Design and Synthesis of Metal free Organic Room Temperature Phosphorescent molecules

M.Sc. Thesis

By

Sandeep Kumar Pandit

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHANOLOGY INDORE

May 2024

Design and Synthesis of Metal free Organic Room Temperature Phosphorescent molecules

A THESIS

Submitted in partial fulfilment of the requirement for the award of the degree

Of

Master of Science

by

Sandeep Kumar Pandit

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHANOLOGY INDORE

May 2024

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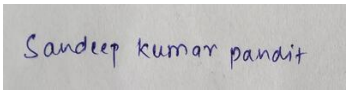
CANDIDATE'S DECLARATION

I affirm that the work which is being presented in the thesis entitled **Design and Synthesis of Metal free Organic Room Temperature Phosphorescent molecules** in the partial fulfilment of the requirements for the award of 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 period of July 2023 to May 2024 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.



17/05/2024

Signature of the student with date

(Sandeep Kumar Pandit)

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

Signature of the Supervisor of M.Sc. Thesis

(Prof. Rajneesh Misra)

Sandeep Kumar Pandit has successfully given the oral his M.Sc. The oral examination was held on **10 May 2024.**

Signature(s) of Supervisor(s) of M.Sc. thesis

Date: 22/05/2024

Convener, DPGC

Date:

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It is essential to acknowledge the indispensable role played by my family, without whose support none of this would have been possible. My deepest love and gratitude are extended to my parents.

Sandeep Kumar Pandit

IIT Indore

DEDICATION

"Gratitude is the bridge that connects the heart to the ones who shape our journey—family for their unwavering support, teachers for their wisdom, and friends for their enduring camaraderie."

ABSTRACT

Currently, the researchers are interested in the development of phenothiazine-based room temperature phosphorescent (RTP) molecules owing to their long-lived lifetime and have excellent phosphorescence characteristics at room temperature. The main aim of this thesis to design and synthesize phenothiazine-based room temperature phosphorescent molecules. The molecules **BT-PTZ-PTZ** and **BT-PTZ-PTZO**, comprised of benzothiazole, phenothiazine and phenothiazine oxide moieties, were synthesized by well-known Buckwald-Hartwig cross coupling reactions. The solvatochromism was performed to support the donor-acceptor character in the molecules, which showed significant red shift with different polarity of solvents. Further, the solid-state emission was recorded for the compound **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** and it was found that the both the compounds being highly emissive in solid state that encouraged to perform the solid-state emission. Both the compounds were characterised by various analytical techniques such as ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

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ABBREVATIONS

mg	Milligram
mol	Mole
g	Gram
°C	Degree Celsius
%	Percentage
h	Hour
min	Minute
mL	Millilitre
π	Pi
λ	Wavelength
δ	Chemical shift

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	Dimethyl formamide
D-A-D	Donor-acceptor-donor
DCM	Dichloromethane
LCMS	Low resolution mass spectrometry
NMR	Nuclear magnetic resonance
PTZ	Phenothiazine
DFT	Density functional theory
TMS	Tetramethyl silane
RTP	Room temperature phosphorescence

CHAPTER 1: INTRODUCTION

1.1 General introduction

Photoluminescence (PL) is a fascinating phenomenon wherein a material emits light after being excited by photons (light particles). When photons of sufficient energy are absorbed by a material, they can excite electrons to higher energy levels within the atoms in the molecule. On returning to its stable state it emits excess amount of energy in the form of light. Molecules which display a strong PL characteristic have gained significant research interest due to their great potential applications in different optoelectronic devices such as organic light emitting diodes (OLEDs), non-linear optics, bio-imaging, and biomedical applications.1–7 When the electronically excited molecules get relaxed or decayed back to its ground state through radiative or non-radiative routes. This radiative relaxation of excited state energy take place via three types of processes namely fluorescence, phosphorescence and delayed phosphorescence. The key difference between fluorescence and phosphorescence which lies in the duration of the excited state. In fluorescence, the excited state is short-lived, where the emission ceased almost immediately after the excitation source is removed. In contrast, phosphorescence involves a longer-lived excited state, allowing for delayed emission of light even after the excitation source is removed.

In the recent years, among scientists, a more intriguing phenomenon have aroused i.e. room temperature phosphorescence, which refers to the emission of light by certain materials at room temperature after being excited by an external energy source and then returning to their ground state. There are two important ways to trigger RTP emission: (I) an efficient ISC process from S1 to T1 and (II) inhibition of non-radiative decay of triplet excitons. Nevertheless, the current pure organic RTP materials are designed by incorporation of heavy atoms such as Br, Cl and I, carbonyl groups, help for efficient intersystem crossing (ISC) in order to populate triplet excitons and exhibit the radiative decay of the lowest triplet state (T1). Moreover, the incorporation of heavy atoms and carbonyl or heteroatom plays key role in enhancing the intermolecular interactions to

inhibit molecular motion, results in the reduction of non-radiative decay of triplet excitons.[8–10] The metal-free organic RTP materials have gained significant attention as compared to the conventional organic and inorganic toxic metal containing RTP luminophores due to low cost, wide variety, appreciable stability, large stokes shifts, and bio-compatibility.[11] Notably, the emergence of transition metal complex-based RTP materials has significantly propelled OLED advancement, leading to the attainment of 100% internal quantum efficiency. In contrast to organometallic compounds, pure organic aromatic materials have shown limited efficiency in RTP emission due to weak spin-orbit coupling (SOC) and a slow radiative transition rate (k_P). Additionally, oxygen and other triplet state quenchers play a crucial role in the occurrence of room-temperature phosphorescence (RTP) in pure organic aromatic materials. In essence, triplet excitons are challenging to populate and prone to quenching. Over the past decade, extensive efforts have been made to address these challenges.

Recent studies have revealed that efficient room-temperature phosphorescence (RTP) materials can be achieved through the manipulation of intermolecular interactions (such as crystallization, polymerization, and rigid matrix) and host-guest assembly, aiming to reduce the non-radiative transitions and protect the phosphors from oxygen exposure as much as possible.[12–15] Additionally, molecular engineering techniques have been employed, including the introduction of heavy atoms (such as Br, I), heteroatoms (N, O, S), or carbonyls into the molecular structure to enhance intersystem crossing (ISC), crucial for populating triplet excitons. Through these approaches, significant advancements have been achieved in RTP materials, including the extension of emission wavelength up to 819 nm, enhancement of phosphorescence quantum yield by more than 95%, and prolongation of afterglow duration beyond 1 hour. To achieve efficient pure organic room-temperature phosphorescence (RTP), priorities should be given to populate the triplet excitons by enhancing intersystem crossing while simultaneously suppressing non-radiative dissipation. Various methodologies have been employed by

different research groups to accomplish this goal. These include polymer aggregation, crystallization, halogen bonding, host-guest composition, self-assembly, H-aggregation, polymer matrix assistance, molecule-metal hybridization, and metal-organic framework hosting, among others, in the development of efficient pure organic RTP systems.

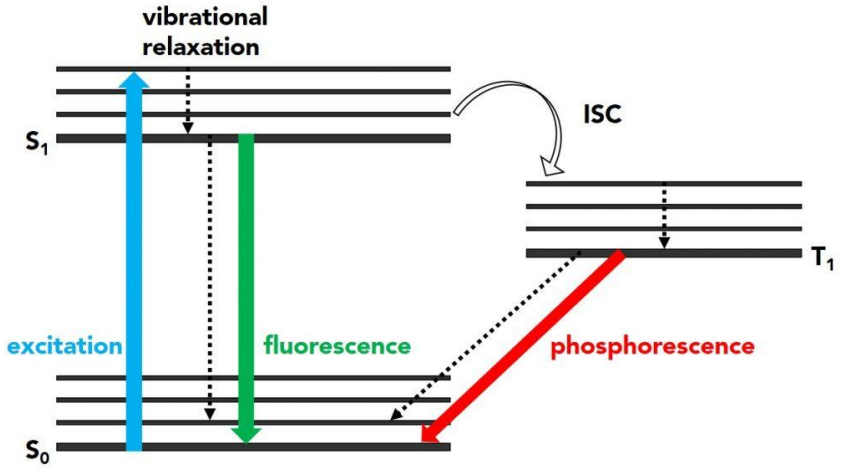


Figure 1: Jablonski diagram

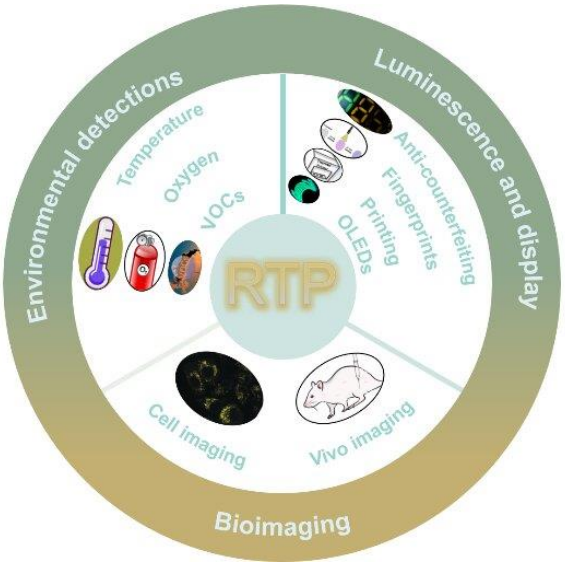


Figure 2: Application of room temperature phosphorescent molecules. (Ref. 10. 1039/D3IM00004D)

In the recent years, oxidised phenothiazine-based molecules have received an increasing interest in the important class of luminophores owing to their

multiple characteristic such as photoluminescence, phosphorescence and room temperature phosphorescence.[16–18] Remarkably, in the oxides phenothiazine molecules, there are three active sites (3-, 7- and 10-positons). Through synthetic modification, the oxidised phenothiazine molecules can be functionalized easily and also by incorporating strong push pull units for extending the π-conjugation. [19,20]

In 1950, Smith and co-workers evolved a method for synthesizing the derivatives of oxidized phenothiazine by using hydrogen peroxide (H_2O_2), which is a strong oxidizing agent. This reaction was performed in the presence of glacial acetic acid. Further many groups have furnished different methods to synthesize the oxidised phenothiazine [21]. In 2021, Li *et al.* reported three space-confined bridged phosphors in which the phenothiazine is interconnected with dibenzofuran, dibenzothiophene, and carbazole through a 9,9-dimethylxantene bridge. It was observed that the nearly pure phosphorescence was exhibited by the crystals in the room temperature. Moreover, it was found that the at room temperature these compounds are non-emissive and only exhibit fluorescence in solutions and amorphous state. The average lifetime for the crystals was found to be 5 ms at room temperature and 77 ms for crystals at 77 K according to the time-resolved decay curves recorded at 532 nm. [22]

Furthermore, Li *et al.* reported a series of phenothiazine-5,5-dioxide-based luminogense exhibiting room temperature phosphorescence (RTP) characterises. Its persistent RTP properties was explained by strong π-π interactions in the solid state. The effect of RTP of the luminogense, which manifested that the luminogense of 4, 5 and 6 having the electron-withdrawing group exhibited the longest RTP lifetime of 268 ms, 256 ms and 410 ms. While the luminogense 1 and 2 having electron-donating groups showed the shortest RTP lifetime of 88 ms amd 96 ms. No RTP was observed for the luminogense of 7 in the single crystal since it contain the trifluromethyl unit which is acting as a strong electron-withdrawing unit. [23]

In 2018, Wei *et al.* reported two blue phosphorescent host materials named as CEPDO and CBPDO wherein, the phenothiazine-5,5-dioxide moiety

considered as a central core, carbazole acting as a end-capping unit and two distinct alkyl units were taken for the improvement of the film-forming features. Both the luminogens exhibit two absorption bands in the UV-visible region , one is corresponding to the π-π* transitions and another is attributed to the n-π* transition. The fluorescence quantum yield of CEPDO and CBPDO was found to be 62.5% and 59.7% which is quite close owing to have a similar structure[24]

The molecules which contain the phenothiazine as a central core is considered a potential luminophores with a characteristics of high triplet emission, owing to its butterfly shaped structure it supress the non-radiative decays of the triplet exciton through reducing the excessive π-π stacking interactions in the solid state.

In 2021, Wang *et al*. reported three phenothiazine based room temperature phosphorescent molecules. Firstly, they cultivated the amorphous films by doping the compounds into a stiff PMMA matrix with a mass fraction of 0.1%. Further, after UV irradiation for around 30 seconds, a distinct photo-induced RTP emission was observed for all for compounds. Which is ranging from almost non RTP emission to the strong RTP emission. Among all of the them the derivative having three phenothiazine moieties attached with a phenyl ring exhibiting excellent RTP efficiency reaching 22% after photo-induction.[25]

Furthermore, researchers have found that the phenothiazine can be a regarded as a promising candidate to construct room temperature phosphorescent molecules. The phenothiazine molecules have multiple features that make it suitable for RTP applications such as the phenothiazine contains heavy atoms like sulfur, which enhances spin-orbit coupling. This leads to longer-lived triplet states, a crucial factor for phosphorescence. It shows efficient ISC, allowing efficient population of the long-lived triplet state necessary for phosphorescence emission. Moreover, the rigid molecular structure of phenothiazine helps in reducing non-radiative decay pathways, favouring the emission of phosphorescence over other processes. Phenothiazine derivatives can be synthesized with

varied substituents and modifications, allowing for the fine-tuning of their phosphorescent properties, such as emission wavelength and quantum yield.

