules, in which, the phenothiazine was used as electron donor unit and the phenanthroimidazole was used as electron acceptor unit. The structure comprises an additional phenyl ring which is directly attached to the N- position of the imidazole ring. We have incorporated heavy atoms, bromine (-Br) to molecular structure of the target molecules which could result significant halogen–halogen bonds in the solid state and hence these halogen–halogen interactions may contribute to the enhancement of aggregation-induced emission by strictly restricting the molecules' vibration and rotation.

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Nomenclature

Hz	Hertz
°C	degree Celsius
ppm	parts per million
mmole	millimole
g	gram
mL	milliliter
min.	minutes
λ	lambda
δ	delta

Acronyms

PI	Phenanthroimidazole
PTZ	Phenothiazine
TADF	Thermally Activated Delayed Fluorescence
NMR	Nuclear Magnetic Resonance
HRMS	High Resolution Mass Spectrometry
DCM	Dichloromethane
EtOAc	Ethyl acetate
RB flask	Round-bottom flask
TLC	Thin layer chromatography
DFT	Density Functional Theory
DMSO	Dimethyl sulfoxide
$CDCl_3$	Deuterated chloroform
THF	Tetrahydrofuran
s	singlet peak
d	doublet peak
t	triplet peak
m	multiplet peak

Chapter 1 Introduction

1.1 General Information

Stimuli-responsive small organic molecules that show luminescence in solid state have been an intriguing area of research over the last decades by virtue of their versatile applications. [1,7] These molecules, favorable for designing of smart novel materials encompassing organic light emitting diodes (OLEDs), mechanical sensors, [3-5,8] fluorescent probes and switches, [6,8,9] photovoltaic devices, memory devices, safety records, bioimaging among others, [9,10] have continuously thrived and are still being explored to expand their applicability. Stimuli-responsive materials are known to respond to different stimuli such as heat, light, pH, mechanical stress, electric field etc. [27] Mechanofluorochromic materials have gained immense popularity and significance as they exhibit reversible and/or switchable changes in their emissive properties upon application of mechanical stimuli that include scarping, grinding, mechanical friction, stretching, shearing etc. [5-7] It is a prerequisite for a molecule to show high emissions in its solid state to manifest prominent mechanofluorochromism. An opposing mechanism, 'aggregation-caused quenching (ACQ)' [8,10,21] poses challenges in achieving the target by quenching the emissions during formation of aggregates. Short-range molecular interactions like π-π stacking emerging from the planarity of the skeleton of the molecule are the most common cause of ACQ. [22] This problem found an address when Tang et. al reported of a mechanism, popularised as Aggregation-induced emission (AIE), through which enhanced emissions were observed in aggregates of solid state. [10,17] Twisted molecular conformations in fluorophores result in restricted intramolecular rotations (RIR), which in turn weaken intermolecular close packing and π-π stacking interactions, thereby facilitating AIE. [21,22] Similarly, introduction of non-planar functional units is also useful for inducing loose packing in the crystalline form of the molecules. [21] Mechanical stimulus damages the loose aggregates,

causing substantial change in colour and fluorescence as a result of changed intermolecular interactions. [21] To tune the mechanochromic properties of the fluorophores, introduction of large π-conjugated frameworks and/or heteroatoms are proven and tested strategies used to enrich the MFC behaviour. [12-14] The heavy-atom effect is a well-known photophysical phenomena in which adding a heavy atom like bromine to a dye molecule enhances the fluorescence yield by restricting the ACQ process. The heavy-atom effect contributes significantly to considerable spin–orbit coupling (SOC), resulting in an increase in the rate of intersystem crossing and radiative processes from T_1 to S_0. As a result, while the heavy-atom effect is frequently overlooked when designing common fluorescent molecules, it has been incorporated into the development of highly efficient organic room-temperature phosphorescent materials and thermally activated delayed fluorescence emitters.

1.2 Literature Survey

Polymers designed along Donor-Acceptor (D-A) framework are an important class of organic semiconductors that find widespread utility in organic semiconductors and photovoltaics, organic light emitting diodes (OLEDs), stimuli-responsive devices, biology etc. [7,18,27] In such a molecule, donor moiety is an electron-rich species whereas the acceptor one is an electron-deficient species. The synthesized molecules are stimulated to check whether they allow intramolecular charge transfer (ICT). ICT is a useful property to tune photophysical properties in the molecule. [6] The optical and electronic properties of the aforementioned systems can be further exploited to our advantage by making simple modifications to the system such as either by changing the strength or number of the donor/acceptor species or by introducing various π linkers in the system or both. Today, we see molecules of types D-π-A, D-A-D′, D-A-A′, D′–A′–D–A–D–A′–D′, D-π-A-π-D, D–A–D–π–D′, and D–A–D–A′–D′ etc. also being reported.

