

# **Design and Synthesis of Donor-Acceptor Functionalized Stimuli-Responsive Materials**

**Ph.D. Thesis**

By  
**Ekbote Anupama Vivek**



**DISCIPLINE OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY INDORE  
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# Design and Synthesis of Donor-Acceptor Functionalized Stimuli-Responsive Materials

**A THESIS**

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

*of*

**DOCTOR OF PHILOSOPHY**

*by*

**Ekbote Anupama Vivek**



**DISCIPLINE 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 entitled “**Design and Synthesis of Donor-Acceptor Functionalized Stimuli-Responsive Materials**” in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** 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 **May 2016** to **December 2021** under the supervision of **Dr. Rajneesh Misra, Professor, Department of Chemistry, IIT 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.

27/04/2022

**Signature of the student with date  
(EKBOTE ANUPAMA VIVEK)**

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

27/04/2022

Signature of Thesis Supervisor #1 with date

**(PROF. RAJNEESH MISRA)**

Signature of Thesis Supervisor #2 with date

**(NAME OF THESIS SUPERVISOR)**

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**EKBOTE ANUPAMA VIVEK** has successfully given his Ph.D. Oral Examination held on **27/04/2022**

27/04/2022

Signature of Thesis Supervisor #1 with date

**(PROF. RAJNEESH MISRA)**

Signature of Thesis Supervisor #2 with date

**(NAME OF THESIS SUPERVISOR)**



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**Anupama Ekbote**

**IIT Indore**



**DEDICATED TO  
MY BELOVED PARENTS,  
MY HUSBAND AND MY  
COUNTRY INDIA**

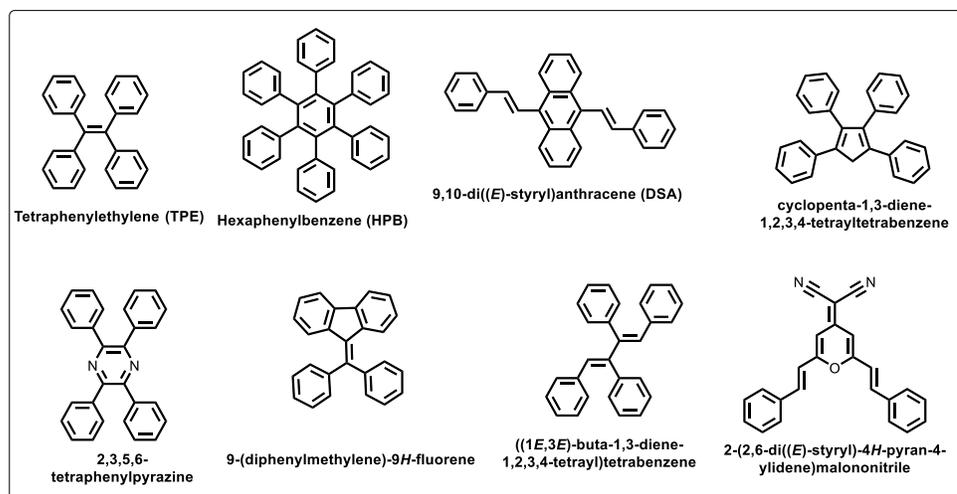
**-Anupama**



## SYNOPSIS

In recent years, the development of luminescent materials which show response to different external stimuli (temperature, pressure, electricity, pH, polarity *etc.*) has gained significant attention considering their utilization in applications such as organic light emitting diodes (OLEDs), information devices, security inks, fluorescent probes, fluorescent sensors, reversible switches, pressure sensors, bioimaging and other optoelectronic devices. Stimuli-responsive materials are new-generation materials which can be constructed by using variety of organic molecules, metal-complexes, metal-organic frameworks and polymeric materials. Mechanochromic materials are stimuli-responsive materials which display reversible changes in their emission on application of mechanical stimuli such as grinding, rubbing, shearing or scratching. In general, majority of the practical applications of stimuli-responsive materials are in the solid state; hence significant amount of solid-state emission is crucial for the design of these materials. The common organic fluorophores such as perylene have been employed in optoelectronic and material devices but their use in the solid-state application is limited due to aggregation caused quenching (ACQ). The organic fluorophores which are often highly emissive in solution state, exhibit ACQ characteristics *i.e.* non-radiative decay of the excited state as an outcome of the extensive  $\pi-\pi$  stacking between the closely lying molecules in the aggregated state. The concept of aggregation-induced emission (AIE) established by Tang *et al.* is beneficial in resolving ACQ and furnishing organic fluorophores with efficient solid-state emission. The AIE luminogens or AIEgens possess a non-planar propeller type structure consisting of rotors attached to a stator that hinder the  $\pi-\pi$  stacking interactions between the molecules on aggregation by the restriction of intramolecular rotations (RIR) resulting in enhanced emission on aggregation or in solid state. The classic examples of AIEgens are tetraphenylethylene (TPE), hexaphenylbenzene (HPB), 9,10-di((E)-styryl)anthracene (DSA) and their functionalized derivatives (Figure 1.).

These AIEgens are non-emissive in solution due to the free rotation of the aromatic rotor rings around the single bond but are highly emissive in solid state *via* RIR. The introduction of AIE active luminogens in conventional organic fluorophores that are usually non-emissive in solid state has proved to be a promising technique for furnishing stimuli responsive materials with efficient solid-state emission. Mechanical stimuli responsive materials or mechanochromic materials usually display physical structural changes such as phase transformation *i.e.* crystalline to amorphous or vice versa or interchange between different crystalline states, E/Z double bond isomerization or conversion between open and closed forms as a response to mechanical force. Reversible mechanochromic behavior is mainly accompanied by morphological transition, changes in molecular conformation and interruption in the molecular stacking interactions. Therefore, subtle changes in the molecular packing and intermolecular interaction by various strategies such as extended  $\pi$  conjugated structures, effective donor-acceptor interaction, inclusion of different substituents (alkyl, aryl, heavy metal or electronegative atoms), positional effects can help in controlling the stimuli-responsive properties. Organic molecules comprising of D-A, D- $\pi$ -A, D-A-D type architecture allow fine tuning of electronic and photophysical properties by use of a variety of donors and acceptors of different strengths. The incorporation of AIE active donors or acceptors render the molecules with conformational flexibility and can function as excellent candidates for design of stimuli-responsive materials suitable for various optoelectronic applications.



**Figure 1.** Common AIE luminogens and its derivatives.

The following thesis work focuses on the donor-acceptor functionalized luminogens showing stimuli-responsive properties possessing different structures such as D-A, D-A-D, D- $\pi$ -A, D-A-A' encompassing different heterocyclic acceptor moieties (quinoxaline, phenanthroimidazole, benzothiazole and benzothiadiazole) and incorporating AIE active donors like tetraphenylethylene and phenothiazine. The main objectives of this work are as follows:

- To design and synthesize donor-acceptor functionalized organic luminogens exhibiting effective emission in both solution state and solid state.
- To study the AIE, photophysical and stimuli-responsive properties such as solvatochromism, mechanochromism, acidochromism of the designed luminogens using different spectroscopic techniques.
- To explore the effect of use of different donor AIEgens, use of different heterocyclic acceptors to modulate intermolecular interactions, positional isomerism, symmetrical and unsymmetrical substitution on the photophysical, electronic and stimuli-responsive properties.

- To investigate the structural features of the donor and acceptor functionalized luminogens required for inducing stimuli-responsive nature *via* single-crystal X-ray diffraction analysis, powder-X-ray-diffraction analysis and density functional theory (DFT) calculations.

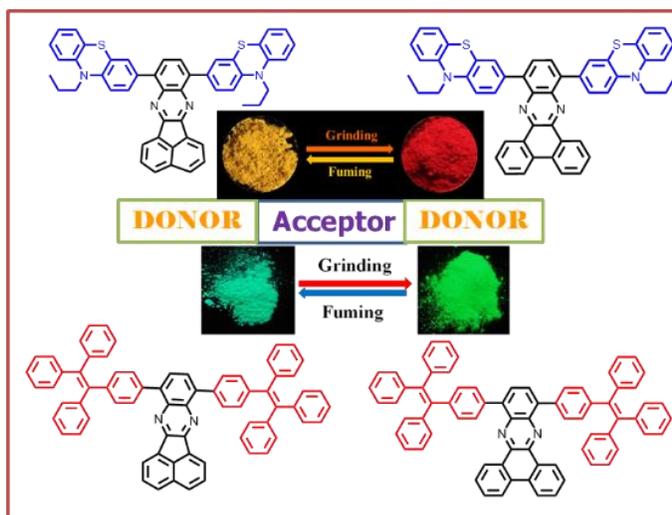
## Chapter 1: Introduction

This chapter discusses about the design strategies for donor-acceptor functionalized stimuli-responsive materials. The chapter also investigates the underlying mechanisms responsible for the stimuli-responsive nature of various materials and their importance in different optoelectronic applications.

## Chapter 2: Materials and experimental techniques

Chapter 2 summarizes the general experimental methods, characterization techniques and details of the instruments used for the characterization.