In the current report, we have synthesized Benzothiozole (BT) and phenothiaizne (PTZ) substituated moleucles named as **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO,** possess high emission in the solid state. We have recored the photophysical propertie of these compound in solution and solid state, wherein it shows good solvatochromic effect and also the high emission in the solid state, which could be useful for many optoeletronic applications.

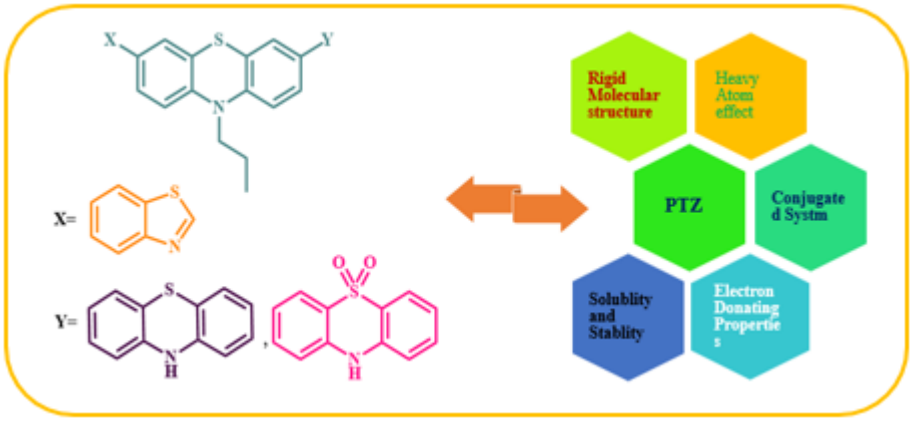
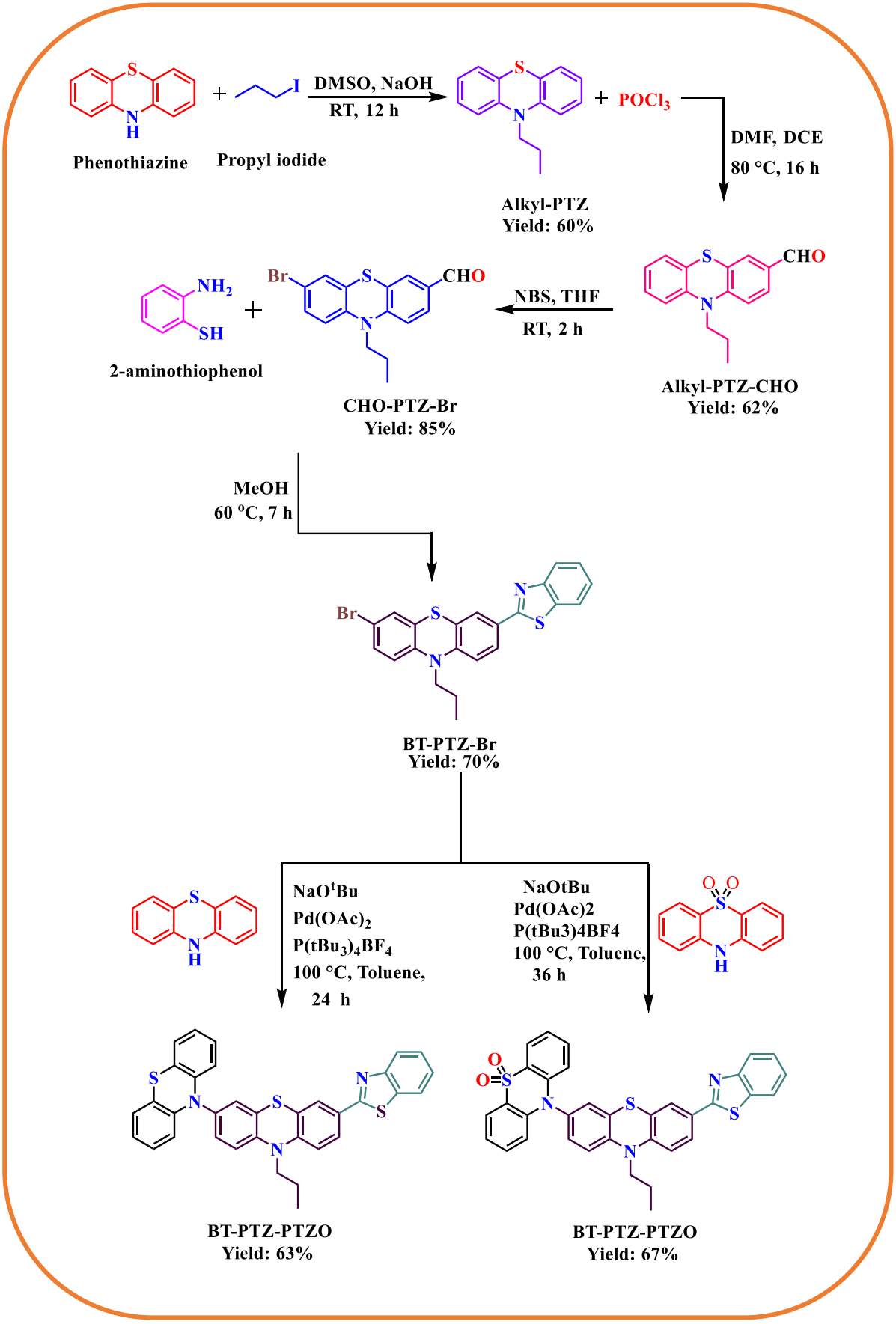


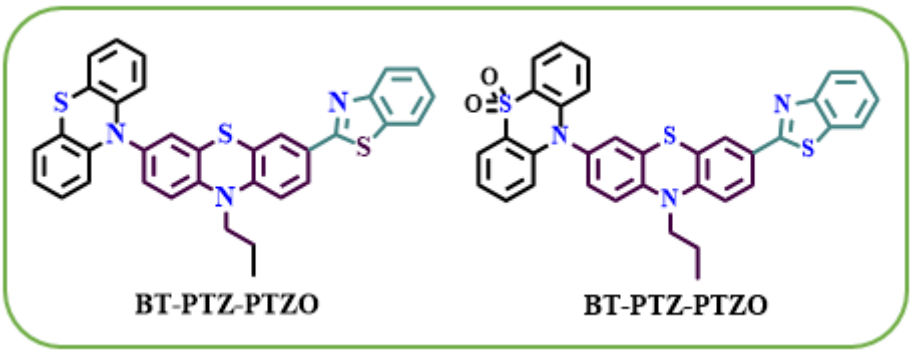
Figure 3: Phenothiazine based room temperature phosphorescent molecules (RTP)

1.2 Aim and Strategy of our work

Herein, we have synthesized Benzothiozole (BT) and phenothiaizne (PTZ) substituated moleucles named as **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO**. Both the molecules were characterised by LCMS, HRMS, ^{1}H NMR and ^{13}C NMR techniques. Here, our aim is to study the photophysical, structural and the theoritical studies of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** molecules. However, BT and PTZ, PTZO substituated PTZ-base RTP molecules were syntheized by the help of Buckwald-Hartwig cross-coupling reaction.



Scheme1: Overall Scheme



Scheme 2: Designed molecule

CHAPTER 2: LITERATURE SURVEY

In 2018, Wei *et al.* reported two blue phosphorescent host materials named as CEPDO and CBPDO in which phenothiazine-5,5-dioxide moiety play a role as a central core, carbazole acting as a end capping unit accompanied with two distinct alkyl units were taken for the improvement of film forming properties. Both the luminogens exhibit two absorption bands in the UV-visible region , one is corresponding to the π-π* transitions and another is attributed to the n-π* transition. The fluorescence quantum yield of CEPDO and CBPDO was found to be 62.5% and 59.7% which is quite close owing to have a similar structure.[24]

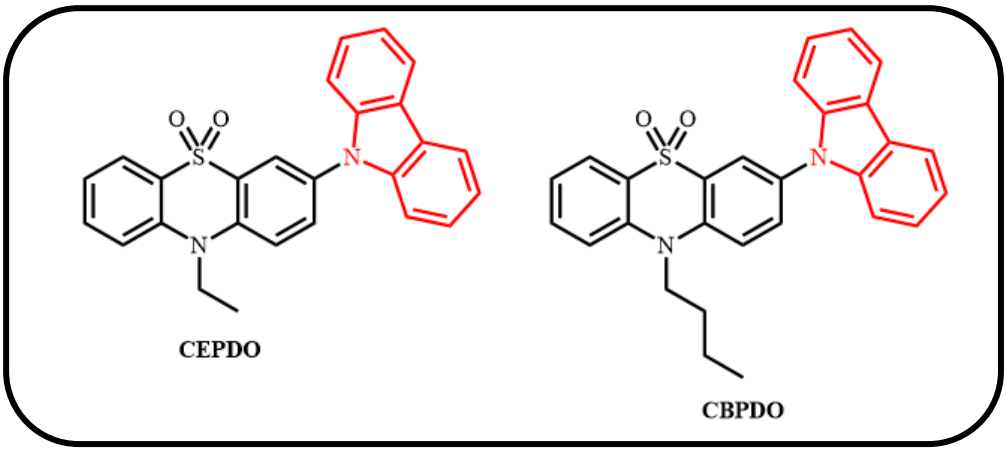


Figure 4: Structure of CEPDO and CBPDO as a RTP molecules

In 2023, Misra *et al.* reported three donor-acceptor isomers (D-π-A) named as *o*-PTZ, *m*-PTZ and *p*-PTZ respectively. These molecules were further characterized by a using a benzothiazole electron-acceptor unit (A), phenothiazine electron-donor portion (D)and a phenyl π-bridge where all the connections occured at the relative ortho, meta, and para positions, denoted as o-PTZ, m-PTZ, and p-PTZ, respectively. A strategy was employed of intramolecular charge transfer (ICT) for theses isomers to increase the strength of the spin-orbit coupling that activate the ISC process. Furthermore, the fluorescence lifetime and quantum yield were calculated for the compounds in various solvents and it was found that the ortho and meta isomers being poorly fluorescent (quantum yield lower than 19 and 13%, respectively), whereas the para isomer showing the highly

fluorescent characteristics in all of the solvents (quantum yield higher than 21%). [26]

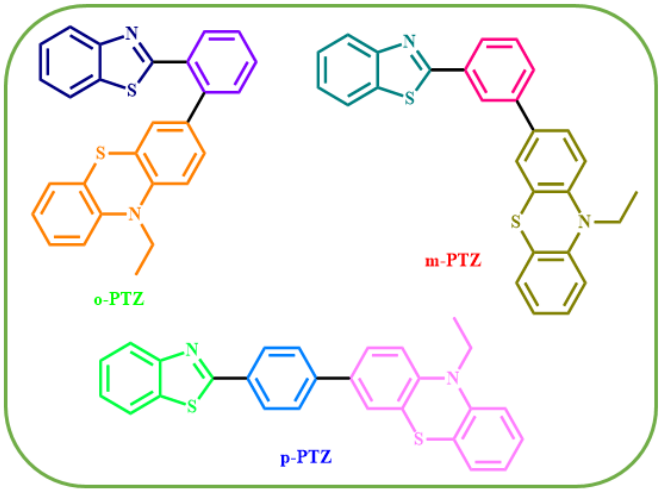


Figure 5: Structures of o-PTZ, m-PTZ and p-PTZ as RTP molecule.

In 2021, Li *et al.* reported three space-confined bridged phosphors in which the phenothiazine is interconnected with dibenzofuran, dibenzothiophene, and carbazole through a 9,9-dimethylxantene bridge. It was observed that the nearly pure phosphorescence was exhibited by the crystals in the room temperature. Moreover, it was found that the at room temperature these compounds are non-emissive and only exhibit fluorescence in solutions and amorphous state. The average lifetime for the crystals was found to be 5 ms at room temperature and 77 ms for crystals at 77 K according to the time-resolved decay curves recorded at 532 nm.[22]

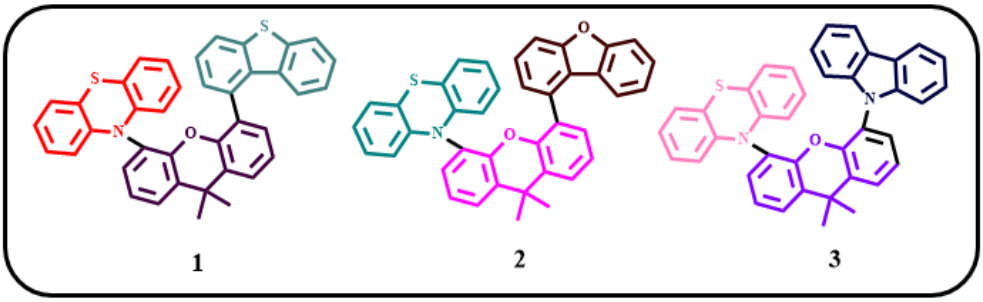


Figure 6: Structure of PTZ containing RTP molecules

In 1978, Bilen *et al.* reported, for the first time pure organic materials exhibiting RTP properties [27] Both the compounds 1 and 2 were synthesized with good yields of 77% and 86% respectively. The chromophores 1 and 2

show two absorption bands corresponding to the n-π* and π-π* transitions. The chromophore 1 show two phosphorescence bands with different lifetime of 234 ms and 455 ms respectively, which suggested that the they mainly produced from two different excited states. While the chromophore 2 exhibit dual emission with having almost equal intensity. The lifetime of compound 1 (455 nm, Φ=3.6%) and for compound 2 (876 ms, Φ=8.2%) was found in the phosphorescence study.