[7,8] Their ability to show strong spectral shifts under stimulus as a result of large transition-dipole-moment make them a preferred choice. [21] Some commonly incorporated donor moieties include thiophene, phenothiazine, tetraphenylethylene, ferrocene, oligothiophenes, carbazoles, triarylamines while phenanthroimidazole (PI), benzothiadiazole (BTD) [27], diketopyrrolopyrrole (DPP) [10], pyrazabole (PY), tetracyanobutadiene (TCBD), tetracynoethylene (TCNE), tetracynoquinodimethane (TCNQ), diarylborons, Dibenzo[b,d]thiophene sulfone (DBTSO), β-diketone boron complexes, borondiiminates are the usually employed acceptor moieties in mechanochromic materials. [21]

Phenothiazine (PTZ) is a non-planar and electron-rich species commonly used to synthesise materials with excellent mechanochromic properties. [21] It has two aromatic rings bridged together by a sulphur and a nitrogen atom. The central six-membered thiazine ring performs two functions: firstly, it enhances the electron-donating ability and secondly, it allows the molecular structure to exist in bent or a structure similar to the shape of a butterfly. The nitrogen and sulphur atoms on the central ring of PTZ moiety induce supramolecular interactions in the solid state which can potentially influence the photophysical properties of the molecule. [22] These structural properties have thus helped phenothiazine (PTZ) gain utility in development of AIE and mechanofluorochromic materials and applications in organic photovoltaic (OPVs) devices, TADF materials etc. [22]

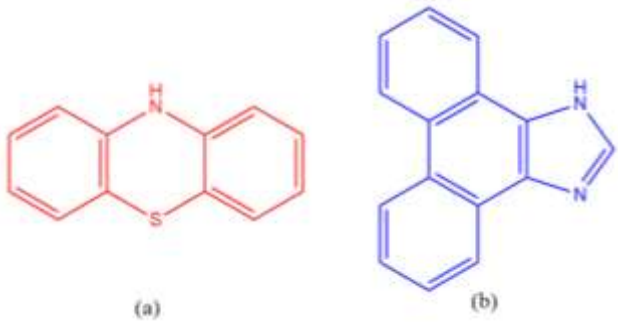


Figure 3: Chemical structure of (a) Phenothiazine and (b) Phenanthroimidazole molecule

The phenanthroimidazole (PI) is an efficient fluorogenic framework wherein an imidazole ring and phenanthrene are fused together. PI has been a point of continuous attention due to its efficient high emissions and remarkable thermal-, chemical- and photo- stability. [12-14] High fluorescence efficiency remains one of the best properties to exploit in order to develop stimuli-responsive fluorescent materials. Apart from significant efficiency, the ambipolar PI core possesses charge transporting ability that makes it suitable for applications in materials. [8,22]

1.3 Aim and Strategy of our work

The development of multiple chromophores-based donor-acceptor molecules e.g., D−A−A′, D−π−A, D-A-D-A′-D, D-π-A-π-D, A−D−D′, etc., frameworks may generate intense AIE emissions and mechanofluorochromism. For this work, we aimed at to design molecules based on D-A approach by incorporating PI as the acceptor (A) and PTZ as the donor (D), and finely tune the electronic and photophysical properties by changing the strength of the attaching moieties. Further, we have introduced heavy atoms, bromine (-Br) to the molecular structures of the target compounds as they are known to intensify the solid-state emission of a fluorophore. The structures of final molecules were characterized with the help of ^{1}H-NMR, ^{13}C-NMR and HRMS.