## Chapter 3: T-shaped donor-acceptor-donor type symmetrical quinoxaline derivatives: Aggregation-induced emission and mechanochromism

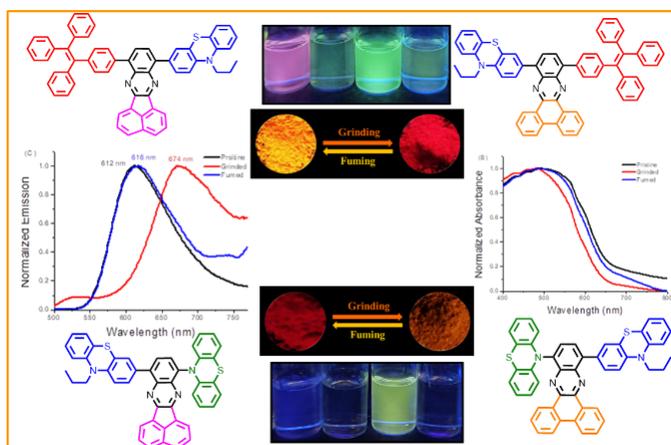


Chapter 3 discusses about the design and synthesis of T-shaped donor-acceptor-donor type phenanthrene-quinoxaline (PQ)-A and acenaphthene-

quinoxaline (AQ)-A' based symmetrical derivatives **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ** and **TPE-PQ-TPE**, **TPE-AQ-TPE** functionalized with phenothiazine (PTZ)-D and tetraphenylethylene (TPE)-D' respectively. The symmetrical quinoxaline derivatives contain two donors TPE and PTZ with contrasting donor character and were synthesized by the Suzuki cross-coupling reaction between TPE/PTZ boronate esters and respective dibromo-quinoxaline derivatives. The effect of substitution of different donors on the solvatochromic, AIE and mechanochromic properties of the symmetrical quinoxaline derivatives were evaluated. The PTZ based symmetrical quinoxaline derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** show increased solvent dependent intramolecular charge transfer (ICT) transitions as compared to the TPE derivatives **TPE-PQ-TPE** and **TPE-AQ-TPE** due to the stronger electron-donating nature of PTZ. The symmetrical quinoxaline derivatives **TPE-PQ-TPE**, **TPE-AQ-TPE** and **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ** exhibit strong AIE behaviour due to incorporation of non-planar TPE and PTZ units. The structural features of the quinoxaline derivatives were explored using density functional theory calculation. The PTZ substituted symmetrical quinoxaline derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** exhibit reversible mechanochromism between yellow-orange to red colour whereas the TPE substituted quinoxaline derivatives **TPE-PQ-TPE** and **TPE-AQ-TPE** exhibit reversible colour-change from green to yellow and a higher grinding induced spectral shift was observed in PTZ quinoxaline derivatives. The higher conformational flexibility of PTZ in comparison to TPE can account for the increased mechanochromic behaviour of PTZ-quinoxaline derivatives. The powder XRD study of the quinoxaline derivatives reveals that the mechanochromic behaviour is related to a morphological change from crystalline to amorphous. The symmetrical quinoxaline derivatives **TPE-PQ-TPE**, **TPE-AQ-TPE** and **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ** are good solid-state emitters, and the donor-acceptor interaction can be modulated by the use of different donors of contrasting abilities. This work provides

strategy to design stimuli-responsive molecules with distinct properties influenced by donor-acceptor interactions.

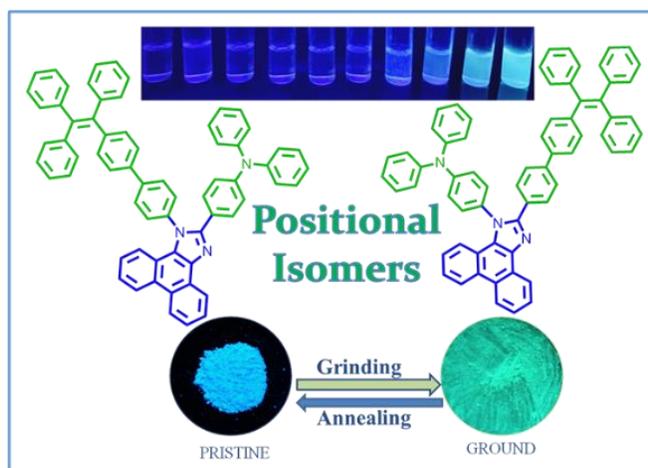
#### Chapter 4: Effect of different donors on mechanochromism of AIE active unsymmetrical D-A-D' type Quinoxaline Derivatives



Chapter 4 summarizes about the design and synthesis of D-A-D'/D-A'-D'' structured unsymmetrical phenanthrene-quinoxaline (**PQ**)-**A** and acenaphthene-quinoxaline (**AQ**)-**A'** derivatives where phenothiazine (PTZ) unit is utilized as donor (D) in combination with tetraphenylethylene (TPE) as donor (D') (**PQ1** and **AQ1**) and N-substituted phenothiazine (N-PTZ) moiety as donor (D'') (**PQ2** and **AQ2**) respectively. The mono-PTZ-substituted bromo intermediate of **PQ** and **AQ** undergoes the Suzuki cross-coupling reaction with TPE boronate ester and Buchwald-Hartwig cross-coupling reaction with PTZ to yield unsymmetrical quinoxaline derivatives **PQ1/AQ1** and **PQ2/AQ2** respectively. The donor-acceptor character of the quinoxaline derivatives can be subtly regulated by unsymmetrical substitution of strong-donor PTZ in combination with donors TPE and N-PTZ and the influence of these structural changes on the photophysical, solvatochromic, AIE and mechanochromic properties have been investigated. The unsymmetrical derivatives show drastic solvatochromic behaviors with highly emissive intramolecular charge transfer (ICT) state in **PQ1** and **AQ1** and quenched twisted intramolecular charge transfer

(TICT) state in **PQ2** and **AQ2** respectively. The unsymmetrical derivatives **PQ1** and **AQ1** incorporating AIEgens PTZ and TPE have efficient solid-state emission and AIE characteristics in contrast to **PQ2** and **AQ2** which are non-emissive in the solid state due to planar N-PTZ moiety. All the unsymmetrical quinoxaline derivatives irrespective of their solid-state emission behavior manifest reversible mechanochromism on application of mechanical stimuli. The reversible mechanochromism involves a phase transformation from crystalline to amorphous which has been studied by powder X-ray diffraction analysis. The presented strategy can help in understanding the influence of different donor-acceptor structures on the AIE and stimuli-responsive characteristics and in further development of donor-acceptor stimuli-responsive materials.

#### **Chapter 5: Stimuli responsive AIE active positional isomers of phenanthroimidazole.**



Chapter 5 discusses about the development of AIE active phenanthroimidazole (PI) based positional isomers **1** and **2** comprising of a triphenylamine (TPA) unit and a tetraphenylethylene (TPE) unit. The positions of triphenylamine (TPA) and tetraphenylethylene (TPE) unit have been interchanged in **1** and **2** and the influence of this change on the AIE and mechanochromism was studied. The phenanthroimidazoles **1** and **2** were synthesized using Suzuki cross-coupling reaction of TPE boronate

ester with iodo-phenanthroimidazoles of TPA and bromo-phenanthroimidazoles of TPA respectively. The PI derivatives **1** and **2** possess significant AIE characteristics by the virtue of propeller orientation of the phenyl rings of the TPE and TPA unit which was further validated by the single crystal X-ray analysis of **1**. Reversible mechanochromism between blue and green color was observed for the phenanthroimidazoles **1** and **2** and the mechanochromic behavior was also studied using the powder X-ray diffraction (PXRD). The PXRD studies demonstrate a phase transition from crystalline to amorphous state associated with the color change. The phenanthroimidazole moiety in combination with TPA and TPE synergistically produces high solid-state emission which can be further employed in optoelectronic applications.

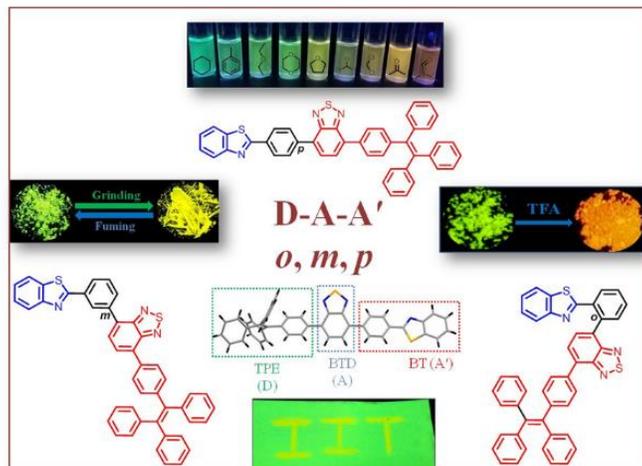
### Chapter 6: Stimuli Responsive Phenothiazine-based Donor-Acceptor Isomers: AIE, Mechanochromism and Polymorphism.



Chapter 6 contributes on the design and synthesis of donor-acceptor (D-A) isomers *p*-PTZ, *m*-PTZ and *o*-PTZ obtained by attaching the phenothiazine (PTZ) moiety at *ortho*, *meta* and *para* positions of the phenyl

benzothiazole (**BT**) unit. This chapter provides in-depth comparison of the structural, photophysical and electronic properties of *p*-**PTZ**, *m*-**PTZ** and *o*-**PTZ** which are influenced as a result of the positional change. The isomers *p*-**PTZ**, *m*-**PTZ** and *o*-**PTZ** were formed by the Suzuki cross-coupling reaction of mono boronate ester of the phenothiazine **PTZ** with corresponding bromo derivatives of phenyl benzothiazole **BT**. The donor-acceptor strength and the molecular packing modes of the isomers can be modulated by attaching the donor **PTZ** at different positions (*para*, *meta* and *ortho*) of the acceptor phenyl **BT** which can result in distinct photophysical and electronic properties. The isomers exhibit contrasting emission properties in different solvents owing to the formation of twisted intramolecular charge transfer (TICT) state. The isomers manifest aggregation-induced emission (AIE) characteristics and reversible mechanofluorochromism (MFC) behavior owing to their twisted structures. The isomers display unique self-reversible color switching mechanism because of the different accessible conformers of **PTZ** moiety. The conformational flexibility of **PTZ** moiety allow the *p*-**PTZ** isomer to occur as polymorphs. The polymorphs of *p*-**PTZ** exhibit structural and morphological difference which were investigated in detail using single crystal X-ray analysis, scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD) studies. The electronic properties of the isomers in ground and excited state were estimated by using the density functional theory (DFT) and time-dependent density function theory (TDDFT) calculations. The isomers were effective in sensing trifluoroacetic acid in solution. The opted design strategy opens possibilities for study of novel stimuli responsive materials.