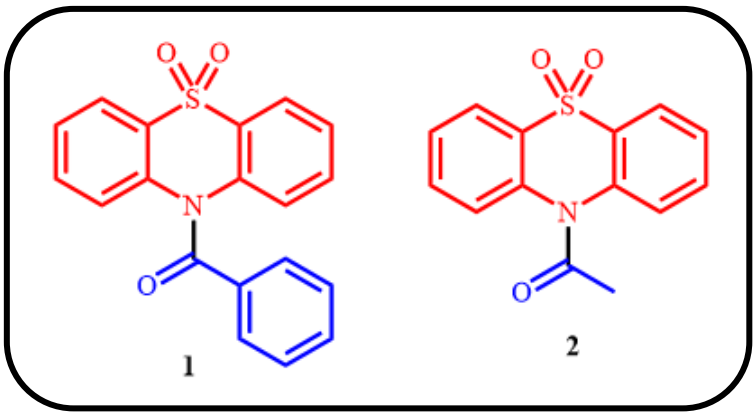


Figure 7: Structure of PTZ oxide based RTP molecules

CHAPTER 3: EXPERIMENTAL SECTION

3.1. Chemicals, reagents, and methods

Chemicals utilized in the 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, ≥99%), $Pd(OAC)_2$ (Sigma-Aldrich, 99%), Na_2SO_4 (Spectrochem, ≥99.5%), NaOH (Sigma-Aldrich, ≥99%), THF, DMF (Spectrochem, >95%), NaOH, $POCl_3$ (Spectrochem, >99%), AcOH (Sigma-Aldrich, 99.99%). All these reactions are mostly moisture-sensitive reactions; therefore, all the oxygen and moisture sensitive reactions were performed in inert conditions like in the presence of (nitrogen/argon) atmospheric condition. ^{1}H and ^{13}C NMR spectra of all compounds were recorded using a Bruker A V 500 and 125 MHz spectrometer respectively. Chemical shifts are described in delts (δ) units, expressed in parts per million downfield from tetramethyl silane (TMS) using left over protonated able to make payment as an internal standard ($CDCl_3$ and DMSO-d_6). The splitting patterns in1HNMR spectra are explained by symbols as "s, singlet; d, doublet; t, triplet, and m, multiplet." Mass spectrometric analysis was done on Bruker-Daltoni, a micro TOF-Q II mass spectrometer.

3.2 General procedure for the preparation of the precursors

The following procedures was adopted for the preparation of the compounds **Alkyl-PTZ-BT-PTZ-NPTZO.**

3.2.1. Synthetic pathway for compound Alkyl-PTZ

A mixture of phenothiazine ((7 g, 35.53 mmol), propyl iodide (6.64 g, 39.08 mmol) and sodium hydroxide (4 g, 100 mmol) was dissolved in 100 ml of dimethyl sulfoxide and was allowed to stir at room temperature for 12 hr. The reaction mixture was diluted with dichloromethane (DCM) and risned with water after the reaction was brought to room temperature. The organic layer was evaporated after drying with Na_2SO_4. The crude product was was

purified by coloum chromatograph. (Hexane: DCM, v/v 100:0) to obtain the compound **Alkyl-PTZ** (6 g, 70% yield) as an off white solid. ^{1}H NMR (500 MHz, CHLOROFORM-d) δ=7.13-7.20 (m, 4H), 6.90-6.96 (m, 4H), 3.82 (br, *J* = 7.2 Hz, 2 H), 1.91 - 1.84 (m, 2 H), 1.06 (t, *J* = 7.2 Hz, 3 H), ^{13}C NMR (125 MHz, CHLOROFORM-d) δ =144.96, 127.38, 127.15, 124.94, 122.45, 115.67, 49.36, 20.06, 11.28. $C_{15}H_{15}NS$: Calculated: 241.35, [M] Found: 241.09

3.2.2. Synthetic pathway for compound PTZ-CHO

A mixture of alkylated phenothiazine (5 g, 20.71 mmol), phosphoryl chloride (7.74 ml) and DMF (6.44 ml) was stirred in ethylene dichloride solvent (80 ml) at 80 ºC for 16 h. On completion of the reaction, chilled water was addded to the reaction mixture. Followed by the reaction mixture was diluted with dichloromethan (DCM) and risned with water. The organic layer was evapoarted after drying with Na_2SO_4. Furthermore the obtained crude product was purified by coloumn chromatography.(Hexane:DCM, v/v 0:100) to obtain the compound **PTZ-CHO** (3.5 g, 62%) as an green fluorecent oily liqiud. ^{1}H NMR (500 MHz, CHLOROFORM-d) δ= 9.82 (s, 1 H), 7.68 - 7.58 (m, 2 H), 7.20 - 7.12 (m, 2 H), 7.05 – 6.86 (m, 3H), 3.89 (t, *J* = 7.2 Hz, 2 H), 1.91 - 1.84 (m, 2 H), 1.06 (t, *J* = 7.2 Hz, 3 H), ^{13}C NMR (125 MHz, CHLOROFORM-d) δ= 190.03, 150.75, 143.41, 131.03, 130.04, 128.40, 127.55, 127.53, 123.56, 115.97, 114.82, 49.68, 20.04, 11.20. HRMS (ESI): calcd for $C_{16}H_{15}NOS$: Calculated: 269.058, [M] Found: 269.086.

3.2.3. Synthetic Pathway for compound CHO-PTZ-Br

A mixture of PTZ-CHO (3 g, 11.74 mmol), N-bromosuccinimide (3.13 g, 17.6 mmol) was dissolved in tetrahydrofuran (THF) solvent (70 ml) and was allowed to stir at room tempearture for 2 h. The reaction mixture was then diluted with dichloromethan (DCM) and risned with water followed by the organic layer was collected and dried with Na_2SO_4 and the obtained crude product was purified by coloumn chromatorgyaphy. (Hexane:DCM, v/v 60:40) to obtain the compound **CHO-PTZ-Br** (2.7 g, 85%) as an

yellow solid. ^{1}H NMR (500 MHz, CHLOROFORM-d) δ= 9.83 (s, 1 H), 7.71 - 7.64 (m, 1 H), 7.63 - 7.58 (m, 1 H), 7.29 (br. s., 2 H), 6.93 (d, *J* = 8.2 Hz, 1 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 3.86 (br. s., 2 H), 1.90 - 1.81 (m, 2 H), 1.05 (t, *J* = 7.2 Hz, 3 H), ^{13}C NMR (125 MHz, CHLOROFORM-d) δ = 189.9, 150.3, 142.7, 131.3, 130.2, 129.8, 128.5, 126.2, 124.4, 117.1, 115.8, 115.1, 49.8, 20.0, 11.2. HRMS (ESI): calcd for $C_{16}H_{14}BrNOS$: Calculated: 348.995, [M] Found: 348.995.

3.2.4. Synthetic pathway for the compound BT-PTZ-Br

A mixture of CHO-PTZ-Br (200 mg, 0.57 mmol) and 2-aminothiophenol (78 mg, 0.631 mmol) was dissolved in methnol solvent (30 ml) and was allowed to stirr at 60 ^{o}C for 7 h. The reaction mixture was then diluted with DCM and risned with water and followed by the organic layer was dried with Na_2SO_4. The obtained crude product was purified by coloumn chromatograply. (Hexane:DCM, v/v 70:20) to otain the compound **BT-PTZ-Br** (0.180 mg, 70%) as an yellowish white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 1.02 (t, *J*=7 Hz, 3 H) 1.78 - 1.88 (m, 2 H) 3.82 (t, *J*=7 Hz, 2 H) 6.71 (d, *J*=9 Hz, 1 H) 6.89 (d, *J*=9 Hz, 1 H) 7.22 - 7.25 (m, 3 H) 7.36 (t, *J*=1 Hz, 5 H) 7.47 (t, *J*=7 Hz, 5 H) 7.80 - 7.90 (m, 12 H) 8.02 (d, *J*=8 Hz, 4 H) ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ(ppm) : 166.8, 154.1, 147.2, 143.4, 134.8, 130.1, 129.8, 128.2, 127.1, 126.3, 126.2, 125.0, 124.7, 122.9, 121.6, 116.8, 115.4, 115.1, 49.56, 20.0, 11.23. HRMS (ESI): calcd for $C_{22}H_{17}BrN_2S_2$ $[M]^+$:452.0011 Found: 451.9970

3.2.5 Synthetic pathway for the compound PTZO

A mixture of phenothiaizne (0.500 mg, 2.5 mmol) and hydrogen peroxide (5.94 ml) was dissolved in acetic acid (5.94 ml) and was allowed to stirr at 70 ^{o}C for 2 h. The recaction mixture was then diluted with DCM and risned with water. Further the organic layer was collected and dried with Na_2SO_4 and the obatined product was then purified by coloumn chromatography. (Hexane:DCM, v/v 0:100) to obtain the compound **PTZO** (0.400 mg, 69%) as an redish white sold. HRMS (ESI): cal. For $C_{12}H_9O_2NS$ $[M]^+$: 231.0349 found 231.0349.

3.3. Synthetic pathway for final compounds

The Buckwald-Hartwig cross coupling reaction was employed to consruct the BT and PTZ, PTZO substituated phenotiazine based RTP molecules.

3.3.1 Synthetic pathway for compound BT-PTZ-NPTZ

A mixture of BT-PTZ-Br (100 mg, 0.220 mmol) and phenothiazine (65 mg, 0.33 mmol), NaO*t*-Bu (63 mg, 0.661 mmol), $Pd(OAc)_2$ (19 mg, 0.088 mmol) and P(*t*-Bu_3)HBF_4 (3.19 mg, 00.011) was dissolved in toluene solvent (30 ml) and was allowed to stir at 100 ºC for 36 h. the reaction was diluted with DCM and rinsed with water when the reaction was brought to room temperature. The organic layer was collected and dried with Na_2SO_4. The obtained crude product was purified by coloumn chromatography. (Hexane: DCM, v/v 6/4) to obtain the compound **BT-PTZ-NPTZ** (80 mg, 63%) as an yellow fluorescent solid. ^{1}H NMR (500 MHz, CHLOROFORM-d), δ (ppm): 8.03 (d, J=7.93 Hz, 1 H), 7.85 - 7.93 (m, 3 H), 7.48 (t, J=8.24 Hz, 1 H), 7.35 - 7.39 (m, 1 H), 7.18 (dd, J=4.43, 2.29 Hz, 2 H), 7.05 (d, J=9.16 Hz, 1 H), 6.94 - 7.01 (m, 3 H), 6.84 - 6.88 (m, 2 H), 6.78 - 6.82 (m, 2 H), 6.27 (dd, J=8.09, 0.92 Hz, 2 H), 3.92 (t, J=10.0 Hz, 2 H), 1.93-2.00 (m, 2 H) 1.10 (t, J=7.40 Hz, 3 H) ^{13}C NMR (125 MHz, CHLOROFORM-d) δ(ppm): 166.80, 154.11, 147.05, 144.21, 134.80, 129.96, 129.83, 127.05, 126.89, 126.70, 126.35, 122.91, 122.50, 121.56, 120.02, 117.01, 115.89, 77.33, 77.01, 76.69. 49.71, 21.12, 11.34.00. HRMS (ESI): calc. for $C_{34}H_{25}N_3S_3$ $[M]^+$ 571.1205 found: 571.1205.