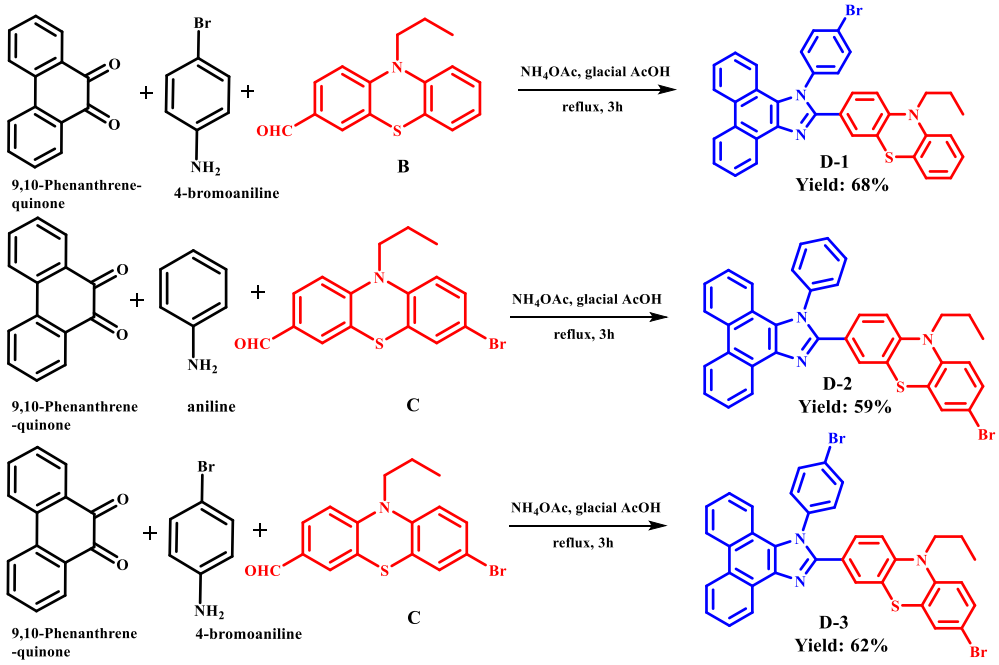


Figure 4: Overall synthetic scheme

Chapter 2 Experimental Details

2.1 Chemicals and Reagents

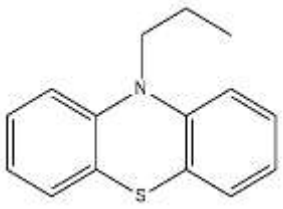
All chemicals used for syntheses were used as received from the commercial sources unless stated otherwise. The chemicals required during the course of this study are: 9,10-phenanthrenequinone (Sigma-Aldrich), Aniline (Sigma-Aldrich), 4-bromoaniline (Sigma-Aldrich), Bromine liq. (Sigma-Aldrich, 99.5%), Phenothiazine (Sigma-Aldrich), Propyl iodide (Sigma-Aldrich, 99%), Dimethyl formamide (Spectrochem), 1,2-Dichloroethane (Spectrochem), Dichloromethane (Spectrochem), Hexane (Spectrochem), Ethyl acetate (Spectrochem), glacial acetic acid, NaOH, NH_4OH, Phosphoryl chloride (Spectrochem), Dimethyl sulphoxide (Sigma-Aldrich).

Moisture sensitive reactions were performed in inert nitrogen/argon atmosphere. ^{1}H-NMR spectra of the final compounds were recorded using a Bruker AV 400 MHz spectrometer. Mass spectrometric analyses were performed on Bruker-Daltonics, microTOF-Q II mass spectrometer. Column Chromatography was performed using 400 mesh silica gel.

2.2 Procedures followed for preparation of the precursors

The precursors A, B and C were synthesized as per the reported procedures.

2.2.1 Synthesis of A



To a clean and dried 100 mL round-bottom flask, phenothiazine (1g, 5.018 mmoles) was transferred. DMSO (15 mL) and NaOH (1g) were added to the phenothiazine and the mixture was left for stirring at RT for 15 minutes. Thereafter, propyl iodide (1.7g, 10.000 mmoles) was added. The mixture was left for stirring for overnight at the room temperature. After the completion of the reaction, it was worked up with H_2O/DCM and the crude sample dried over high vacuum rotary evaporator. Column chromatography was used to obtain purified 'A'. The solvent used for this purpose was hexane only. Colour: oily white, Yield: 91%.

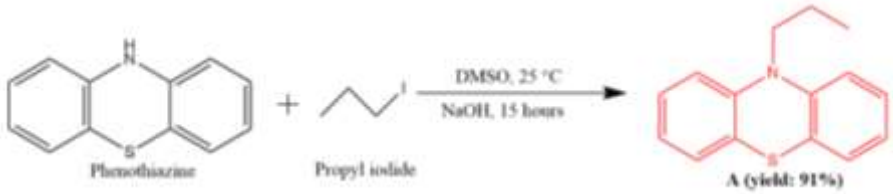
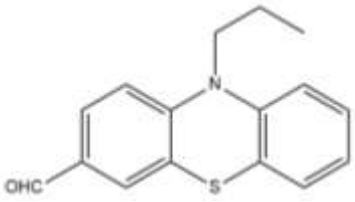


Figure 5: Synthetic route of precursor '**A**'

2.2.2 Synthesis of B



To a clean and dried 100 mL round-bottom flask, A (0.5g, 2.071 mmoles) and DMF (0.6374 mL, 8.284 mmoles) were transferred. DCE (10 mL) was added to the RB, the reaction mixture was cooled to 0°C and then $POCl_3$ (0.78 mL, 8.284 mmoles) was added to the reaction mixture in one portion and left for stirring at 0°C for 10 min. and later for reflux at 80°C for 16 hours. After the completion of reaction, it was worked up with H_2O/DCM and the crude sample dried over high vacuum rotary evaporator. Column chromatography was used to obtain purified 'B'. The solvent mixture used for this purpose was DCM/Hexane taken in volume ratio of 2:3. Yield: 79%

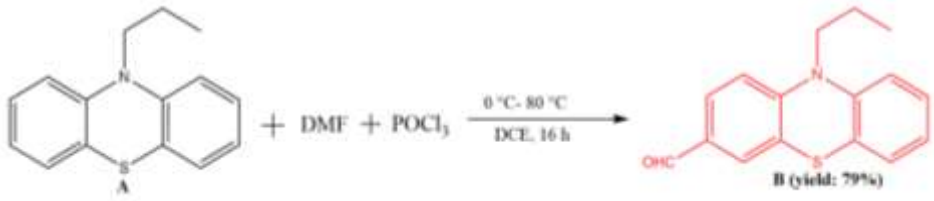
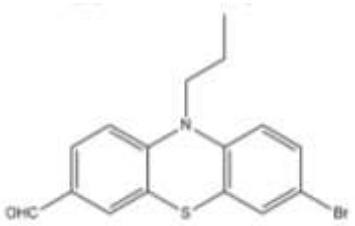


Figure 6: Synthetic route of precursor '**B**'

2.2.3 Synthesis of C



To a clean and dried 100 mL round-bottom flask, after transferring B (1g, 3.913 mmoles) and THF (3 mL), the solution was cooled to 0°C. NBS (1.0450g, 5.870 mmoles) was added to the RB and the reaction mixture was left at 0°C for 10 minutes. The reaction mixture was then left undisturbed to stir for 2 hours at RT. After the completion of reaction, it was worked-up with H_2O/DCM and the crude compound dried over high vacuum rotary evaporator. Yellow-coloured purified 'C' was obtained with the help

of column chromatography with solvent mixture EtOAc/hexane taken in volume ratio 1:9. Yield: 88%