## Chapter 7: Structure-property relationship in multi-stimuli responsive D-A-A' benzothiazole functionalized isomers.



Chapter 7 discusses about the design and synthesis of multichromophoric D-A-A' positional isomers *p*-BT, *m*-BT and *o*-BT involving benzothiazole (BT)-A', benzothiadiazole (BTD)-A and tetraphenylethylene (TPE)-D formed by incorporating the BTD-TPE moiety at *ortho*, *meta* and *para* positions of the phenyl BT unit. The regio-isomerism in *p*-BT, *m*-BT and *o*-BT is accomplished by exploiting the available *ortho*, *meta* and *para* positions of phenyl BT and allows successful tuning of the acceptor strength and molecular packing. A comparative analysis of the photophysical, AIE and MFC properties of the isomers has been done to investigate the effect of positional change. The *p*-BT and *m*-BT isomers were synthesized by the Suzuki coupling reaction of BTD-TPE with boronate esters of BT; whereas the Stille cross-coupling reaction between stannyl reagent *o*-TBT-BT6 and BTD-TPE was employed for the isomer *o*-BT. The structural aspects of the isomers render molecules with aggregation-induced emission and excellent stimuli-responsive properties such as solvatochromism, mechanochromism, acidochromism, which were studied using emission and absorption spectroscopy. The reversible mechanochromism of the isomers was accompanied by phase transition from crystalline to amorphous and was used to develop rewritable ink free paper. The single crystal X-ray analysis

reveals that the mechanochromism of *p*-BT and *o*-BT synergistically depends on both the flexibility and twisting in the donor and acceptor moieties. The isomers display changes in emission in solution and solid state in response to trifluoroacetic acid. The opted strategy allows modulation of fluorescence properties making them potential stimuli responsive materials with applications in mechano-sensors, security inks and optoelectronic-devices.

### **Chapter 8: Conclusions and Future Scope.**

Chapter 8 summarizes the salient features of the work and provides insights to develop new D-A stimuli responsive materials which can be employed for a wide range of optoelectronic applications.

### **LIST OF PUBLICATIONS**

- [1] **Ekbote, A.**, Mobin, S. M., Misra, R. (2020) Stimuli-responsive phenothiazine-based donor–acceptor isomers: AIE, mechanochromism and polymorphism, *J. Mater. Chem. C*, 8, 3589–3602 (DOI: 10.1039/C9TC05192A)† (Impact Factor = 7.393)
- [2] **Ekbote, A.**, Han, S. H., Jadhav, T., Mobin, S. M., Lee, J. Y., Misra, R. (2018) Stimuli responsive AIE active positional isomers of phenanthroimidazole as non-doped emitters in OLEDs, *J. Mater. Chem. C*, 6, 2077–2087 (DOI:10.1039/C7TC05450E)† (Impact Factor = 7.393)
- [3] **Ekbote, A.**, Mobin, S. M., Misra, R. (2018) Structure–property relationship in multi-stimuli responsive D–A–A' benzothiazole functionalized isomers, *J. Mater. Chem. C*, 6, 10888–10901 (DOI: 10.1039/C8TC04310H)† (Impact Factor = 7.393)
- [4] **Ekbote, A.**, Jadhav, T., Misra, R. (2017) T-Shaped donor–acceptor–donor type tetraphenylethylene substituted quinoxaline derivatives: aggregation-induced emission and mechanochromism. *New J. Chem.*, 41, 9346–9353 (DOI: 10.1039/C7NJ01531C)† (Impact Factor = 3.591)

- [5] Khan, F.,<sup>§</sup> **Ekbote, A.**,<sup>§</sup> Mobin, S. M., Misra, R. (2021) Mechanochromism and Aggregation-Induced Emission in Phenanthroimidazole Derivatives: Role of Positional Change of Different Donors in a Multichromophoric Assembly, *J. Org. Chem.*, 86, 1560–1574 (DOI: 10.1021/acs.joc.0c02404) (Impact Factor = 4.354)
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## ACRONYMS

D-A	Donor-acceptor
SCXRD	Single Crystal X-ray diffraction
NMR	Nuclear Magnetic Resonance
DMF	Dimethylformamide
DCM	Dichloromethane
THF	Tetrahydrofuran
UV-Vis	UV-Visible Spectroscopy
Calcd.	Calculated
CDCl <sub>3</sub>	Chloroform-d
ESI-MS	Electrospray Ionization- Mass Spectrometry
EtOH	Ethanol
MeOH	Methanol
TLC	Thin Layer Chromatography
AIE	Aggregation-induced emission
TPE	Tetraphenylethylene
TPA	Triphenylamine
PTZ	Phenothiazine
PI	Phenanthroimidazole
BT	Benzothiazole
BTD	Benzothiadiazole
QY	Quantum yield
PXRD	Powder X-ray diffraction
MFC	Mechanfluorochromic

## NOMENCLATURE

$\lambda$	Wavelength
$\varepsilon$	Extinction coefficient
$\alpha$	Alfa
$\beta$	Beta
$\gamma$	Gamma
$\pi$	Pi
$\phi_f$	Fluorescence quantum yield
$\sigma$	Sigma
$\text{\AA}$	Angstrom
nm	Nanometer
cm	Centimeter
$^{\circ}$	Degree
$^{\circ}\text{C}$	Degree Centigrade
mmol	Millimol
mL	Milliliter
$\mu\text{L}$	Microliter
a. u.	Arbitrary Unit





# Chapter 1

## Introduction

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### 1.1 Background

Luminescent materials have received significant interest of the scientific community, with the advent of new-age technologies such as optoelectronic devices,<sup>[1]</sup> stimuli-responsive materials,<sup>[2]</sup> bioimaging,<sup>[3]</sup> fluorescent probes,<sup>[4]</sup> sensors,<sup>[5]</sup> data storage,<sup>[6]</sup> solid-state lasers,<sup>[7]</sup> biomedical applications<sup>[8]</sup> and material devices<sup>[9]</sup>. Researchers have been constantly intrigued by the various luminescence phenomena and have made efforts in deciphering the processes involved in obtaining effective luminescence which can be further applied for developing multifunctional materials.<sup>[10]</sup> Luminescence in general is the process of spontaneous emission of light not occurring because of heat.<sup>[11]</sup> Photoluminescence is a process involving emission of light caused by relaxation of electronically excited states formed by absorption of photons from a given light source by a chromophoric molecule.<sup>[12]</sup> Emission of light is often generated by radiative relaxation of the excited state primarily by two processes namely fluorescence and phosphorescence whereas the non-radiative relaxation of the excited state via different processes results in quenching of emission.<sup>[13]</sup> Organic luminescent materials have emerged as promising candidates for future applications and can be effectively constructed from a range of organic luminogens and chromophores which allow development of diverse structures and accurate tuning of optical properties.<sup>[14]</sup> Organic luminescent materials are preferable over their inorganic and polymeric counterparts for application in different technologies due to the following benefits like definite chemical structures, easy reproducibility, low-cost purification, design versatility and compatibility with different substrates.<sup>[15]</sup> Organic luminescent materials are usually associated with  $\pi$ -conjugated structures and precise alteration in the  $\pi$ -conjugation length or incorporation of

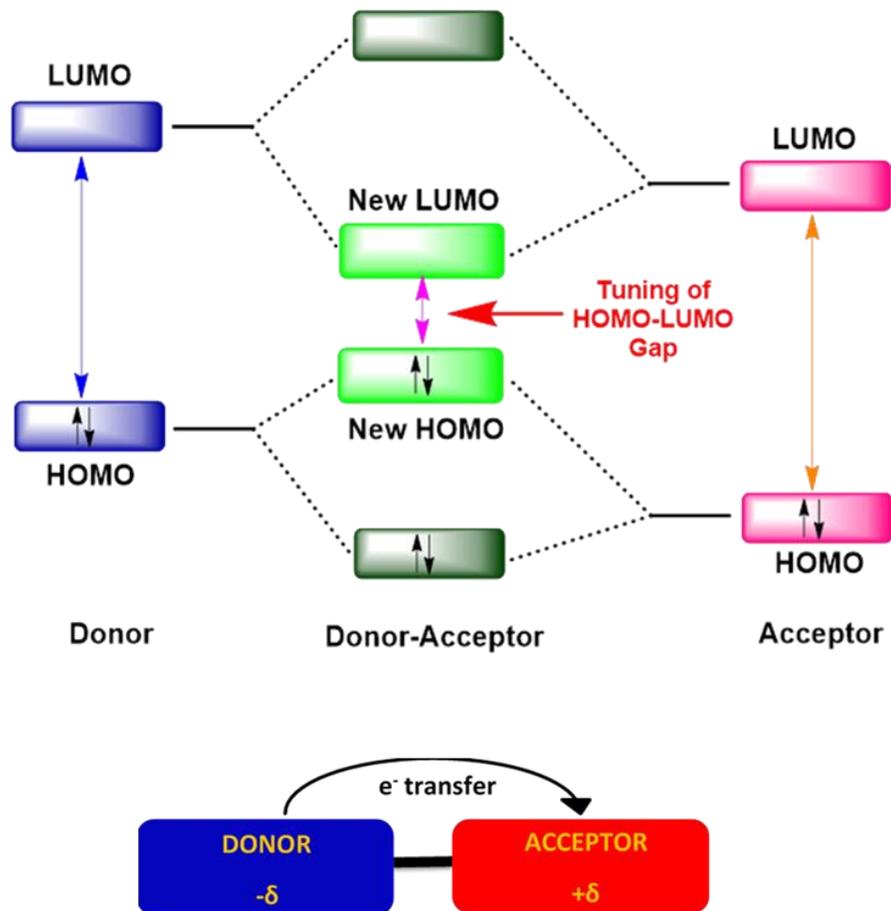
different electron donating or electron withdrawing units enable modulation of luminescence properties.<sup>[16]</sup> Emissive organic  $\pi$ -conjugated small molecules comprising of an electron donor and an electron acceptor display interesting electronic and optical features such as broad absorption spectra, higher absorption coefficients, small HOMO-LUMO gap, narrow emission peaks and formation of strong dipoles.<sup>[17]</sup> The fusion of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the individual donor and acceptor moieties results in formation of distinct HOMO and LUMO energy levels in the donor-acceptor functionalized organic molecules (Figure 1.1). Donor-acceptor systems possess induced dipoles on their donor and acceptor fragments which contribute to the charge transfer processes.<sup>[18]</sup> The process of electron transfer from a donor unit to an acceptor unit located in the same molecule is known as intramolecular charge transfer (ICT) and is a crucial factor in tuning the optical and electronic properties of donor-acceptor systems.<sup>[18]</sup> The ICT process imparts new absorption and emission characteristics which can be effectively controlled by integration of suitable donor and acceptor units.