3.3.2. Synthetic pathway for compound BT-PTZ-NPTZO

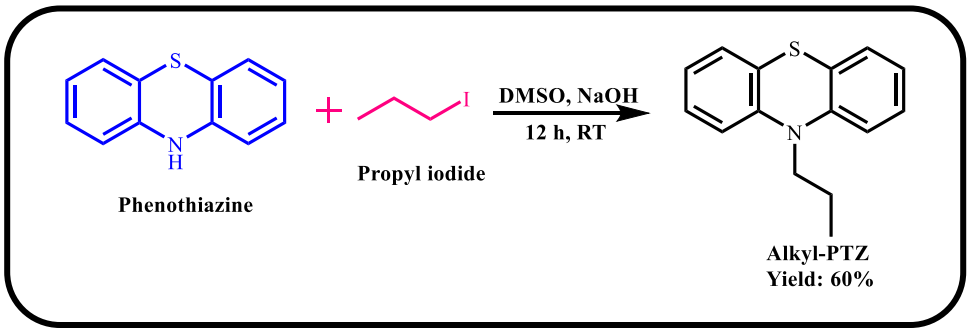
A mixture of BT-PTZ-Br (100 mg, 0.220 mmol), PTZO (76 mg, 0.330 mmol), NaO*t*-Bu (63 mg, 0.661 mmol), P(*t*-Bu_3) HBF_4 (3.19 mg, 0.011 mmol) and $Pd(OAc)_2$ (20 mg, 0.088 mmol) was dissolved in toluene (30 ml) and was allowed to stir at 100 ºC for 36 h. the reaction mixture was diluted with water and risned with water when the reaction mixture was

brought to room temperature. The organic layer was collected ad dried with Na_2SO_4 and the obtained crude product was purified with coloumn chromatography. (Hexane/DCM, v/v 3/7) to obtain the compound **BT-PTZ-NPTZO** (90 mg, 67% yield) as an green solid. ^{1}H NMR (500 MHz, CHLOROFORM-d) δ(ppm): 8.16 (dd, J=7.93, 1.22 Hz, 2 H) 8.04 (d, J=8.24 Hz, 1 H) 7.87 - 7.95 (m, 3 H) 7.47 - 7.51 (m, 1 H) 7.35 - 7.43 (m, 3 H) 7.22 - 7.26 (m, 2 H) 7.14 - 7.17 (m, 2 H) 7.09 - 7.12 (m, 1 H) 7.00 (d, J=8.54 Hz, 1 H) 6.75 (d, J=8.55 Hz, 2 H) 3.95 (t, J= 10 Hz, 2 H) 1.96 (sxt, J=7.29 Hz, 2 H) 1.12 (t, J=7.40 Hz, 3 H) ^{13}C NMR (125 MHz, CHLOROFORM-d) δ(ppm): 166.54, 154.16, 146.60, 145.60, 140.78, 134.86, 132.84, 126.42, 126.39, 123.43, 122.15, 121.61, 117.29, 115.78. HRMS (ESI): calc. for $C_{34}H_{25}N_3O_2S_3$ $[M]^+$: 603.1103 Found 603.1103.

CHAPTER 4: RESULT AND DISCUSSION

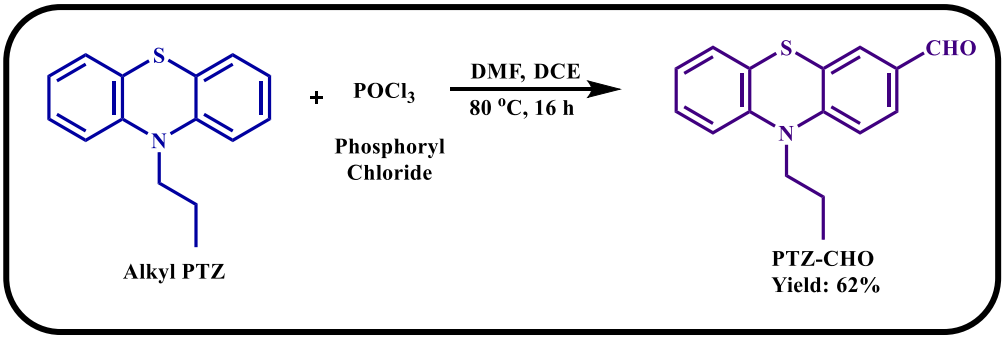
4.1 Synthetic pathway and chacterization

The synthesis of BT and PTZ, PTZO substituted PTZ based compounds form **Alkyl-PTZ** to **BT-PTZ-PTZO** are shown in different schemes one by one. The compound **alkyl-PTZ** was synthesized by simple alkylation reaction of phenothiazine with propyl iodide in dimethyl sulfoxide solvent with NaOH as a base was performed at room temperature. The compound **alkyl-PTZ** was obtained with a 60% yield.



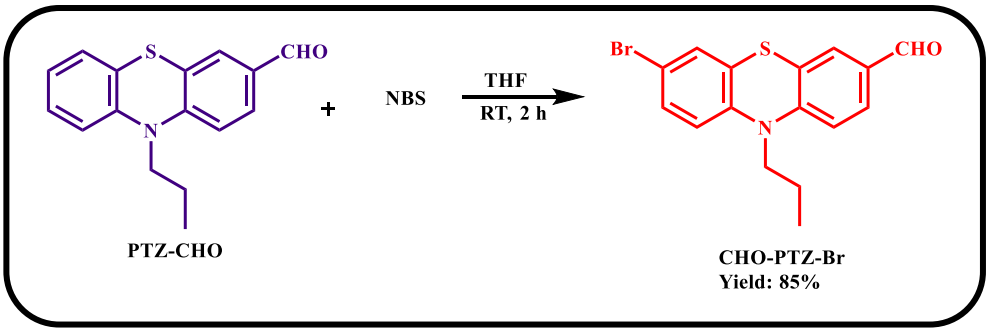
Scheme 3. Synthetic pathway for compound **Alkyl-PTZ**

Compound **PTZ-CHO** was sythesized by a well-known reaction Viels Mayer Heck reaction between alkyl-PTZ, phosphoryl chloride ($POCl_3$) and dimethyl formamide (DMF) in ethylene dichloride solvent and was preformed at 80^{o}C for 16 h. The compound **PTZ-CHO** was obtained with a 62% yield.



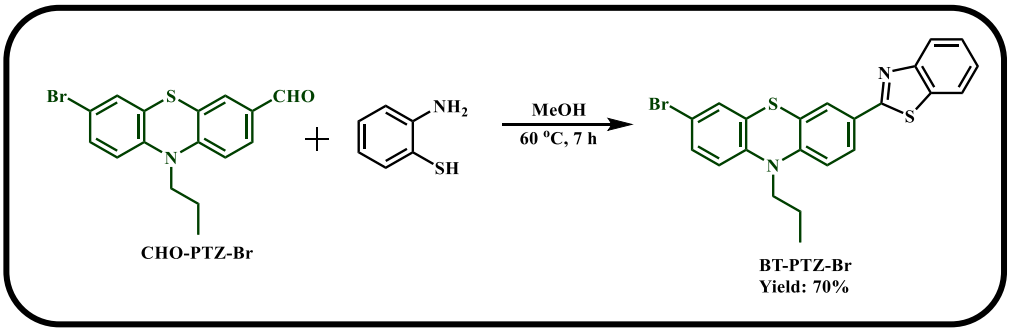
Scheme 4. Synthetic pathway for compound **PTZ-CHO**

Compound **CHO-PTZ-Br** was synthesized by simple bromination reaction of PTZ-CHO with N-bromosuccinamide in tetrahydrofuran (THF) solvent and the reaction was performed at room temperature for 2 h. The compound **CHO-PTZ-Br** was obatined with a yield of 85%.



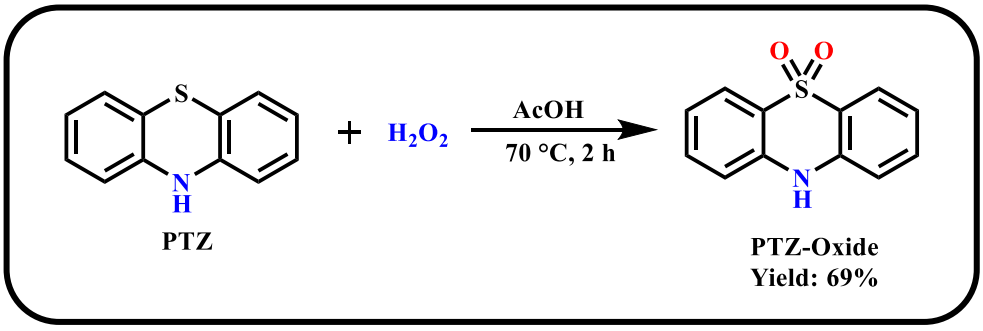
Scheme 5. Synthetic pathway for Compound **CHO-PTZ-Br**

Compound **BT-PTZ-Br** was synthesized by a simple condenstaion reaction between CHO-PTZ-Br and 2-aminotthiophenol in methanol solvent which was performed at 60 ^{o}C for 7 h. The compound **BT-PTZ-Br** was obatined with a yield of 70%.



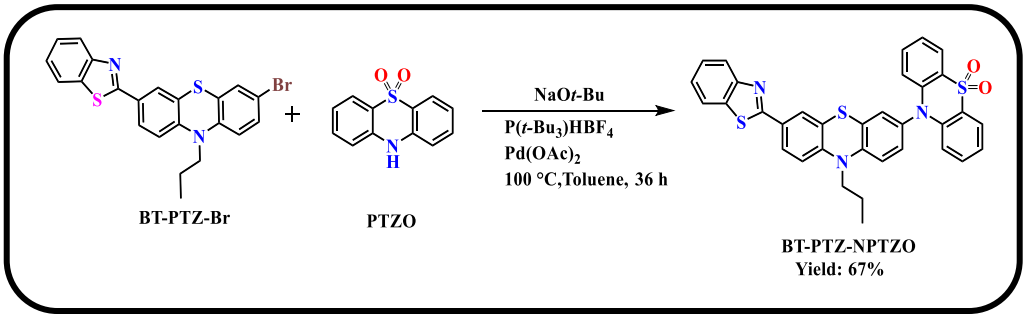
Scheme 6. Synthetic pathway for Compound **BT-PTZ-Br**

Compound **PTZ-Oxide** was synthesized by a simple oxidation reaction of phenothiaizne with hydrogen peroxide in acetic acid solvent which as performed at 70 ^{o}C for 2 h. The compound **PTZ-Oxide** was obtained with a yield of 69%.



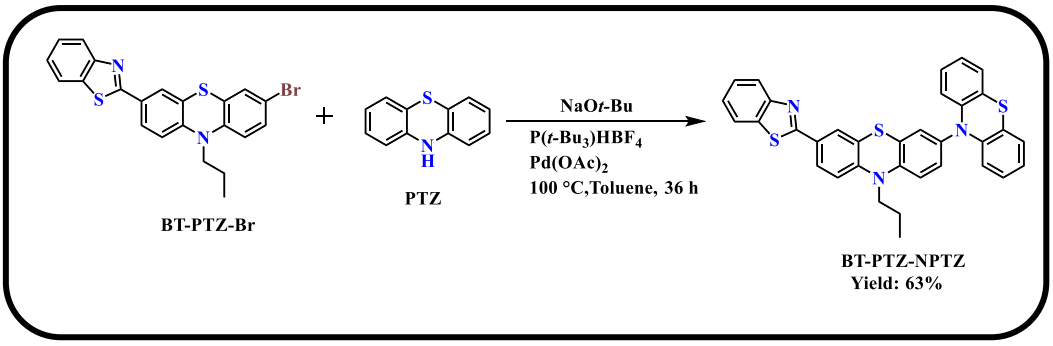
Scheme 7. Synthetic pathway for Compound **PTZO**

The compound **BT-PTZ-NPTZO** was synthesized by a Buckwald-Hartwig cross coupling reaction between **BT-PTZ-Br** and **PTZO** in toluene solvent with NaO*t*-Bu as a base, P(*t*-Bu_3)HBF_4 and $Pd(OAc)_2$ as a catalyst at 100 °C for 24 h to obtain the compound **BT-PTZ-PTZO** with a yield of 67%.



Scheme 8: Synthetic pathway for the compound **BT-PTZ-NPTZO**

The compound **BT-PTZ-NPTZ** was synthesized by Buckwald-Hartwig cross coupling reaction between **BT-PTZ-Br** and **PTZO** in toluene solvent with NaO*t*-Bu as a base P(*t*-Bu_3)HBF_4 and $Pd(OAc)_2$ as a catalyst at 100 °C for 36 h to obtain the compound **BT-PTZ-NPTZ** with a yield of 63%.



Scheme 9: Synthetic pathway for the compound **BT-PTZ-PTZ**

4.2. Photophysical Properties

The photo-physical properties of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** were studied using absorption (Figure 8A and B) and emission spectroscopy (Figure 8C and D) in various polarity of solvents i.e from non-polar to polar (Toleue, 1,4 Dioxane, tetrahydrofuran, dichloromethane, chloroform, dimethyl sulfoxide). The absorption bands with high intensity

in the region at 280-340 nm for **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** are owing to the π-π* transition from the different aromatic units. The absorption spectra of BT-PTZ-1 and BT-PTZ-2 also exhibits absorption band in the region of 350-450 nm which is due to the intramolecular charge transfer transition (ICT) occurring between the donors phenothiazine (PTZ) and the acceptor benzothiazole unit respectively. Since these molecules exhibited donor-acceptor characters, we performed solvatochromic study to support the intramolecular charge transfer (ICT) present in these molecules. The absorption spectra of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** was not much affected by solvent polarity compared to emission spectra, which showed remarkable shift in emission with increasing the solvent polarity. The compound **BT-PTZ-NPTZ** showed green emission at 501 nm in toluene, further on increasing the solvent polarity to DMSO showed orange colour emission at 570 nm. This could be due to the excited state get well stabilized by the more polar solvent, which reduces the energy resulting in more red shifted emission. Similar phenomenon was observed for **BT-PTZ-NPTZO**, which initially showed the cyan colour emission in toluene at 490 nm due to ICT emission with along with shoulder peak of locally excited (LE) emission, which further red shifted to 520 nm in DCM and 560 nm in DMSO with orange colour emission.