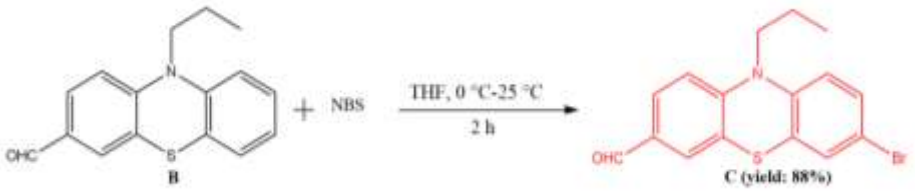


Figure 7: Synthetic route of precursor '**C**'

2.2.4 Synthesis of final molecules

2.2.4.1 Synthesis of D-1

In a clean and dried 250 mL round-bottom flask, 9,10-phenanthrenequinone (1g, 4.741 mmoles), 4-bromoaniline (1.2231g, 7.111 mmoles) and **B** (1.2105g, 4.742 mmoles) were transferred. In a separate conical flask, ammonium acetate (3.68g, 47.4 mmoles), dissolved in glacial acetic acid (40 mL) was mixed into the RB. The reaction mixture was left undisturbed for refluxing in an oil bath for 3 hours. Upon completion of the reaction, the mixture was left to cool. After cooling, the reaction mixture was transferred to an RB containing water (200 mL) and continuously stirred for 10 minutes. The green ppt. obtained was filtered, dried, and purified with the help of column chromatography using solvent mixture DCM-hexane taken in volume ratio 2:3. The final product (**D-1**, 2.031g, yield: 68%) was a light green solid.

(**D-1**) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.84 (d, J = 8 Hz, 1H), 8.73 (d, J = 8 Hz, 1H), 8.66 (d, J = 8 Hz, 1H), 7.71 (d, J = 8 Hz, 3H), 7.63 (t, J = 8 Hz, 1H), 7.48 (m, 2H), 7.34 (d, J = 8 Hz, 2H), 7.28 (t, J = 8 Hz, 1H), 7.11 (m, 4H), 6.89 (t, J = 8 Hz, 1H), 6.79 (d, J = 8 Hz, 1H), 6.66 (d, J = 8 Hz, 1H), 3.74 (t, J = 8 Hz, 2H), 1.77 (m, 2H), 0.97 (t, J = 8 Hz, 3H) in ppm. ^{13}C{1 H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.2, 145.9, 144.5, 137.9, 137.5, 133.5, 130.8, 129.2, 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 127.4, 127.1, 126.4, 125.8, 125.1, 125.0, 124.3,

124.1, 123.9, 122.8, 122.8, 120.6, 115.5, 114.7, 49.3, 20.1, 11.3 ppm. HRMS (ESI): calculated for $C_{36}H_{26}BrN_3S$ $[M + H]^+$, 612.1104; found, 612.1096.

2.2.4.2 Synthesis of D-2

In a clean and dried 100 mL round-bottom flask, 9,10-phenanthrenequinone (0.5g, 2.37 mmoles), aniline (0.33g, 3.58 mmoles) and **C** (0.8 g, 2.37 mmoles) were transferred. In a separate conical flask, ammonium acetate (1.76g, 23.72 mmoles), dissolved in glacial acetic acid (20 mL) was mixed into the RB. The reaction mixture was left undisturbed for refluxing in an oil bath for 3 hours. When the reaction mixture cooled, it was added to 100 mL of water and continuously stirred for 10 minutes. A green ppt. formed, that was later filtered, dried and purified with the help of column chromatography using DCM-hexane taken in volume ratio 2:3. The final product obtained (D-2, 0.837g, yield: 59%) was a light green solid.

(**D-2**) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.86 (d, J = 8 Hz, 1H) 8.76 (d, J = 8 Hz, 1H), 8.70 (d, J = 8 Hz, 1H), 7.74 (t, J = 8 Hz, 1H), 7.65 (m, 4H), 7.51 (m, 3H), 7.38 (s, 1H), 7.30 (s, 1H), 7.19 (m, 4H), 6.66 (dd, J = 8 Hz, 2H), 3.72 (t, J = 8 Hz, 2H), 1.76 (m, 2H), 0.97 (t, J = 8 Hz, 3H) in ppm. ^{13}C{1 H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 149.7, 145.4, 143.7, 138.6, 130.4, 130.1, 130.0, 129.7, 129.3, 129.1, 128.6, 128.3, 128.2, 127.4, 126.6, 126.4, 125.8, 125.0, 124.2, 124.0, 123.1, 123.0, 120.8, 116.6, 114.9, 114.8, 49.4, 19.9, 11.2 ppm. HRMS (ESI): calculated for $C_{36}H_{26}BrN_3S$ $[M + H]^+$, 612.1104; found, 612.1115.

2.2.4.3 Synthesis of D-3

In a clean and dried 100 mL round-bottom flask, 9,10-phenanthrenequinone (0.5g, 2.37 mmoles), 4-bromoaniline (0.592g, 3.58 mmoles) and C (0.8g, 2.37 mmoles) were transferred. In a separate conical flask, ammonium acetate (1.76g, 23.72 mmoles) was dissolved in glacial acetic acid (20 mL). It was mixed into the RB and the reaction mixture was put to reflux in an oil bath for 3 hours. When the reaction

mixture cooled, it was added to 100 mL of water and continuously stirred for 10 minutes. A green ppt. formed, that was consequently filtered, dried and purified with the help of column chromatography using DCM-Hexane taken in volume ratio 2:3. The final product obtained (D-3, 0.995g, 62%) was a light green solid.