The luminescent properties of donor-acceptor systems can be perturbed by (1) Utilizing donor and acceptors of varying strengths, (2) By using different heterocyclic donor and acceptor moieties having various intermolecular interactions, (3) Regulating the donor-acceptor character by using different alkyl, aryl or halogen substitutions and using  $\pi$ -linker or spacer moieties between donor and acceptor units.<sup>[19]</sup>

Organic chromophores containing electron donating or withdrawing components can be employed in various donor-acceptor structures such as D-A, D-A-D, D- $\pi$ -A, D-A-A', D-A-D' *etc.* to produce luminescent molecules useful in different applications such as

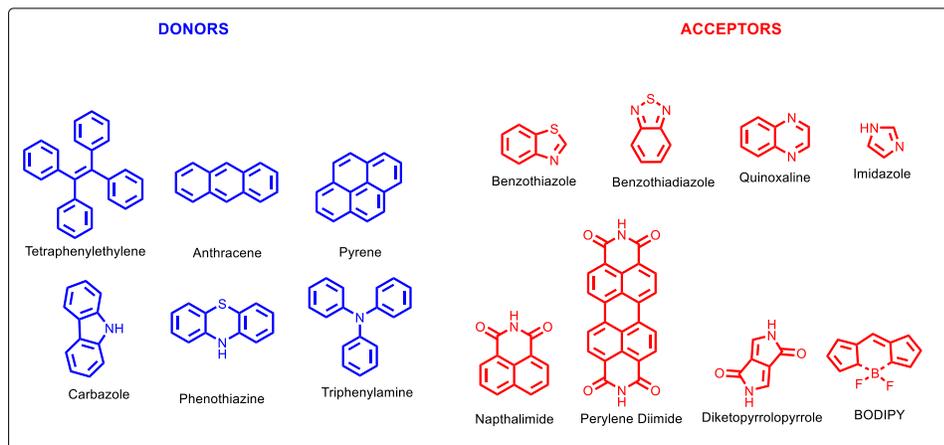
- Organic light emitting diodes (OLEDs)<sup>[20]</sup>
- Bioimaging and photodynamic therapy<sup>[21]</sup>

- Stimuli-responsive materials<sup>[22]</sup>
- Sensors<sup>[23]</sup>
- Organic field effect transistors (OFETs)<sup>[24]</sup>
- Flat panel Displays<sup>[25]</sup>
- Non-linear optics (NLOs)<sup>[26]</sup>



**Figure 1.1** Schematic representation of frontier orbitals and intramolecular charge transfer in donor-acceptor molecules.

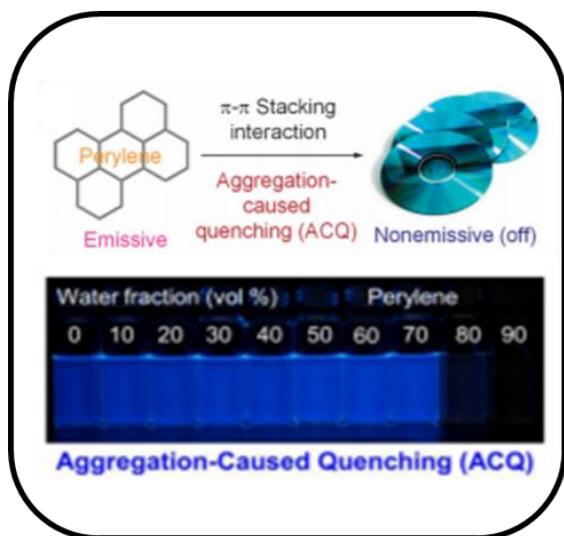
The different donor and acceptor chromophores are as shown in Chart 1.1.



**Chart 1.1** Examples of donor and acceptor moieties.

Organic luminescent molecules find place in different applications in solution as well as solid state, however most of the applications such as OLEDs, OFETs, stimuli-responsive materials *etc.* exploit the solid state of emissive molecules.<sup>[27]</sup> For instance, the fabrication of OLEDs or OFETs is done by preparation of vacuum deposition of emissive substances over solid films. Furthermore, the biological or sensing applications are mostly performed in aqueous media in which most of the organic luminophores are partially soluble leading to formation of nanoaggregates, which are invisible in naked eye. Over the past few years, a wide variety of photoluminescent organic molecules have been developed and the mechanisms related to the photoluminescence processes of these molecules have been extensively studied.<sup>[28]</sup> In the earlier stage, the photoluminescent processes for organic dyes were mostly studied in dilute solutions where the dyes exist as an isolated species not affected by any interactions with other dye molecules. It was observed that most of the organic dyes were highly luminescent in their dilute solution but on increasing the concentration the luminescence drastically decreased owing to the “concentration-quenching” effect. Jean Perrin in 1923 investigated the concentration effect on photoluminescence of uranine and discovered that the increase in concentration of uranine

initially leads to increase in photoluminescence intensity owing to higher number of dye molecules but at higher concentrations the photoluminescence intensity decreases significantly.<sup>[29]</sup> In 1955 Theodor Förster found that the fluorescence of pyrene decreases on increasing concentration which was ascribed to the formation of excimers at higher concentration facilitated by collisional interactions between the aromatic rings. It was thus concluded that the concentration quenching of organic molecules at higher concentrations could be due to strong  $\pi$ - $\pi$  interactions or face to face interactions between the aromatic rings.<sup>[30]</sup> J.B. Birks in “*Photophysics of Aromatic Molecules*” published in 1970 has summarized that such type of concentration quenching effect is displayed by most of the well-known organic aromatic molecules.<sup>[31]</sup> The established organic luminophores in their aggregated or solid state have slightly diminished or completely quenched emissions as compared to their dilute solutions, and the phenomenon in general is referred to as “Aggregation caused quenching” (ACQ).<sup>[31]</sup> The aromatic molecules in their solutions are well-separated and do not interact with each other thereby exhibiting strong emission. However, the molecules on aggregation come in close proximity of each other and the aromatic rings of the luminophores undergo extensive  $\pi$ - $\pi$  stacking interaction (like discs or rods stacked on one another) creating non-radiative channels for relaxation of their excited states resulting in quenched emission of organic luminophores in their aggregated state. The ACQ effect is a common obstacle resulting in non-emissive aggregated states of organic molecules.<sup>[32]</sup>



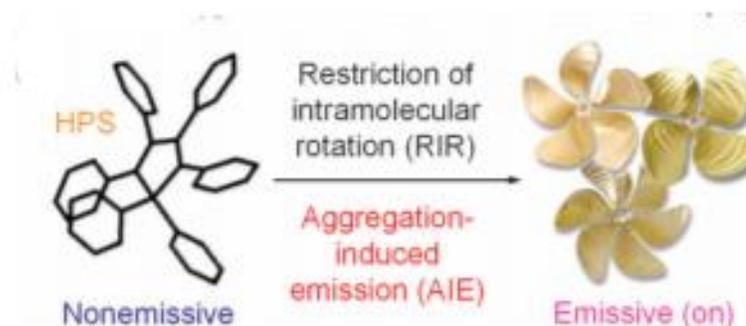
**Figure 1.2.** Schematic representation of ACQ effect in perylene molecules.

Figure 1.2 represents the ACQ effect observed in perylene dye. The solution of perylene in THF is highly emissive. Perylene is insoluble in water and hence a gradual increase of water fraction in THF results in increased concentration of perylene molecules which thereby leads to aggregation of the molecules. The perylene dye molecules shows diminished or quenched emission at 80% and 90% THF-water mixtures of due to  $\pi$ - $\pi$  stacking between the planar rings on aggregate formation.

Several chemical strategies have been executed by researchers to reduce the ACQ effect such as addition of polar groups, bulky substituents or branched alkyl chains on aromatic cores which could reduce the hydrophobicity of aromatic rings thereby decreasing the possibility of aggregation in aqueous media.<sup>[33]</sup> Also, physical processing methods such as mixing of transparent polymers and organic luminophores could avoid the molecules from coming together on aggregation thereby decreasing ACQ effect.<sup>[34][38]</sup> However, all these strategies have failed to lessen the ACQ effect making the organic molecules difficult to be used in practical applications. Hence, researchers have made efforts to come up with an approach which rather than obstructing the spontaneously occurring aggregation process could utilize it constructively to enhance the emission of organic molecules in the solid state.<sup>[35][39]</sup>

## 1.2. Aggregation-induced emission

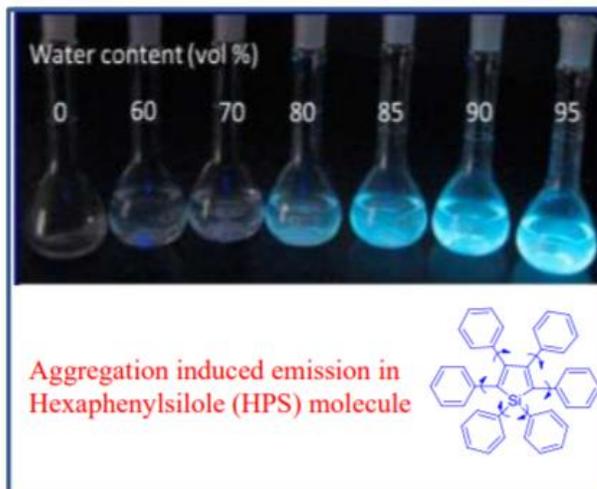
In 2001, Tang and coworkers discovered “Aggregation-induced emission” (AIE) which takes the advantage of the aggregation process to produce effective emission.<sup>[36]</sup> AIE is an anti-ACQ effect which was first detected in hexaphenylsilole (HPS) and its derivatives.<sup>[37]</sup> The HPS molecule has a unique propeller type confirmation with the central silole ring acting as stator for the six-phenyl ring which act as rotors (Figure 1.3).