The molecules **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** are highly emissive in solid state, encouraged to execute the solid-state emission property. The compound **BT-PTZ-NPTZ** exhibited yellow emission at 536 nm, while the **BT-PTZ-NPTZO** showed green emission at 526 nm. Both the compounds possess high emission intensity in solid owing to their twisted structure, shown in fig 9.

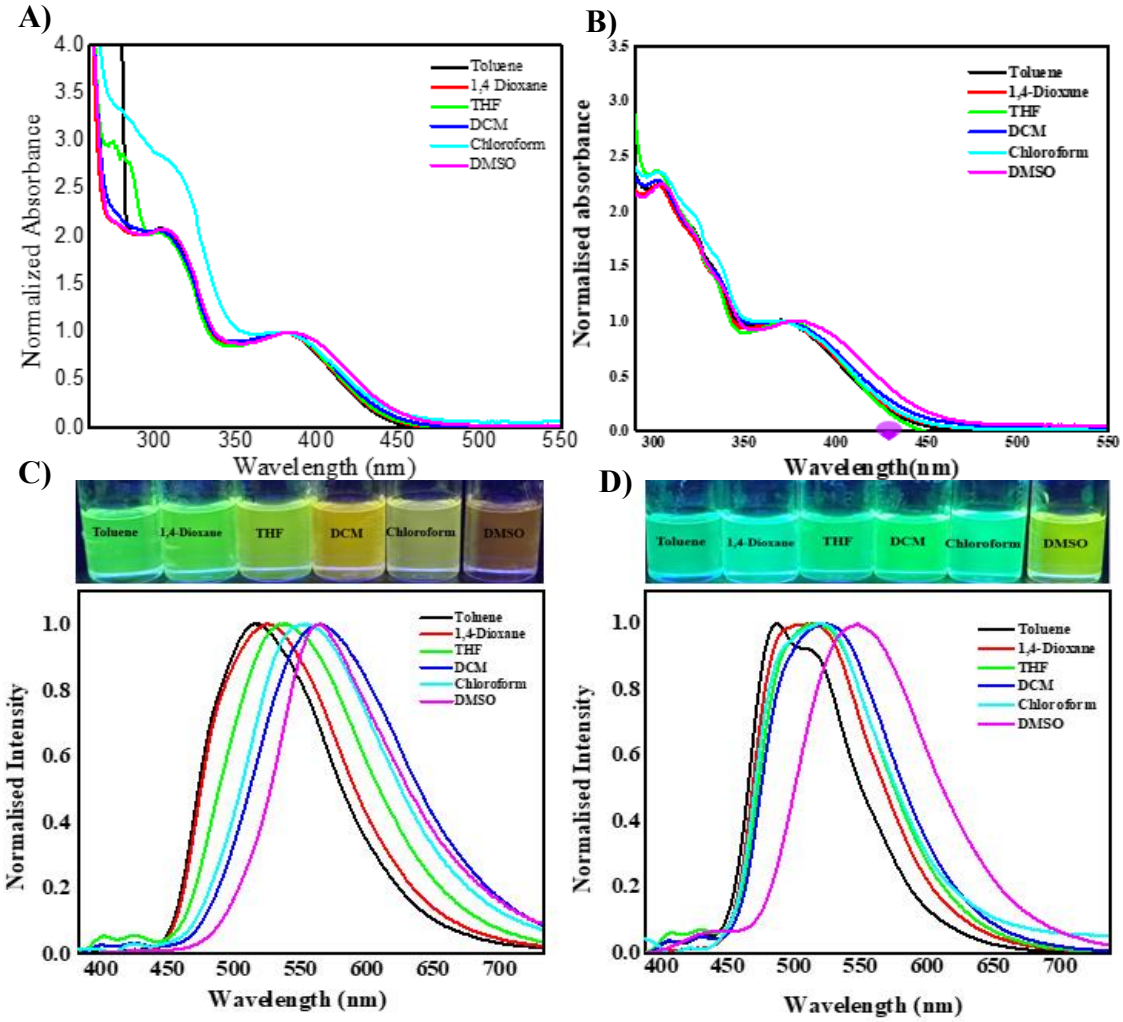


Figure 8: Absorption (A and B) and Emission Spectra (C and D) of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** in different polarity of solvents.(λ_{exc} = 380 nm).

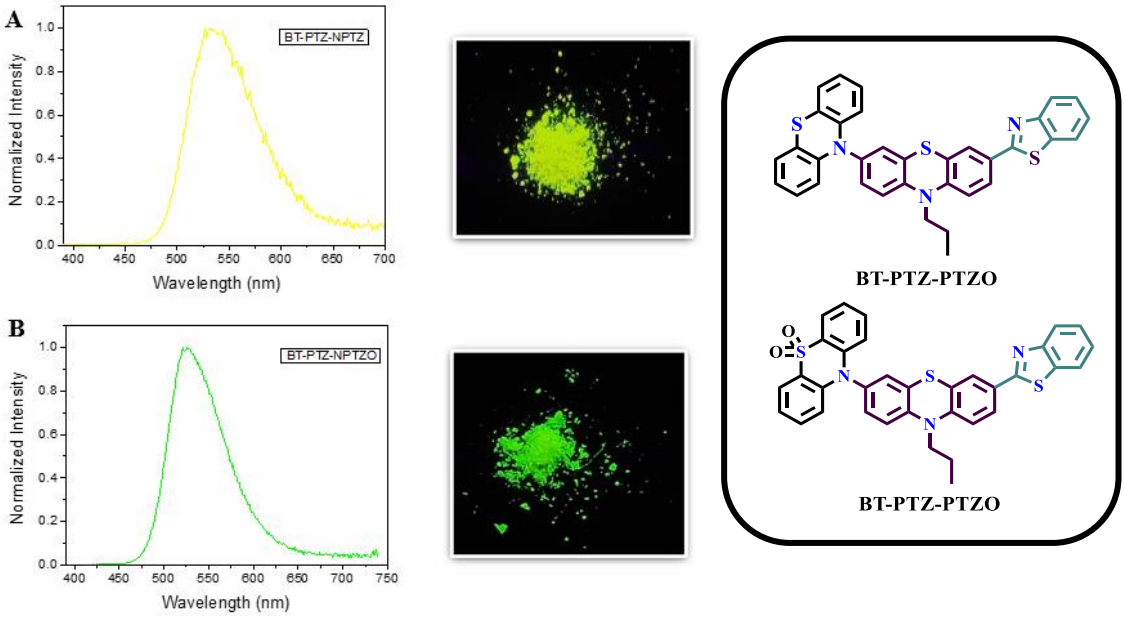


Figure 9: Solid state emission spectra (A and B) of Compound **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO.**

4.3 Density Functional Theory Calculations

The density functional theory calculations were performed on **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** in order to get better understanding about the geometries and electronic distribution in the ground state of these molecules. The calculations were performed at B3LYP/631G (d, p) level and the frontier molecular orbitals (FMOs) were calculated, the calculated highest occupied molecule orbital (HOMO), lowest occupied molecular orbital (LUMO) and the HOMO-LUMO gaps are shown in (Figure 10). The highest occupied molecule orbital (HOMO) is localized on terminal phenothiazine and phenothiazine oxide unit in in **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO,** respectively, while The Lowest unoccupied molecule orbital (LOMO) is localized over benzothiazole unit and slightly extending to the central phenothiazine unit in case of **BT-PTZ-NPTZ . W**hereas in **BT-PTZ-NPTZO,** it localized over the phenothiazine oxide unit. The HOMO-LUMO energy gap for **BT-PTZ-NPTZ and BT-PTZ-NPTZO was** found to be 3.30 eV and 3.43 eV, respectively.

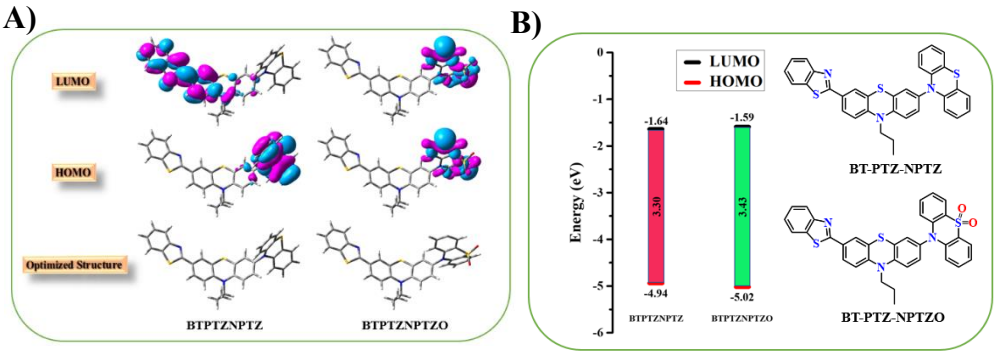


Figure 10: A) Optimized structure of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** , B) Energy level diagram showing the HOMO and LUMO levels of **BT-PTZ-NPTZ** and **BT-PTZ-NPTZO** determined at the B3LYP/6-31G(d) level

CONCLUSION

In this report, we have synthesized metal free pure organic phenothiazine-based molecules **BT-PTZ-NPTZO** and **BT-PTZ-NPTZ** by Buckwald-Hartwig cross coupling reaction. In solvatochromic study the compound **BT-PTZ-NPTZ** exhibited around 60 nm of redshift emission wavelength, while the compound **BT-PTZ-NPTZO** showed 70 nm red shift. The density functional theory was performed to calculate the HOMO-LUMO energy gap and to optimize the geometry. All the compounds were synthesized and well characterized by various spectroscopic techniques such as ^{1}H and ^{13}C NMR, and LCMS, HRMS techniques. The molecules are expected to show room temperature phosphorescence owing to its structural modification, which could be useful for various applications.

In future, our main aim will be in the developing of new RTPMs with improved properties like longer phosphorescence lifetime, higher quantum yields, and better stability. These kinds of advancements are crucial for expanding the practical applications of RTMs. The Room Temperature Phosphorescent molecules hold promise for next-generation lighting and display technologies. Its ability to emit light after excitation without putting continuous excitation source makes it and energy-efficient and suitable for making OLEDs and quantum dot display.