(**D-3**) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.84 (d, J = 8 Hz, 1H) 8.77 (d, J = 8 Hz, 1H), 8.70 (d, J = 8 Hz, 1H), 7.74 (m, 3H), 7.65 (t, J = 8 Hz, 1H), 6.67 (dd, J = 8 Hz, 2H), 7.52 (t, J = 8 Hz, 1H), 7.45 (s, 1H), 7.39 (d, J = 8 Hz, 2H), 7.31 (t, J = 8 Hz, 1H), 7.19 (m, 4H), 3.74 (t, J = 8 Hz, 2H), 1.77 (m, 2H), 0.99 (t, J = 8 Hz, 3H) in ppm. ^{13}C{1 H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 149.9, 145.6, 143.7, 137.8, 133.6, 130.8, 130.0, 129.7, 129.3, 128.4, 127.9, 127.5, 126.6, 126.5, 125.9, 125.1, 124.4, 124.3, 124.0, 122.9, 122.7, 122.2, 120.6, 116.7, 114.9, 49.4, 20.0, 11.2 ppm. HRMS (ESI): calculated for $C_{36}H_{25}Br_2N_3S$ $[M + H]^+$, 690.0209; found, 690.0227.

2.3 Analytical Techniques used

2.3.1 NMR Spectroscopy

Solid state NMR spectroscopy is a sensitive and powerful technique used in structure elucidation. It reports in terms of its chemical shift and splitting of signals by virtue of the magnetic behaviour of nucleus of neighbouring atoms. NMR occurs in the radio frequency region of the electromagnetic spectrum. It is a trusted technique used to determine the presence and position of the functional groups. It was used in this project to confirm whether the synthesized product was in accordance with the expected design.

2.3.2 High Resolution Mass Spectrometry (HRMS)

As the most effective analytical tool, the Fourier Transform-based HRMS techniques blend and provide high sensitivity detection,

unambiguous identify cation and precise elucidation of immense chemical compounds present during a forensic examination as traces in recovered samples. In contrast to any other analytical technique, resolution is a property of instrument rather than of the analyte or experiment. High resolution separates extremely close signals.

2.3.3 TLC and Column Chromatography

TLC and Column chromatography both work on the principle of adsorption. Column chromatography is a simple and popular lab technique used to separate and purify a mixture of constituents dissolved in the mobile phase in the column, wherein the constituents can either be solid or liquid. Column chromatography has two components: stationary phase (adsorbent) and mobile phase. Most common choices for stationary phase are silica gel and alumina, however calcium phosphate, magnesia and calcium carbonate are also seldomly used. The selection of solvent used depends upon the solubility of the components in the mixture. Also, solvents with low boiling point are preferred so as to obtain the eluted material readily.

Chapter 3 Results and Discussion

3.1 Syntheses of precursors and final molecules

The synthesis of PTZ incorporated PI derivatives **D-1**, **D-2** and **D-3** is shown in Figure 2. The **A**, **B**, and **C** were the precursors of the target structures that have been synthesized as per the reported procedures (Figure 3, 4, and 5) [28]. The reaction of phenothiazine with n-propyl iodide in the presence of NaOH resulted in the formation of **A** in 91% yield. The Vilsmeier–Haack formylation

reaction of **A** with an equivalent amount of $POCl_3$ and DMF resulted in the formation of **B**, in 79% yield. B, on reaction with NBS, resulted in the formation of **C** in 88% yield.

The final molecules (**D-1**, **D-2** and **D-3**) were synthesized by the condensation reactions between 9,10-phenanthrenequinone and the corresponding aldehydes and amines in the presence of ammonium acetate. The condensation reaction of 9,10-phenanthrenequinone and 4-bromoaniline with the precursor **B** in the presence of ammonium acetate for 3 hours gives **D-1** in 68% yield. The condensation reaction of 9,10-phenanthrenequinone and aniline with the precursor **C** in the presence of ammonium acetate for 3 hours gives **D-2** in 59% yield. The condensation reaction of 9,10-phenanthrenequinone and 4-bromoaniline with the precursor **C** in the presence of ammonium acetate for 3 hours gives **D-3** in 62% yield.

The purification of all phenanthroimidazole derivatives were carried out using 400 mesh silica gel column chromatography, and all the compounds were characterized by ^{1}H NMR, ^{13}C NMR and Mass spectra.