**Figure 1.3.** Schematic presentation of mechanism involving AIE as restricted intramolecular rotation in hexaphenylsilole (HPS) luminogen.

In solution, the phenyl rings undergo continuous intramolecular rotations around the single bond attached with the stator silole ring generating non-radiative decay channels for its excited state resulting in quenching of emission. In contrast to the quenched emission of HPS in solution, it displays excellent emission in the aggregated state due to restriction of intramolecular rotation (RIR).<sup>[37]</sup> In the aggregated state, the HPS molecules retain their non-planar framework which interrupts the stacking process observed in planar disc type molecules and are also unable to rotate freely as they lie close to each other which allows the molecules to relax their excited state radiatively making their aggregated state highly emissive. The non-planar frameworks of the luminogens with AIE or AIE gens works in a positive way to generate emission in aggregated state via RIR contrary to the planar structures of the ACQ molecules.

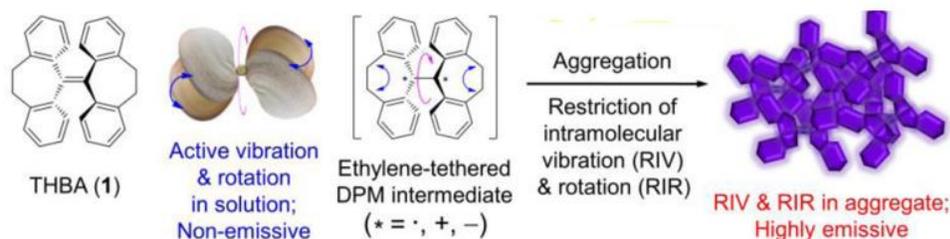
The AIE effect have been explored in detail using fluorescence and absorption spectroscopy. The HPS molecules were dissolved in acetonitrile and HPS being insoluble in water, the aggregates were produced by slowly increasing the water amount from 0-90% in acetonitrile solution of HPS. In pure acetonitrile solution, the HPS molecules have reduced emission with a quantum yield ( $\Phi_F$ ) 0.22%. The emission of HPS remains constant even at 50% water fraction but increases significantly at 80-90% water fraction with quantum yield ( $\Phi_F$ ) reaching to 56%. The absorption spectra of HPS molecules on aggregation *i.e.* at 80-90% water fraction exhibit the Mie scattering effect prominently observed in nanoparticles which is confirmed for HPS molecules by the extended tail-type absorption in higher wavelength region.<sup>[38]</sup> The aggregates of size 190 nm and 130 nm are formed at 80% and 90% water fractions respectively, which confirms the generation of nanoparticles on aggregation in HPS molecules. Figure 1.4 shows pictorial representation of AIE effect in acetonitrile-water mixture of HPS molecules. The AIEgens emit efficiently on aggregation by RIR and this hypothesis has also been validated by activating the RIR process externally *i.e.* by controlling the intramolecular interactions using experiments such as decreasing the temperature of system, increasing the viscosity of a solution system and applying pressure.<sup>[39]</sup> All these physical changes affect the intramolecular interactions and improve the emission by triggering the RIR process in AIEgens. Thus, effective emission in solid state could be obtained by exploring different non-planar propeller type structures which can emit via RIR.<sup>[40]</sup>



**Figure 1.4.** Fluorescence photographs of HPS in acetonitrile/water mixtures with different water fractions.

Several non-planar AIEgenes have been investigated whose AIE activity is ascribed to a different mechanism namely restriction of intramolecular vibrations (RIV) rather than RIR. The organic molecule 10,10',11,11'-tetrahydro-5,5'-bidibenzo[a,d][7]annulenyliene (THBA) is non-emissive in its solution but exhibits substantial emission as aggregates.<sup>[41]</sup> The THBA molecule has phenyl rings which are connected by an ethylene bond which brings a restraint on the rotational motions of the phenyl rings. The phenyl rings in THBA can undergo vibrational motions which can non-radiatively decay the excited state energy in solution similar to the rotational motions. (Figure 1.5).<sup>[42]</sup> However, in the aggregated state the emission is enhanced by the restriction of intramolecular vibrations (RIV). The quantum mechanics and molecular mechanics studies reveal that the single THBA in solution possesses six normal vibrational modes which can significantly utilize the excited state energy. However, in the aggregated state, THBA possesses only three normal vibrational modes which limits the consumption of excited state energy to approximately 30%, allowing THBA to display radiative emissions in aggregated state. Thus, in addition to RIR the RIV mechanism also effectively results in AIE behavior for luminogens with structures similar to THBA. In general, the restriction of any kinds of

motions (rotation, vibration, flapping, twisting, scissoring *etc.*) that result in non-radiative decay of excited state can result in AIE activity. Hence, the AIEgens can be elucidated as systems working on restriction of intramolecular motions (RIM) mechanism where (M) is any kind of motion including vibration (V) and rotation (R).<sup>[37]</sup>

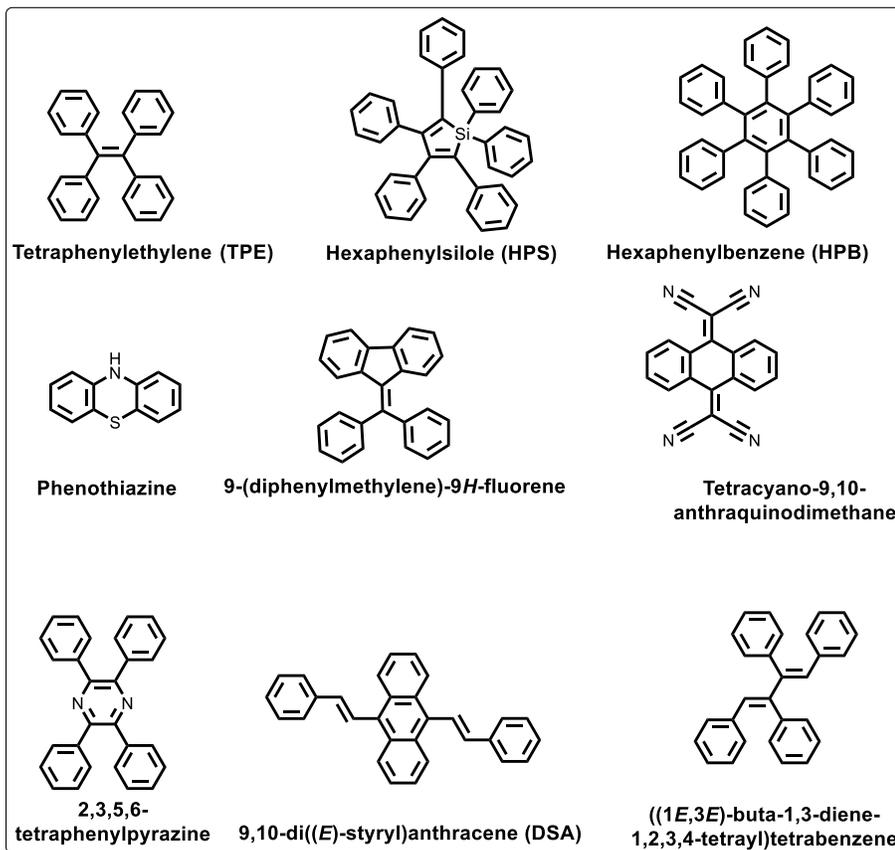


**Figure 1.5.** Schematic presentation of mechanism involving AIE as restricted intramolecular vibration in 10,10',11,11'- tetrahydro-5,5'-bidibenzo[a,d][7]annulenyliene (THBA) luminogens.

### 1.3. Aggregation-induced emission type luminogens

Organic molecules which are emissive in aggregated state are termed as aggregation-induced emission (AIE) luminogens or AIEgens and are suitable for developing solid-state emissive molecules.<sup>[43]</sup> The AIE luminogens possess unique non-planar twisted frameworks which produce intense emission in the aggregated state due to RIR or RIV process.<sup>[40]</sup> The AIEgens are usually non-emissive in solution owing to the continuous intramolecular rotations of the aromatic rings which render non-radiative decay of their excited state. A variety of AIE luminogens with the ability to generate emission via RIR, have been developed over past few years by careful structural manipulation of organic molecules.<sup>[40]</sup> The well-known AIE luminogens rely on a structure consisting of a fixed central unit (olefin or aromatic unit) acting as stator surrounded by different aromatic units which behave as rotors attached by freely rotating single bond. Chart 1.2 depicts the structures of commonly employed AIE luminogens.<sup>[44]</sup> Tetraphenylethylene (TPE) and hexaphenylsilole (HPS) are widely used

AIEgens displaying high emission on aggregation and have rotor-stator based structures.<sup>[45]</sup> Similar to the RIR mechanism, certain non-planar molecules apart from the rotor-stator type molecules that exhibit any kind of restricted intramolecular motions (RIM) in their aggregated state also have efficient emission in their aggregated states.<sup>[41]</sup> [45]



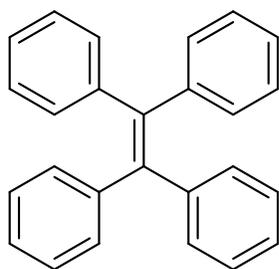
**Chart 1.2.** Examples of different aggregation-induced emission (AIE) type luminogens.