APPENDIX-A

Chacterization of Compound Alkyl-PTZ

1.1 ^{1}H NMR and ^{13}C NMR Spectra of Compound Alkyl-PTZ

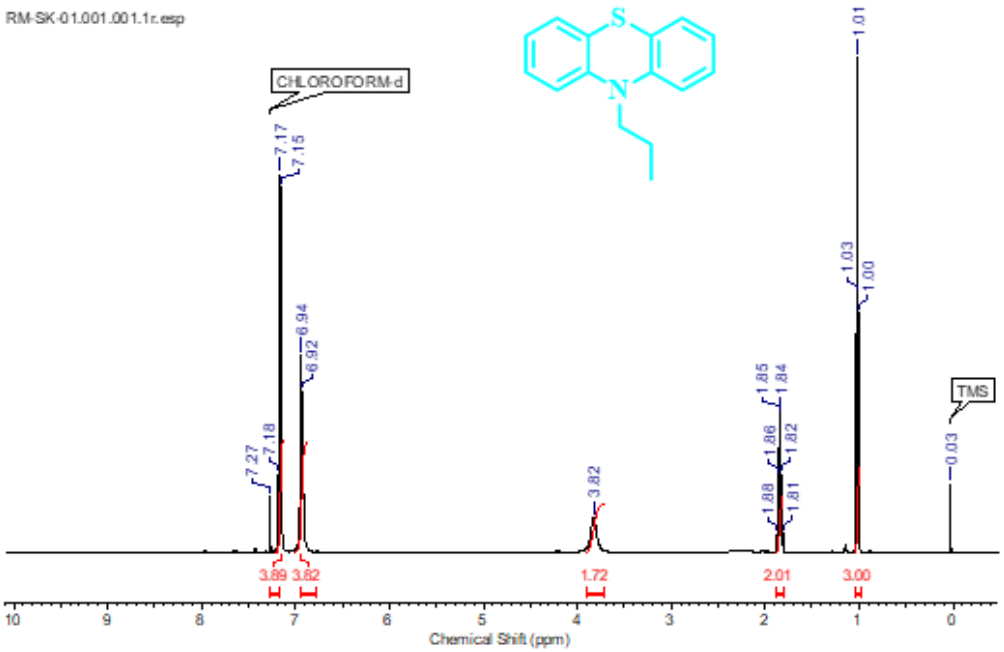


Figure 11: ^{1}H NMR Spectrum of Compound **Alkyl-PTZ**

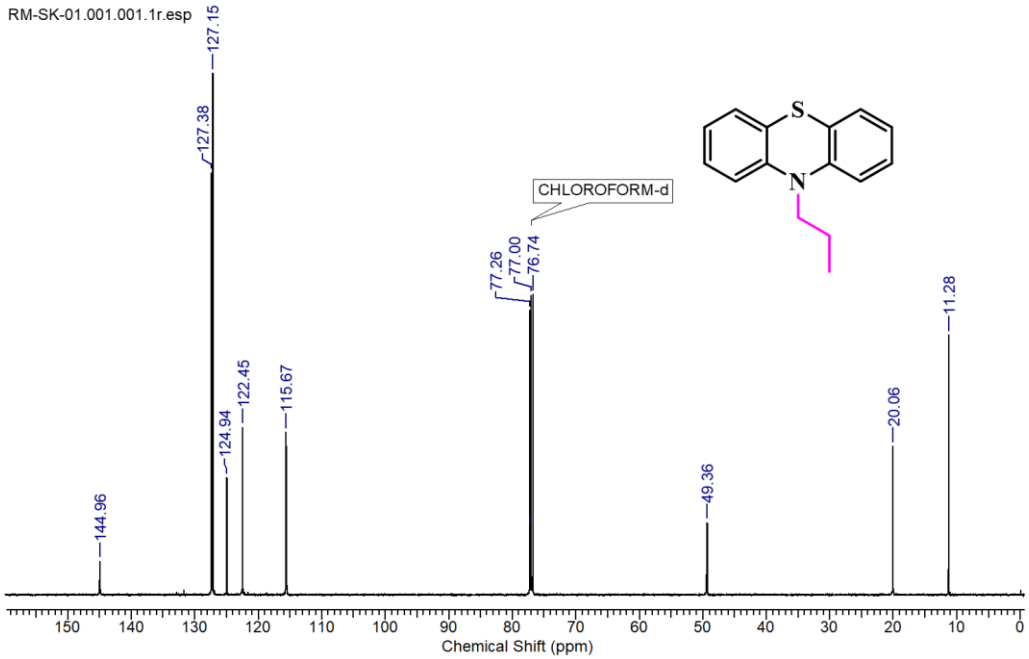


Figure 12. ^{13}C NMR Spectrum of Compound **Alkyl-PTZ**

1.2 HRMS of Compound Alkyl-PTZ

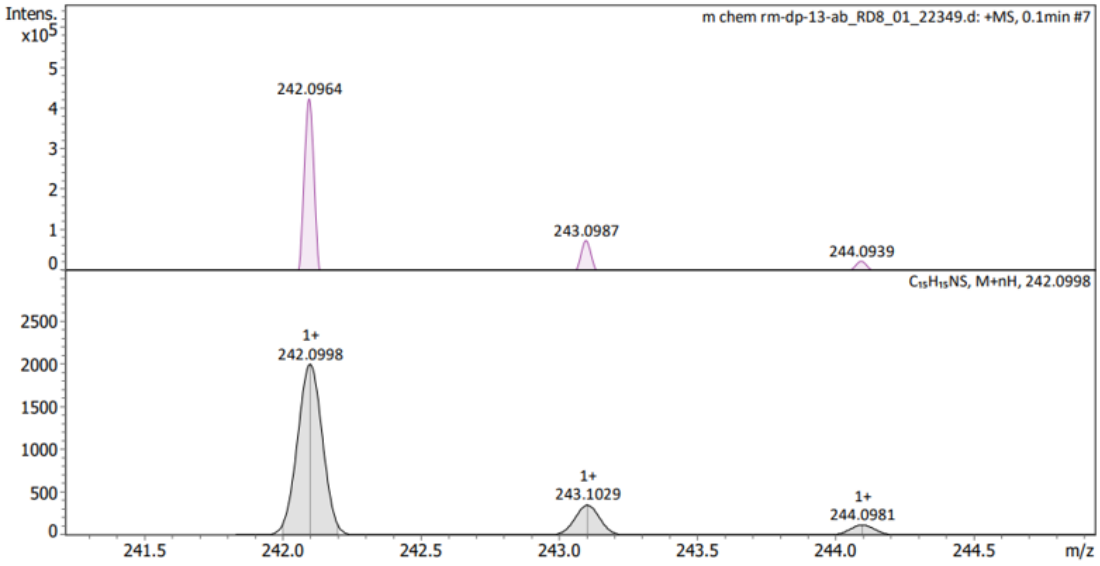


Figure 13: HRMS of Compound **Alkyl-PTZ**

Chacterization of Compound PTZ-CHO

2.1 ^{1}H and ^{13}C NMR Spectrum of Compound PTZ-CHO

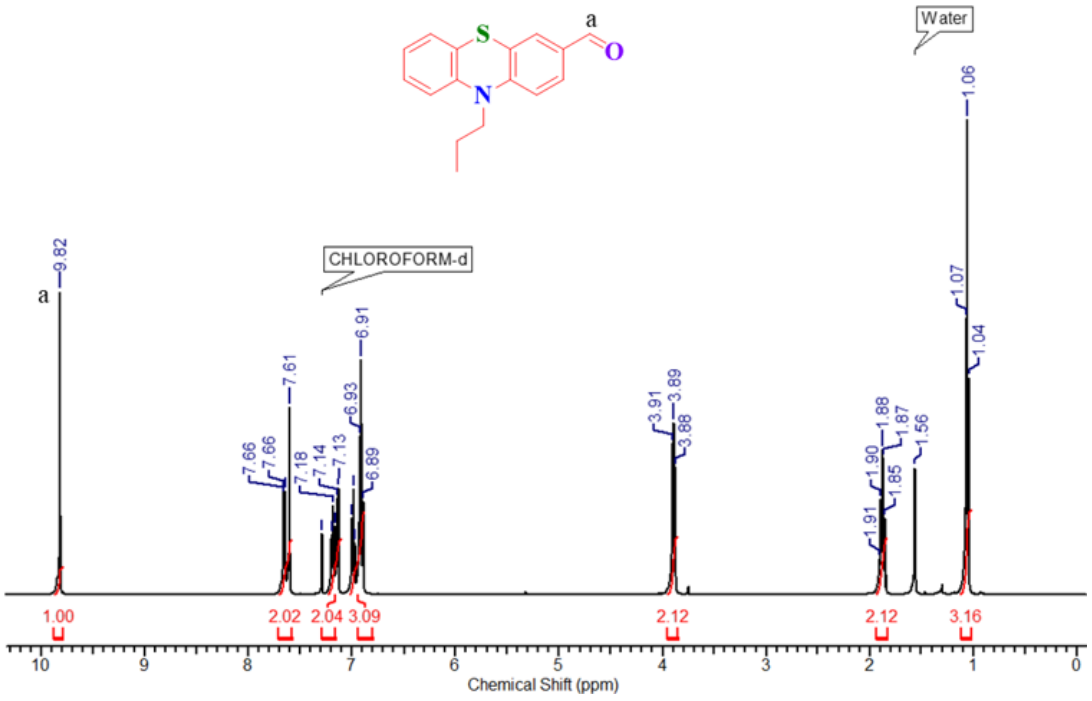


Figure 14. ^{1}H NMR Spectrum of Compound **PTZ-CHO**

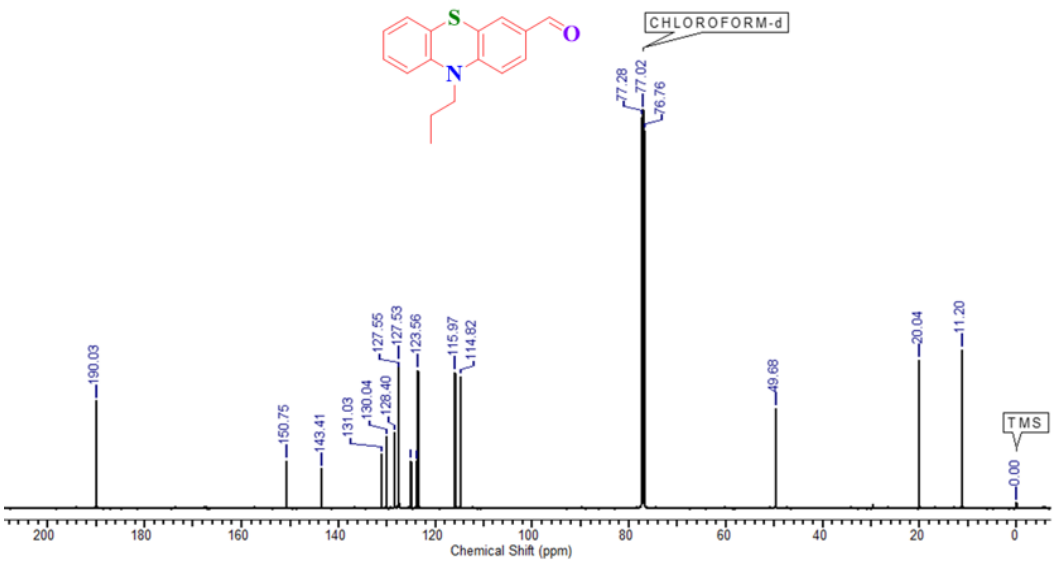


Figure 15: ^{13}C NMR Spectrum of Compound **PTZ-CHO**

2.2 HRMS Spectrum of Compound PTZ-CHO

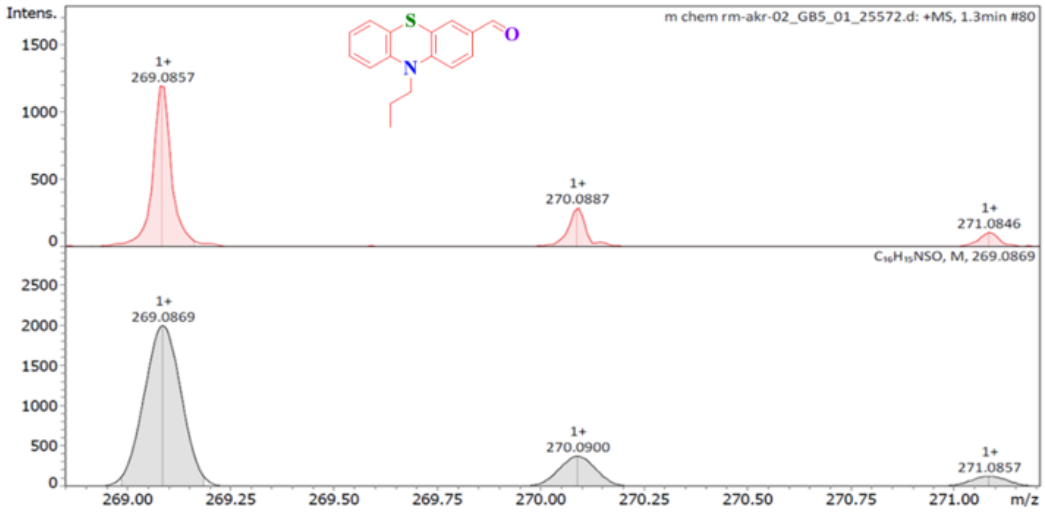


Figure 16: HRMS Spectrum of Compound **PTZ-CHO**

Chacterization of Compound CHO-PTZ-Br