3.2 ^{1}H and ^{13}C NMR Spectroscopy Data

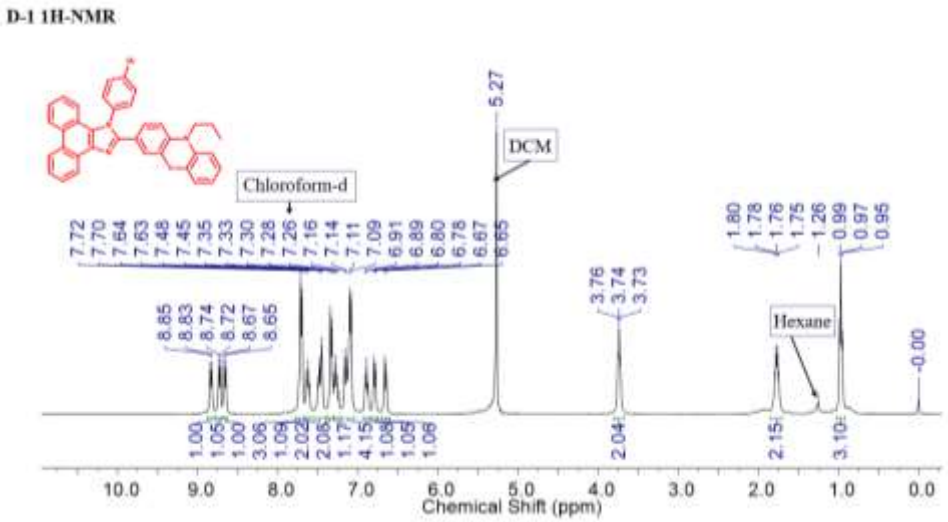


Figure 6: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **D-1**

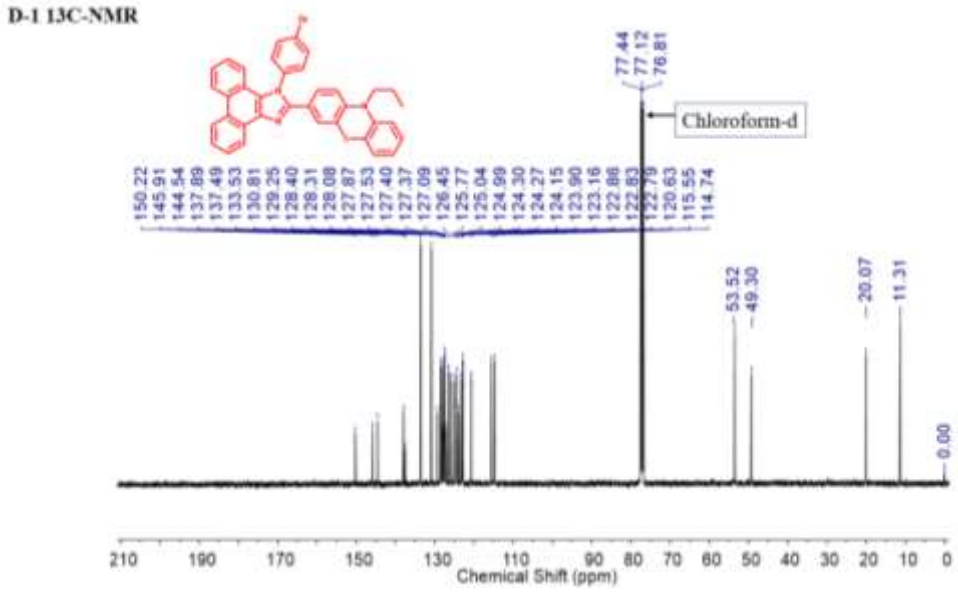


Figure 7: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **D-1**

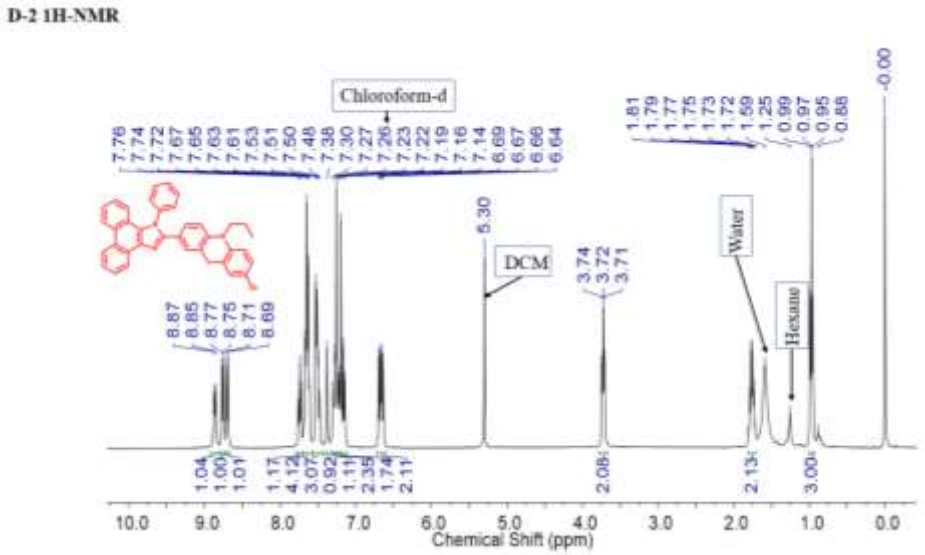


Figure 8: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **D-2**

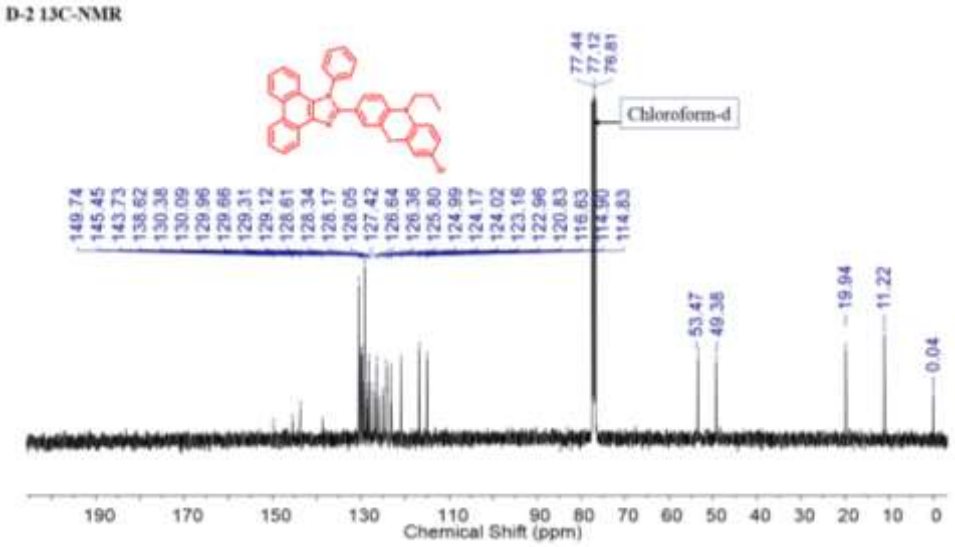


Figure 9: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **D-2**

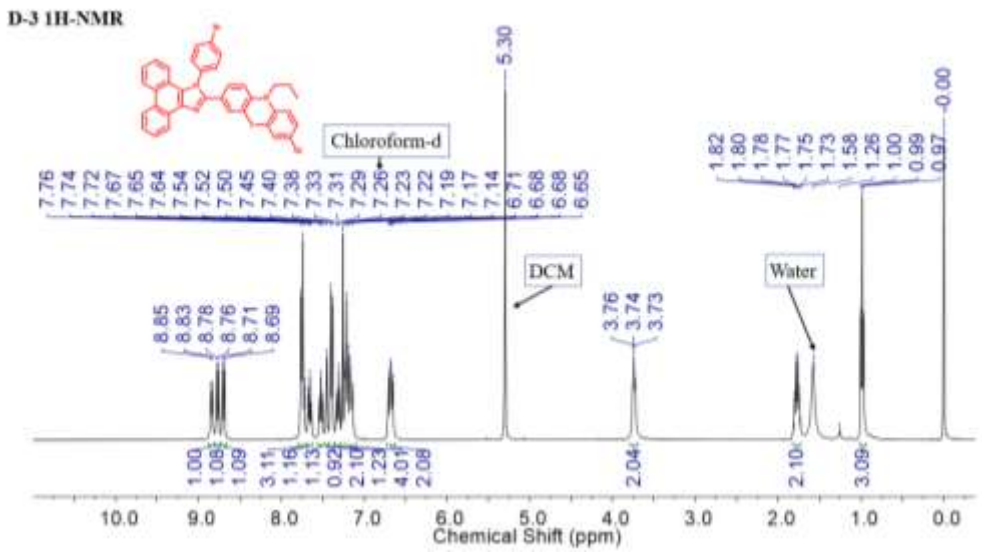


Figure 10: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **D-3**

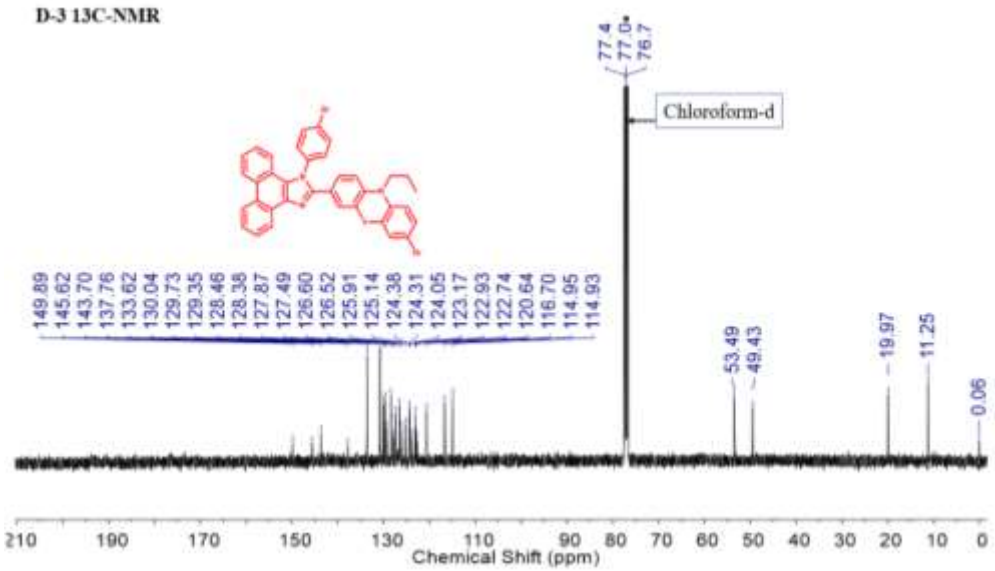


Figure 11: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **D-3**

3.3 HRMS Data

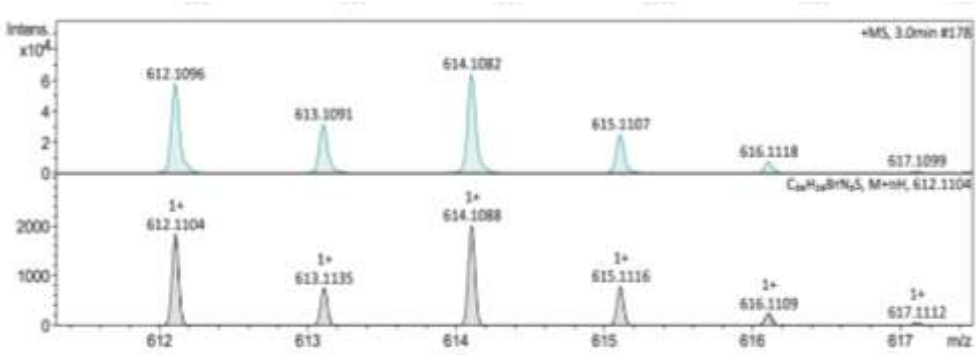


Figure 12: HRMS spectrum of compound **D-1**

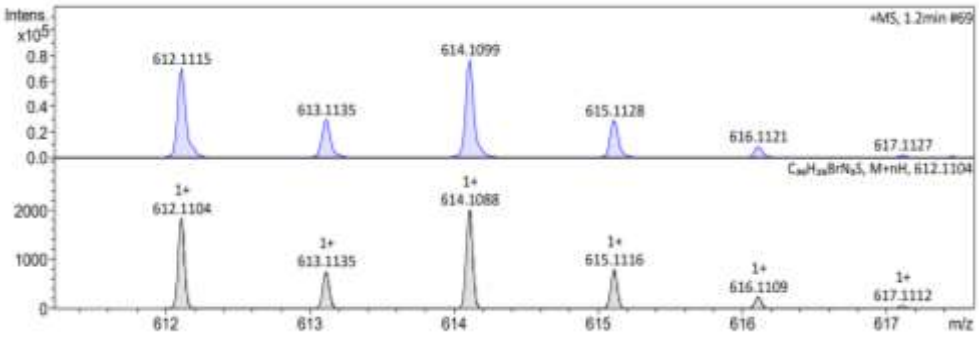


Figure 13: HRMS spectrum of compound **D-2**

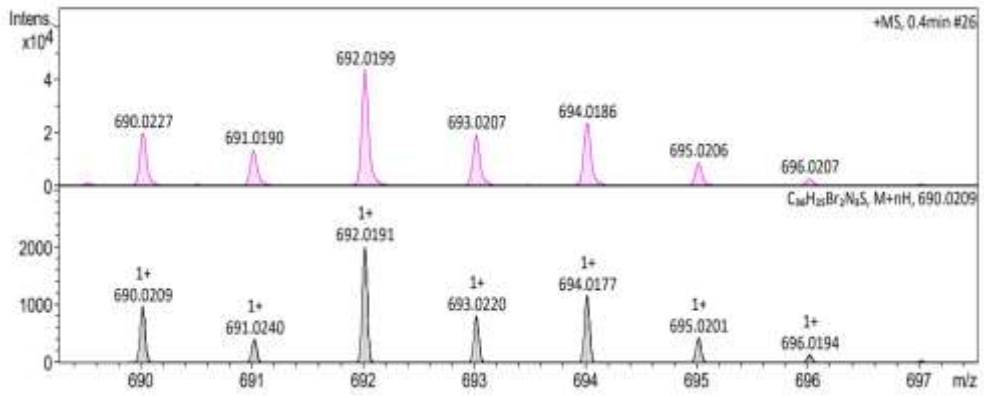


Figure 14: HRMS spectrum of compound **D-3**

Chapter 4 Conclusion and Scope for Future Work