Phenothiazine (PTZ) with a bent butterfly structure manifests AIE characteristics by restriction of intramolecular vibrations (RIV).<sup>[46]</sup> Similarly, anthraquinodimethane derivatives retain bent structures and manifest AIE nature by restricting the flapping and vibrations of its aromatic cores.<sup>[47]</sup> Thus, a wide variety of AIEgens having non-planar, bent, propeller type twisted architectures that carefully restrict any kind of intramolecular motions which create non-radiative decay channels thereby emitting efficiently in aggregated state have been reported in literature. The

inclusion of AIE units in traditional ACQ chromophores is a decent approach to induce intense emission into the non-emissive aggregated states of ACQ chromophores. The integration of AIE units acting as electron donors and conventional ACQ chromophores acting as electron acceptors result in donor-acceptor systems with high solid-state emission.<sup>[48]</sup>

#### 1.4. Tetraphenylethylene

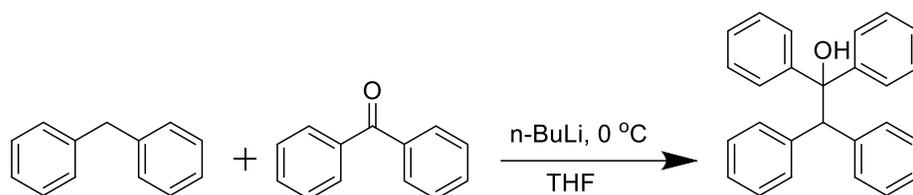
Tetraphenylethylene (TPE) is a conventional AIE luminogen and has many uses in organic light emitting diodes (OLEDs), non-linear optics (NLOs), mechanochromic materials and bioimaging.<sup>[49]</sup> Tetraphenylethylene has an exclusive non-planar architecture with an ethylene double bond in the center working as stator unit with the four phenyl rings surrounding it which act as rotor units (Figure 1.6.). The TPE moiety maintains a propeller confirmation which was confirmed by Hong *et al.* from its crystal structure analysis and has twisting angle of  $\sim 50^\circ$ .<sup>[50]</sup> The phenyl rings attached to the central olefin can freely rotate in solution via the single bond attachment and produce non-radiative decay paths for the excited state decay. However, the propeller framework of TPE renders the aggregated emissive via RIR process and absence of stacked structures.<sup>[51]</sup> TPE moiety by virtue of its rigid structure possess good thermal and chemical stability and can be easily synthesized and functionalized to its different bromo, hydroxy or other halogenated derivatives.



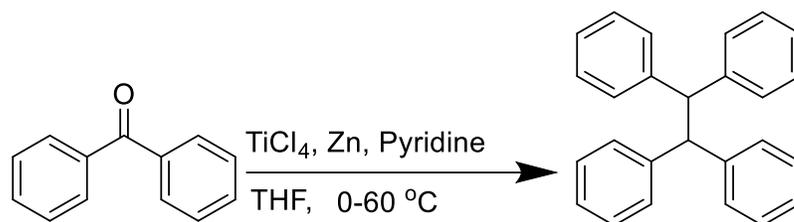
**Figure 1.6.** Structure of tetraphenylethylene.

De Boissieu synthesized TPE for the first time in 1888 *via* dry distillation of diphenylmethane in the presence of bromine.<sup>[52]</sup> Numerous synthetic methods for TPE preparation have been published in the literature

(Scheme 1.1–1.4). Some of these methods can also be used to make functionalized TPEs. TPE can be easily synthesized *via* a condensation process similar to Knoevenagel condensation. Wang *et al.* synthesized TPE *via* a Knoevenagel-like condensation process (Scheme 1.1).<sup>[53]</sup> To make tetraphenylethanol, diphenylmethane was first deprotonated with n-BuLi in THF at 0 °C, then benzophenone was progressively added. The water was removed using the Dean-Stark apparatus *via* an azeotropic combination with toluene, and the resultant tertiary alcohol was dehydrated using catalytic para-toluene sulphonic acid (PTSA). This method is also essential in the design of different functionalized TPEs, such as halogenated TPE. However, the n-BuLi approach has constraints in terms of using substituted diphenylmethane or benzophenone derivatives, such as the production of unstable anion when using electron donating substituents on the diphenylmethane unit.



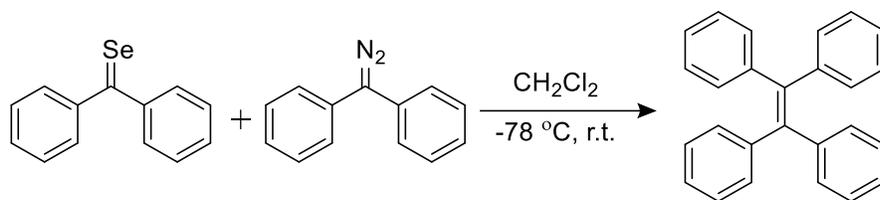
**Scheme 1.1.** Synthesis of TPE by using Knoevenagel like condensation reaction.



**Scheme 1.2.** Synthesis of TPE by using McMurry like condensation reaction.

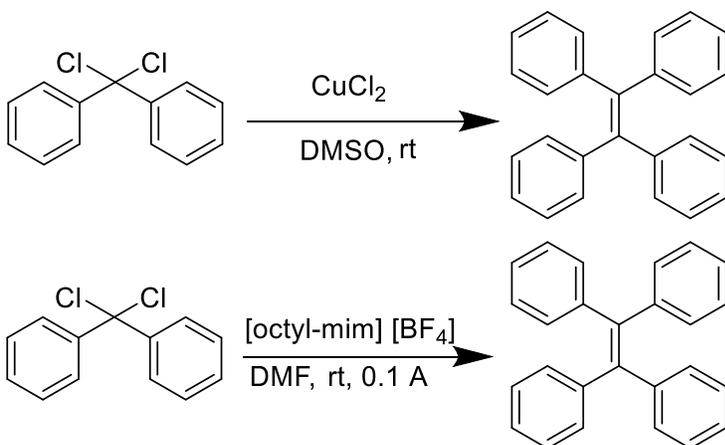
TPE can be effectively synthesized utilizing a McMurry-like condensation process (Scheme 1.2).<sup>[54]</sup> The McMurry coupling is a second significant technique for manufacturing TPE and its derivatives. The two ketones

(benzophenone) get fused to form TPE in the presence of Ti(IV) and Ti(IV) salts, as well as the reducing agent Zn (Scheme 1.2).



**Scheme 1.3.** Synthesis of TPE by using selenobenzophenones with diphenyldiazomethane.

The synthesis of TPE was achieved by reacting selenobenzophenones with diphenyldiazomethane in dichloromethane at  $-40\text{ }^\circ\text{C}$ , as shown in Scheme 1.3.<sup>[55]</sup> This reaction is initiated by a 1,3,4-selenadiazoline intermediate, followed by deselenization and nitrogen gas evolution. Unsymmetrical TPE derivatives can also be obtained using this technique.



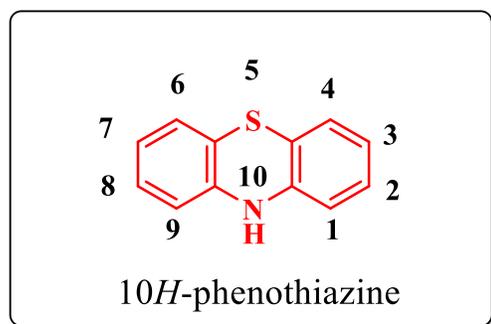
**Scheme 1.4.** Synthesis of TPE from diphenyldichloromethane.

The synthesis of TPE from diphenyldichloromethane is shown in Scheme 1.4. In DMSO, diphenyldichloromethane undergoes an exothermic reaction with stoichiometric copper metal to produce TPE (Scheme 1.4).<sup>[56]</sup> A copper carbenoid intermediate is thought to be involved in this process. Barhadi *et al.* synthesized TPE using electrochemical coupling reactions of

diphenyldichloromethane with nickel catalyst at room temperature ionic liquids (Scheme 1.4)<sup>[56]</sup>.

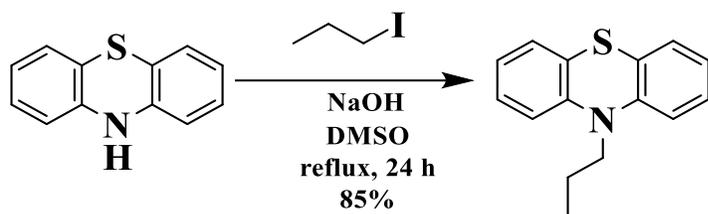
### 1.5. Phenothiazine

Phenothiazine is one of the most attractive cores amongst all heterocyclic organic compounds because of its remarkable photophysical and electrochemical characteristics. Phenothiazine (PTZ) is a tricyclic heteroarene with a nonplanar butterfly shaped structure and behaves as a strong electron donor due to the presence of electron-rich sulphur and nitrogen heteroatoms in the thiazine ring.<sup>[57]</sup> Phenothiazine has multiple active positions (5 (S), 10 (N), 3 and 7-positions) which improve the photophysical and electrochemical properties by extending the  $\pi$ -conjugations (Figure 1.7).<sup>[58]</sup> Phenothiazine unit shows electrophilic substitution at 3 and 7-positions, nucleophilic substitution at *N*-position and oxidation at the S-position.<sup>[58]</sup> The phenothiazine derivatives have been mostly used as electron donor in various optoelectronic applications due to its low reversible oxidation potentials produced by sulfur atom. In recent years, phenothiazine based  $\pi$ -conjugated derivatives have been used in several applications like photovoltaic devices like dye-sensitized solar cells (DSSCs) and bulk heterojunction solar cells, organic light emitting diodes (OLEDs), as phosphorescent materials and thermally activated delayed fluorescence (TADF) materials, aggregation-induced enhanced emission (AIEE) luminogens, sensors and mechanochromic materials.<sup>[59]</sup>



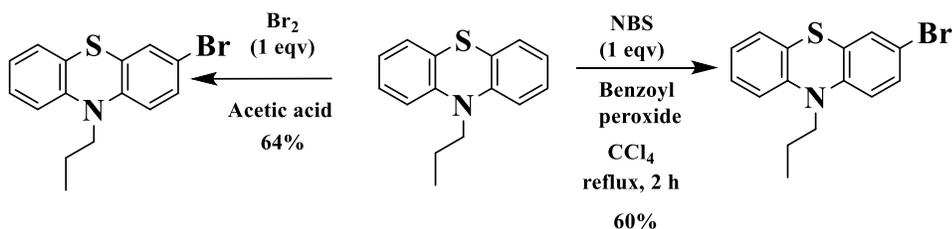
**Figure 1.7.** Structure of phenothiazine.