3.1. ^{1}H and ^{13}C NMR Spectrum of Compound CHO-PTZ-Br

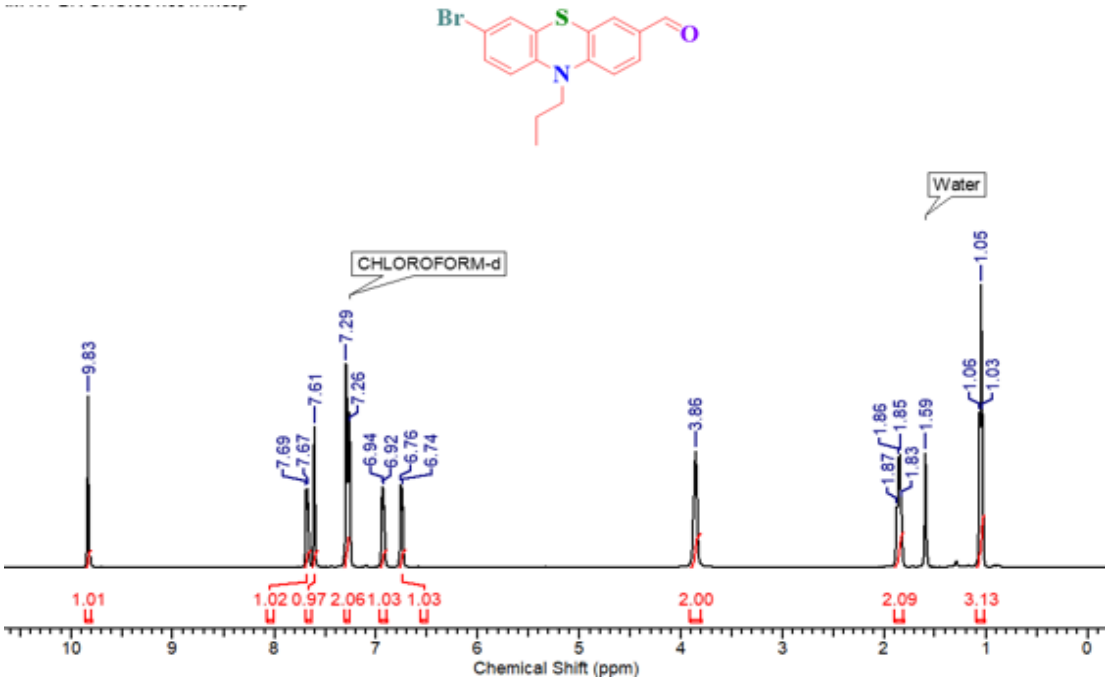


Figure 17: ^{1}H NMR Spectrum of Compound **CHO-PTZ-Br**

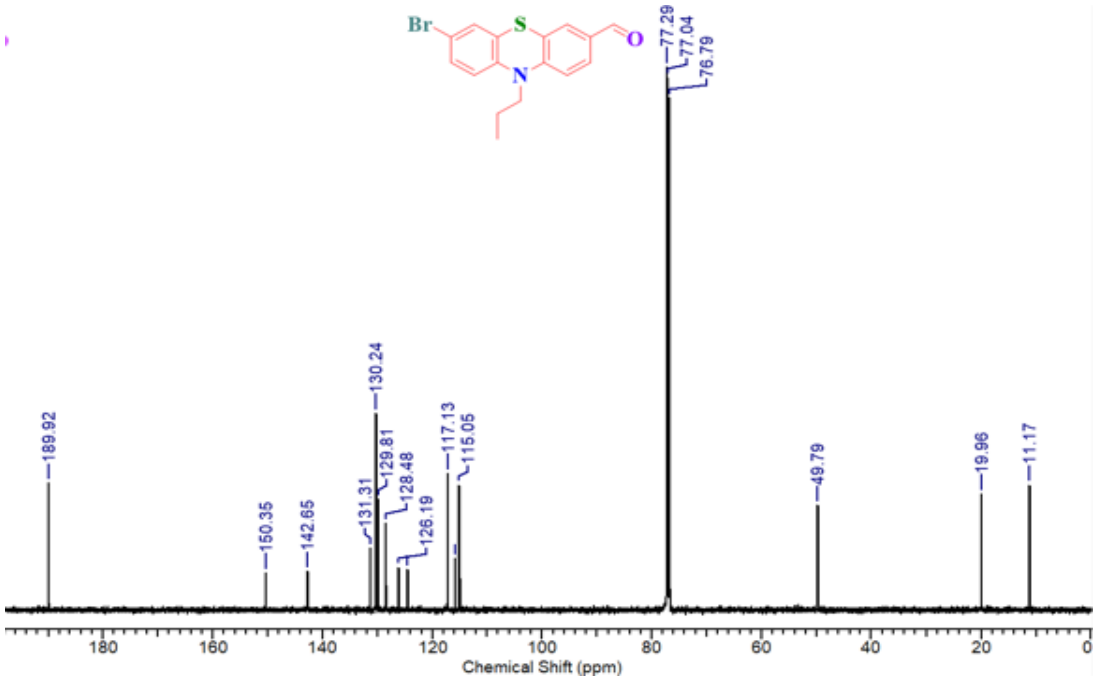


Figure 18. ^{13}C NMR Spectrum of Compound **CHO-PTZ-Br**

3.2 HRMS Spectrum of Compound CH-PTZ-Br

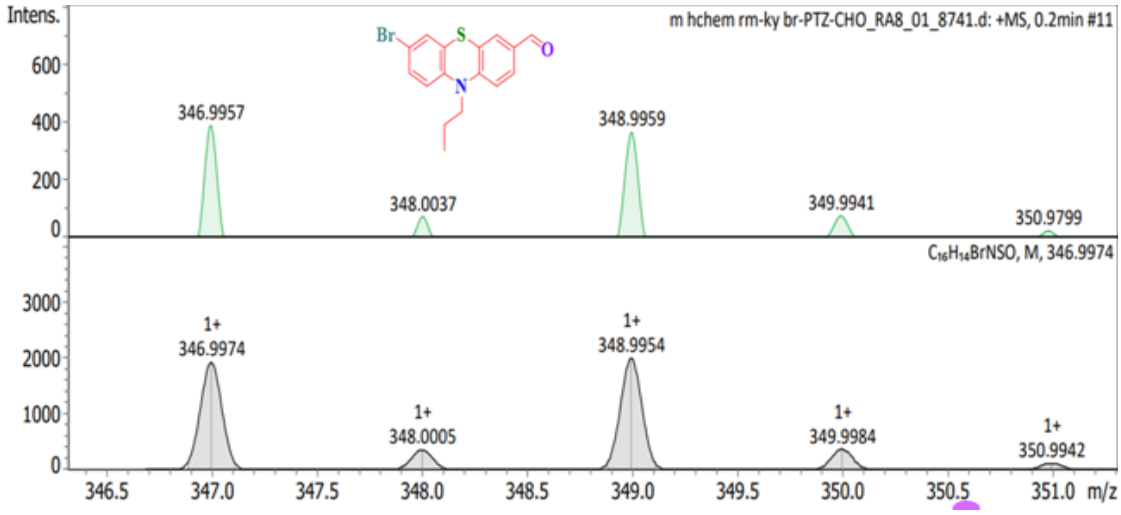


Figure 19: HRMS Spectrum of Compound **CHO-PTZ-Br**

Chacterization of Compound BT-PTZ-Br

4.1 ^{I}H and ^{13}C NMR Spectrum of Compound BT-PTZ-Br

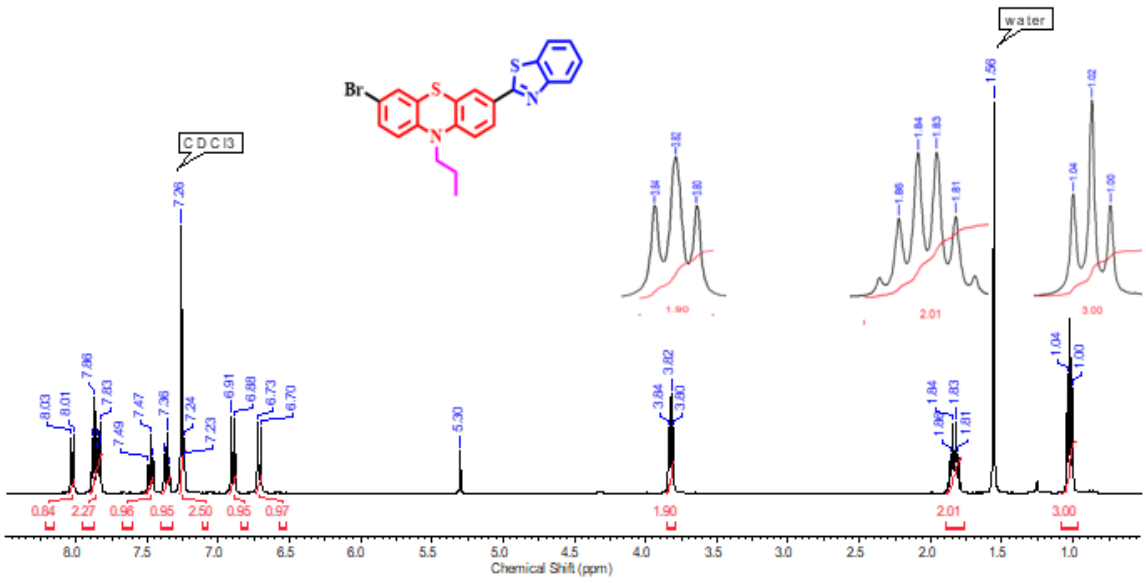


Figure 20: ^{1}H NMR Spectrum of Compound **BT-PTZ-Br**

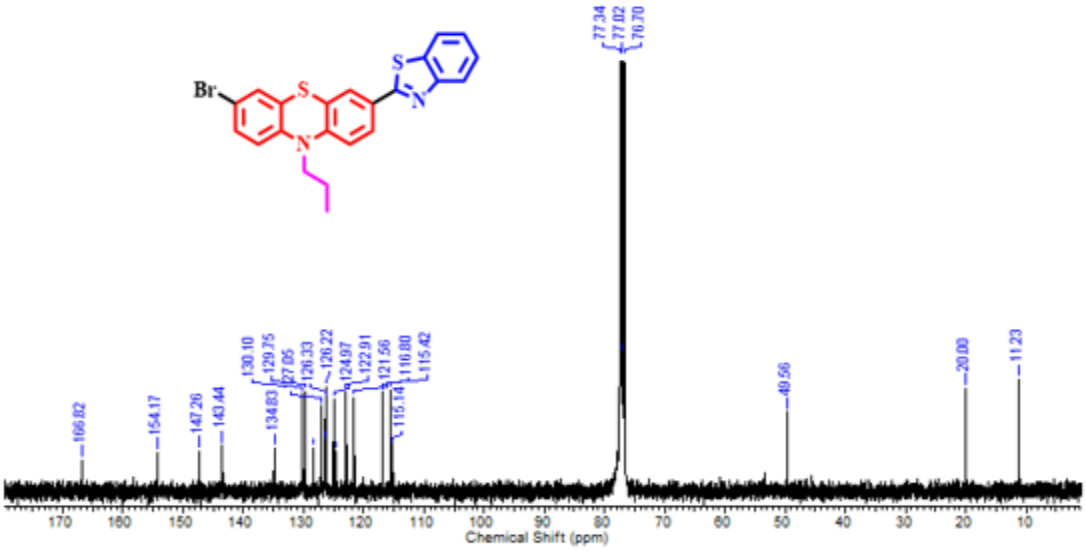


Figure 21: ^{13}C NMR Spectrum of Compound **BT-PTZ-Br**

4.2. HRMS of Compound BT-PTZ-Br

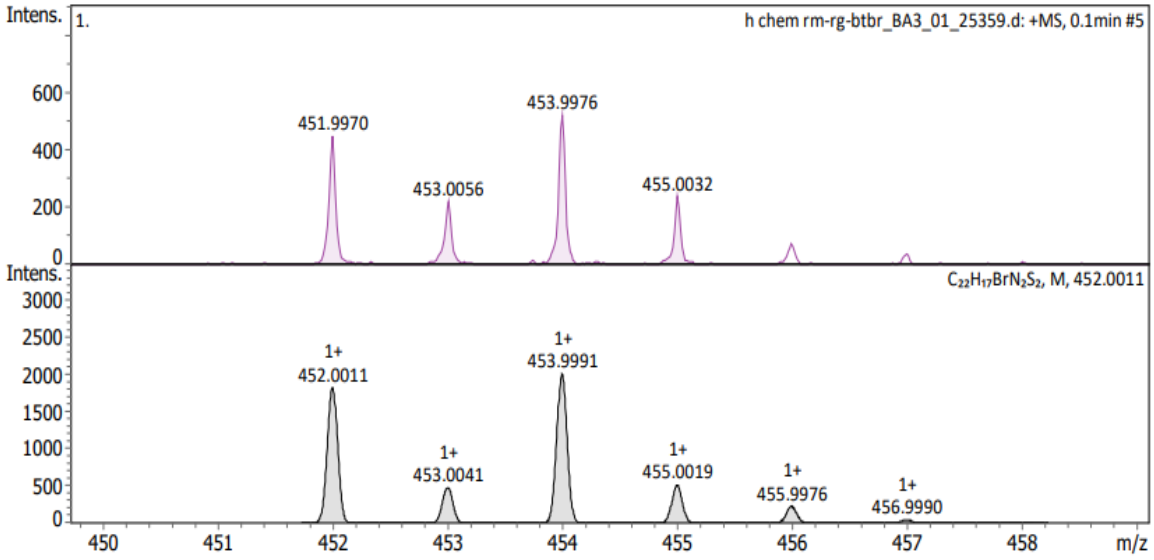


Figure 22: HRMS Spectrum of Compound **BT-PTZ-Br**

Chacterization of Compound BT-PTZ-NPTZ