We have successfully synthesized a strong donor, phenothiazine incorporated phenanthroimidazole derivatives, **D-1**, **D-2** and **D-3** by the condensation reaction of the corresponding diketone, aldehyde and amine in the presence of ammonium acetate. The reaction was accomplished in glacial acetic acid. The **D-1** was synthesized by refluxing 9,10-phenanthroquinone with 4-bromoaniline and the precursor **B**. The **D-2** was synthesized by refluxing 9,10-phenanthroquinone with aniline and the precursor **C**. The **D-3** was synthesized by refluxing 9,10-phenanthroquinone with 4-bromoaniline and the precursor **C**. All the target molecules were synthesized in good yield and have well characterized by ^{1}H NMR, ^{13}C NMR and high-resolution mass spectrometry techniques. We have introduced bromine atoms to the molecular structure of the target compounds **D-1**, **D-2** and **D-3**. The introduction of heavy atoms like bromine to a fluorophore generally induces halogen-halogen bonds in the crystalline lattice of the fluorophore. Such halogen-halogen interactions restrict the vibrations and rotations of the molecules and hence reduces the rate of non-radiative energy decay which enhances the aggregation induced emission. The heavy-atom effect also contributes significantly to considerable spin–orbit coupling (SOC), resulting an increase in the rate of intersystem crossing and radiative processes between T_1 and S_0 states. As a result, while the heavy-atom effect is frequently overlooked when designing common fluorescent molecules, it has been incorporated into the development of highly efficient organic room-temperature phosphorescent materials and thermally activated delayed fluorescence emitters. The presence of halo group also provides the possibility of derivatization through various metal catalyzed cross coupling reactions such as palladium catalyzed Sonogashira and Suzuki cross coupling reactions. These reactions are very useful to synthesize organic chromophores which show near infra-red

absorption. The chromophores with NIR absorption have diverse utility in various optoelectronic applications.

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