The N-position of the 10*H*-phenothiazine unit is readily alkylated through nucleophilic substitution. In the presence of dry DMSO, the reaction of 10*H*-phenothiazine with 1-iodopropane, and sodium hydroxide produced 10-propyl-10*H*-phenothiazine (Scheme 1.5).<sup>[60]</sup> At the 3,7-positions, phenothiazine is extremely sensitive to electrophilic substitution reactions. The most widely utilised compounds are 3,7-brominated phenothiazine derivatives.



**Scheme 1.5.** Synthesis of 10-propyl-10*H*-phenothiazine.

The reaction of 10-propyl-10*H*-phenothiazine with bromine (1 equivalent) in acetic acid or with *N*-bromosuccinimide (NBS) (1 equivalent for monobromination) in presence of catalytic amount of benzoyl peroxide in  $\text{CCl}_4$  results in mono brominated phenothiazine.<sup>[61]</sup>



**Scheme 1.6.** Synthesis of 3-bromo-10-propyl-10*H*-phenothiazine.

## 1.6. Stimuli-responsive materials

Stimuli-responsive materials termed as *smart* materials manifesting evident changes as a response to different external stimuli (mechanical force or pressure, temperature, polarity, ions, pH *etc.*) are of great importance for different optoelectronic applications.<sup>[62]</sup> Luminescent materials are suitable for designing stimuli-responsive materials as the detection of stimuli by visualizing optical changes is preferred because of its higher response speed

and sensitivity, good resolution, easy tuneability and visible in-situ changes.<sup>[63]</sup> Stimuli-responsive changes in emission can be observed in both solution state and solid state; however the application of most stimuli like pressure, vapor or electricity is possible for solid-state materials. Additionally, the luminescence in solution is prone to quenching processes and is suitable for only observing stimuli-responsive changes associated to non-radiative processes (turn on-turn off emission changes).<sup>[64]</sup> On the contrary, the solid-state emission can be easily regulated and is best suited for observing response for all kinds of external stimuli and different optoelectronic and material applications. Hence, it is essential for stimuli-responsive materials to possess efficient emission in its solid state which can be easily achieved by utilization of AIE active luminogens. Organic  $\pi$ -conjugated donor-acceptor systems fused with AIE luminogens can exhibit exceptional solid-state emission and can serve as effective functionalities for stimuli-responsive materials.<sup>[65]</sup> The luminescence of organic systems hugely depends on the choice of donor/acceptors and AIEgens, level of conjugation, molecular conformation and intermolecular interactions.<sup>[66]</sup> The response on application of different external stimuli is achieved by variations in the molecular conformation which can be attained by AIEgens which own a certain degree of flexibility owing to their non-planar frameworks.<sup>[67]</sup> Furthermore, the external stimuli also exert influence on the intermolecular interactions present between the molecules in the solid state and hence regulation of the intermolecular interactions results in tunable emission in solid state.<sup>[66]</sup> The broad class of stimuli-responsive materials can be further classified based on the external stimuli applied.

### **1.6.1. Mechanochromic materials**

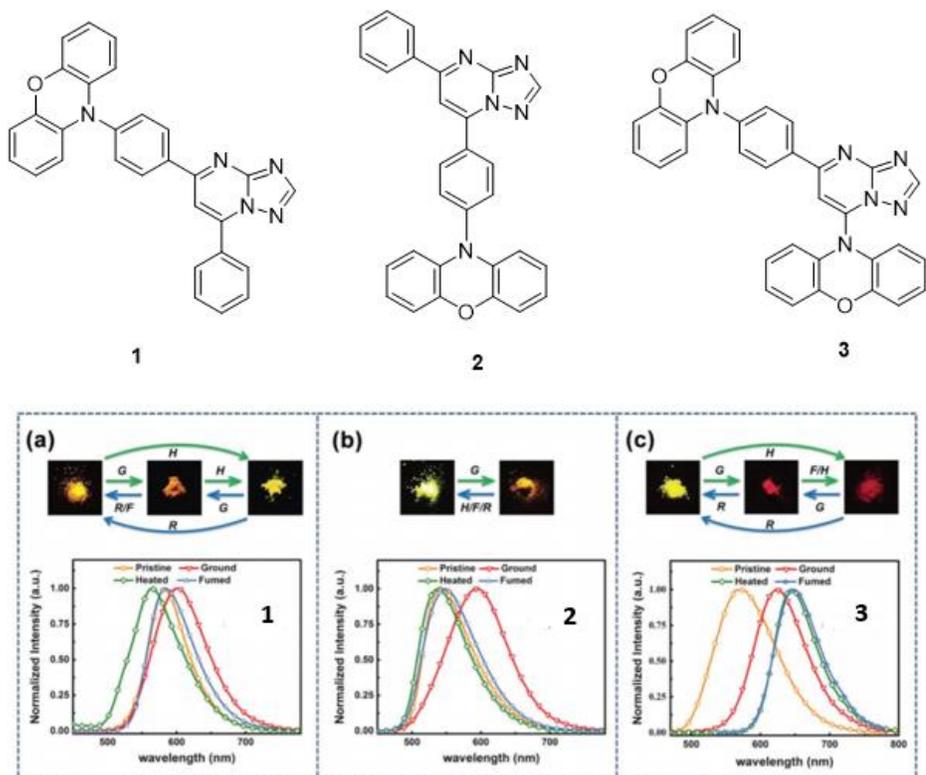
The category of stimuli-responsive materials that change their emission wavelength or intensity on applying mechanical force like grinding, scratching, rubbing *etc.* are known as mechanochromic materials.<sup>[68]</sup> Mechanochromic materials have acquired immense importance amongst all the stimuli-responsive materials because of its use as pressure sensors,

rewritable inks, data storage devices and in optoelectronics.<sup>[69]</sup> The mechanical stimuli induced response is achieved either by alterations in chemical structure or in physical structure. Chemical changes induced by mechanical stimuli involve bond breaking or formation and very few reports relate to this are present in literature due to the drawbacks such as low reversibility, incomplete reaction and higher pressure required for chemical transformation. Mechanochromic materials displaying emission switching brought about by physical structural changes are reversible in nature, hence being more common.<sup>[70]</sup> The mechanochromic emission switching is therefore greatly affected by fine physical structural changes associated with changes in the molecular packing of the system, disruption of intermolecular interactions, fluctuations in conformation or dihedral angle, phase transitions (one crystalline state to another, crystalline to amorphous and vice versa), ring opening/closing and configurational changes (E/Z).<sup>[71]</sup> The initial state of mechanochromic materials available before grinding can be restored either by solvent fumigation, thermal annealing or by self-recovery. Mechanochromic behavior essentially requires emission in the solid state which can be easily attained by incorporation of AIE luminogens such as TPE or PTZ. Organic  $\pi$ -conjugated molecules are appropriate for mechanochromism as their solid-state emission can be tuned by regulating the intermolecular interactions using different donor-acceptor, different alkyl/aryl/halogen/heteroatom substituents or by positional changes.<sup>[72]</sup>

The first ever emission color switching was reported in 2000 by Weder *et al.* for oligo(p-phenylene) vinylene (OPV) dyes blended with linear low-density polyethylene (LLDPE).<sup>[73]</sup> Different emission colors were observed for the polymer-dyes blends by regulating the composition of blends, aggregation processes and temperature and the tensile deformation resulted in solid-state emission color changes. Park *et al.* in 2010 presented the first AIE based mechanochromic material which was a cyano substituted distyrylbenzene derivative and displayed mechanochromic behavior corresponding to the modification in the

molecular sheet type crystal arrangement.<sup>[74]</sup> Following these two initial discoveries, a variety of mechanochromic materials have been developed over past few years.

Yang *et al.* in 2018 designed stimuli-responsive D-A derivatives **1-3** based on [1,2,4]triazolo[1,5-a]pyrimidine (TzPm) as acceptor and phenoxazine as donor attached at 5-position, 7-position and 5,7-positions of TzPm respectively.<sup>[75]</sup> The molecules **1-3** have high PLQY 0.45-0.70 in films and can act as thermally activated delayed fluorescence (TADF) emitters owing to the favorable singlet-triplet splitting energy  $\Delta E_{ST}$  0.06-0.10 eV which allows easy reverse intersystem crossing (RISC).