5.1 ^{1}H and ^{13}C NMR Spectrum of Compound BT-PTZ-NPTZ

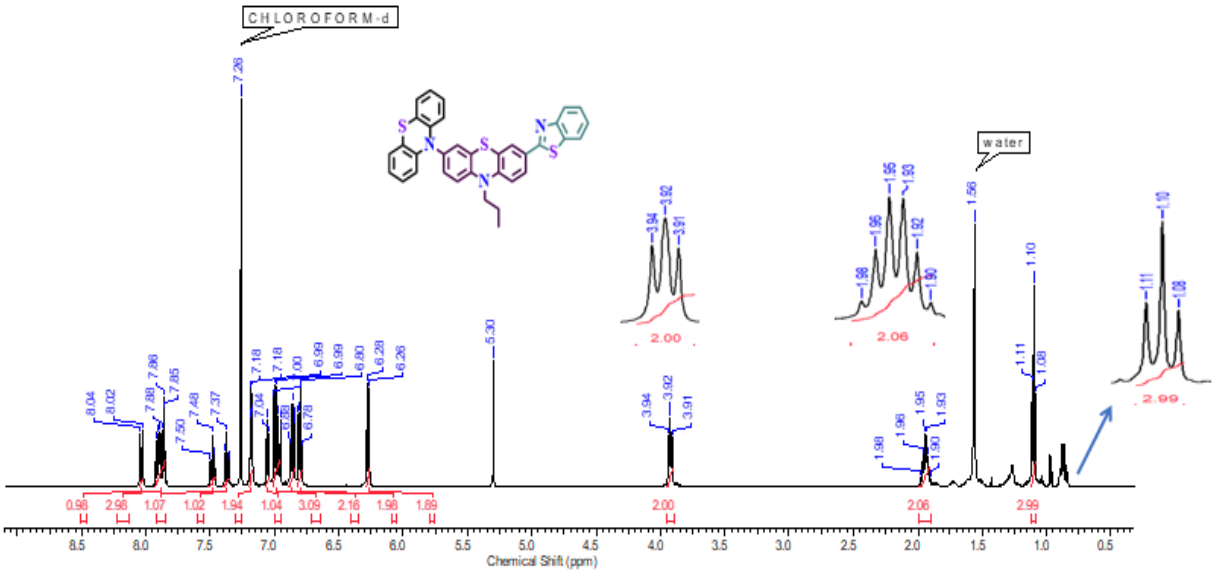


Figure 23: ^{1}H NMR Spectrum of Compound **BT-PTZ-NPTZ**

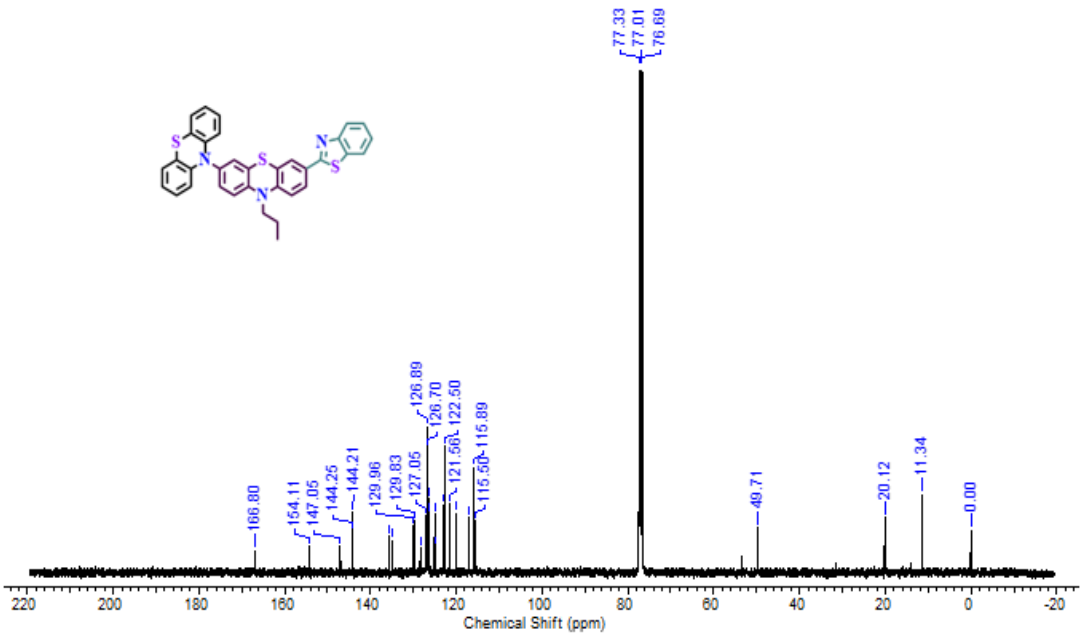


Figure 24: ^{13}C NMR of Compound **BT-PTZ-NPTZ**

5.2 HRMS of Compound BT-PTZ-NPTZ

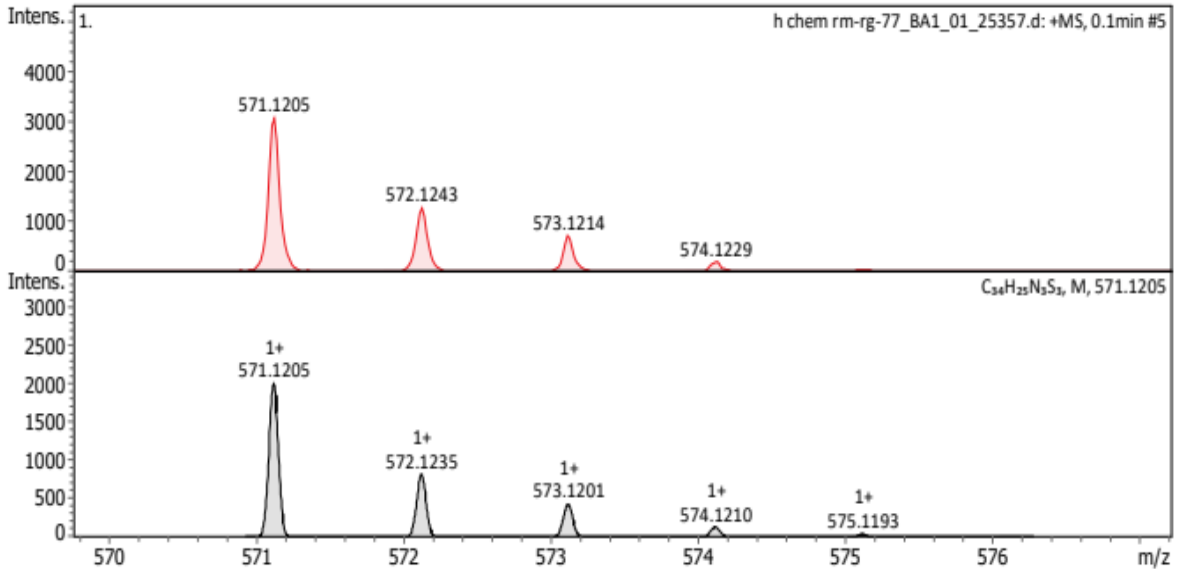


Figure 25: HRMS of Compound **BT-PTZ-NPTZ**

Chacterization of Compound BT-PTZ-NPTZO

6.1 1H and 13C NMR Spectrum of Compound BT-PTZ-NPTZO

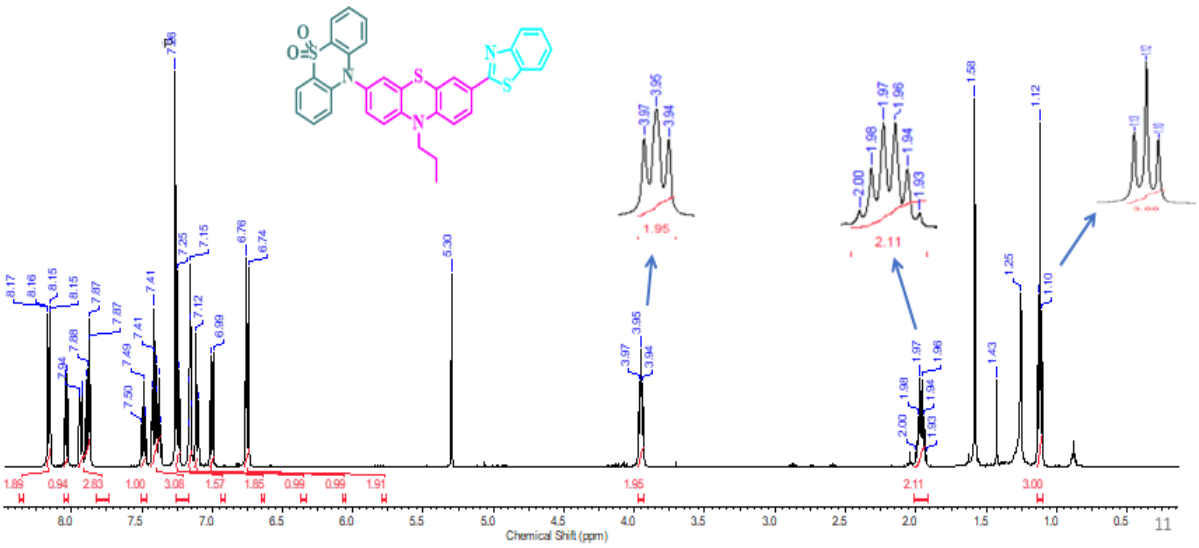


Figure 26: ^{1}H NMR Spectrum of Compound **BT-PTZ-NPTZO**

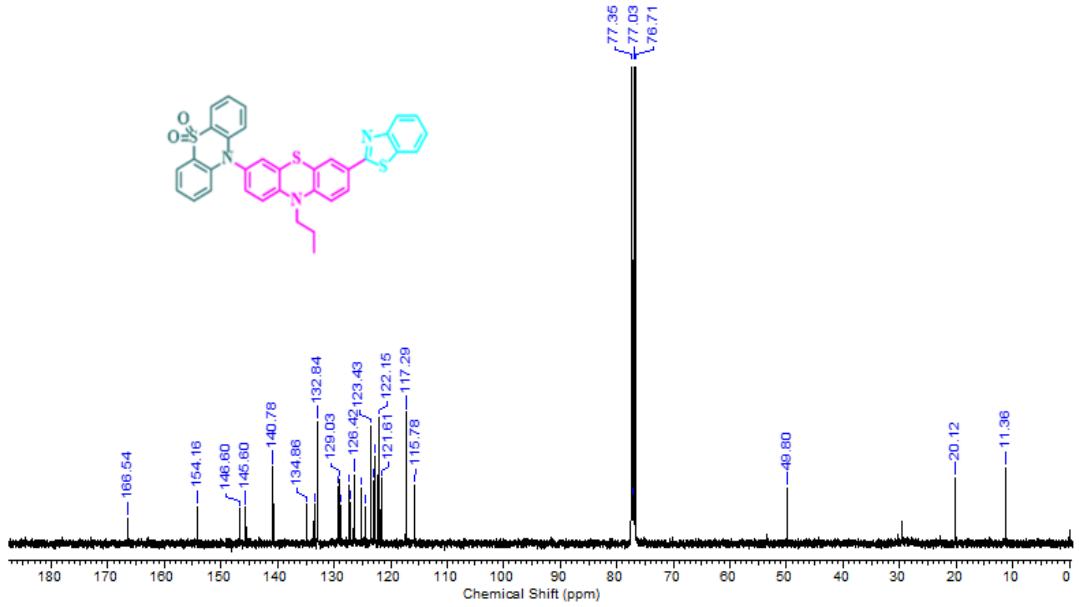


Figure 27: ^{13}C NMR Spectrum of Compound **BT-PTZ-NPTZO**

6.2 HRMS of Compound BT-PTZ-NPTZO

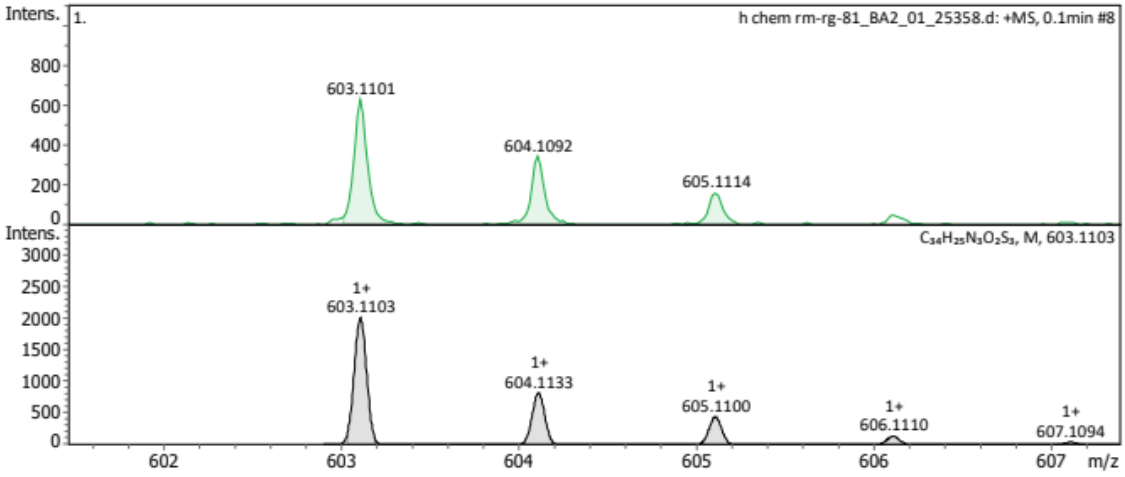


Figure 28: HRMS Spectrum of Compound **BT-PTZ-NPTZO**

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