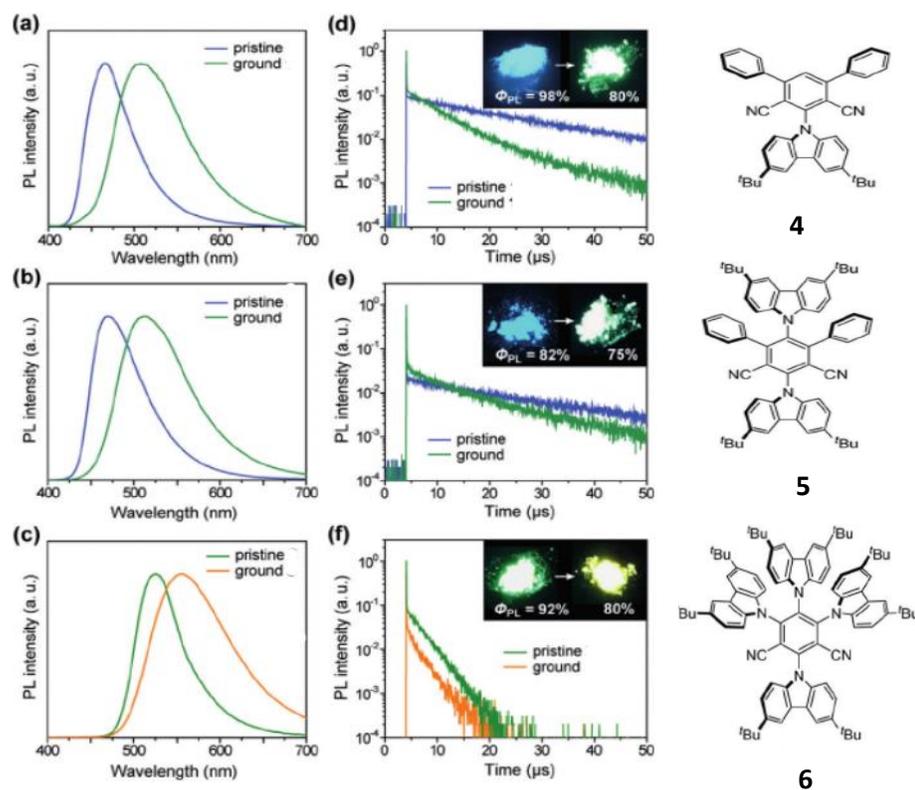
**Figure 1.8.** Chemical structure of triazole-pyrimidine-phenoxazine based mechanochromic materials **1-3** and solid-state emission spectra of pristine, ground, fumed and heated forms of **1-3**.

Molecules **1,2** and **3** in its pristine form emit at 583 nm, 541 nm and 570 nm respectively. The grinding of **1,2** and **3** red-shift the emission to 599

nm, 593 nm and 623 nm respectively. The grinded solids of **1** and **2** can return to their pristine form on fuming with dichloromethane, however the fumigation of grinded form of **3** results in additional red-shift upto 648 nm. Thermal annealing of the ground samples of **1**, **2** and **3** results in blue-shifted emission at 563 nm for **1**, retaining the pristine emission for **2** whereas red-shifted emission at 645 nm for **3**. Thus, the molecule **2** exhibited two-color mechanochromic switching while **1** and **3** display tri-color mechanochromism. The mechanochromism for **1-3** was related to phase change between different micro-crystalline to amorphous. All the three molecules were fabricated as OLEDs and reached a maximum external quantum efficiency of 14.3 % with yellow emission. Figure 1.8 shows the molecular structures of D-A derivatives **1-3** and their mechanochromic behavior.

Yasuda *et al.* have recently reported mechanochromic TADF emission change in three carbazole isophthalonitrile D-A molecules **4-6**.<sup>[76]</sup> The photoluminescence (PL) spectra for pristine powders of **4** and **5** shows peaks at 470 nm ( $\Phi_{\text{PL}}=98\%$ ) and 466 nm ( $\Phi_{\text{PL}}=98\%$ ) which on mechanical grinding with mortar and pestle is red shifted to 515 nm ( $\Phi_{\text{PL}}=80\%$ ) and 512 nm ( $\Phi_{\text{PL}}=75\%$ ) respectively. The pristine form of compound **6** emits at 525 nm ( $\Phi_{\text{PL}}=92\%$ ) whereas the grinded form emits at 557 nm ( $\Phi_{\text{PL}}=80\%$ ) with a striking color change from green to yellow. A color change from blue to green is observed in **4** and **5** with the photoluminescence quantum yield ( $\Phi_{\text{PL}}$ ) being very high in pristine and grinded forms which suggest effective reduction of ACQ processes owing to the non-planar propeller type structures. The pristine form for **4-6** were regained on exposing the grinded forms to vapors of tetrahydrofuran or chloroform confirming the reversible mechanochromic behavior. The time-resolved PL decay of the pristine and grinded forms for **4-6** reveal two-component decay (nanoseconds prompt fluorescence and microseconds delayed fluorescence) which is a character of TADF process suggesting the mechanochromic behavior is linked to TADF color changes. The unusual TADF based color

changing behavior is associated to change in dihedral angles between donor and acceptor in intramolecular charge transfer (ICT) excited states. The change from pristine form to grinded form display crystalline to amorphous morphological transformation. The amorphous state possesses almost perpendicularly oriented donor-acceptor moieties in excited states which are absent in the crystalline state due to densely packed structures which are disordered on griding. The TADF mechanochromic behavior of compounds **4-6** was exploited to develop bicolor non-doped OLEDs with simultaneous blue and green emission originating from a single emitter.



**Figure 1.9.** Chemical structure of D-A TADF-mechanochromic emitters **4-6**. PL spectra of pristine and ground form of (a) **4**, (b) **5** and (c) **6** and PL decay measurements of pristine and ground forms of (d) **4**, (e) **5** and (f) **6**.

Figure 1.9. depicts chemical structure of D-A TADF-mechanochromic emitters **4-6**, their PL spectra and their PL decay measurements in pristine and ground forms.

*The main objectives of the current work are:*

- To design and synthesize luminescent donor-acceptor systems using various architectures such as D-A-D, D-A, D- $\pi$ -A, D-A-D' or D-A-A' for developing AIE active stimuli-responsive materials.
- To design and synthesize donor-acceptor functionalized organic luminogens with effective emission in the solution state and in the solid state.
- To investigate the AIE, photophysical and stimuli-responsive properties such as solvatochromism, mechanochromism, acidochromism of the D-A luminogens using different spectroscopic techniques.
- To alter the intermolecular interactions and molecular packing in solid state by employing different donor AIEgens or different heterocyclic acceptors, positional isomerism, symmetrical and unsymmetrical substitution of donor/acceptor.
- To study the impact of the above-mentioned structural changes on the photophysical, electronic and stimuli-responsive properties.
- To explore the structural features of the donor-acceptor functionalized luminogens essential for inducing AIE nature and stimuli-responsive nature via single-crystal X-ray diffraction analysis, powder-X-ray-diffraction analysis and density functional theory (DFT) calculations.

## **1.7 Organization of thesis**

**Chapter 1** provides background about donor-acceptor functionalized stimuli-responsive materials, the underlying mechanisms responsible for the stimuli-responsive nature, their importance in different optoelectronic applications and the design strategies used to obtain AIE active stimuli-responsive materials.

**Chapter 2** summarizes the general experimental methods, characterization techniques and details of the instruments used for the characterization.

**Chapter 3** discusses the design and synthesis of T-shaped donor-acceptor-donor type symmetrical quinoxaline derivatives functionalized with tetraphenylethylene (TPE) and phenothiazine (PTZ) as donors. The effect of use of two different donors on the photophysical, AIE, solvatochromic and mechanochromic properties of the quinoxaline derivatives have been studied in detail. This work provides strategy to design stimuli-responsive molecules with distinct properties influenced by donor-acceptor interactions.

**Chapter 4** summarizes about the design and synthesis of unsymmetrical quinoxaline derivatives utilizing phenothiazine, tetraphenylethylene and N-substituted phenothiazine as different terminal donor units. The donor-acceptor character of the quinoxaline derivatives can be subtly regulated by unsymmetrical substitution and the influence of these structural changes on the photophysical, solvatochromic, AIE and mechanochromic properties have been investigated. The presented strategy can help in understanding the influence of different donor-acceptor structures on the AIE and stimuli-responsive characteristics and in further development of donor-acceptor stimuli-responsive materials.

**Chapter 5** discusses about the development of AIE active mechanochromic phenanthroimidazole (PI) derivatives which are positional isomers incorporating a triphenylamine and tetraphenylethylene unit. The influence of positional change on AIE and mechanochromism of PI derivatives were studied. The combination of phenanthroimidazole, TPA and TPE synergistically result in the high solid-state emission which can be further employed in optoelectronic applications.

**Chapter 6** contributes on the design and synthesis of donor-acceptor (D-A) isomers obtained by attaching the phenothiazine (**PTZ**) moiety at *ortho*, *meta* and *para* positions of the phenyl benzothiazole (**BT**) unit. This chapter provides in-depth comparison of the photophysical, electronic, structural, AIE and stimuli-responsive properties such as solvatochromism,

mechanochromism and acidochromism properties of the *o/m/p* positional isomers with an aim to study the outcome of the positional change.

**Chapter 7** discusses about the design and synthesis of multichromophoric D-A-A' positional isomers involving benzothiazole, benzothiadiazole and tetraphenylethylene formed by incorporating the BT-D-TPE moiety at *ortho*, *meta* and *para* positions of the phenyl BT unit. A comparative study of the photophysical, AIE and MFC properties of the isomers has been carried out to investigate the effect of positional change. The opted strategy allows modulation of fluorescence properties making them potential stimuli responsive materials with applications in mechano-sensors, security inks and optoelectronic-devices.

**Chapter 8** summarizes the salient features of the work and provides insight to develop new D-A stimuli responsive materials which can be employed for a wide range of optoelectronic applications.

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## Chapter 2

### Materials and experimental techniques

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#### 2.1. Introduction

This chapter describes the materials, general synthetic procedures, characterization techniques and the instrumentation employed in this thesis.

#### 2.2. Chemicals for synthesis

The common solvents used for syntheses were purified according to established procedures.<sup>[1]</sup> The solvents and reagents were used as received unless otherwise indicated. Photophysical and electrochemical studies were performed with spectroscopic grade solvents.

2,1,3-Benzothiadiazole, 9,10-phenanthroquinone, acenaphthaquinone, n-BuLi, 4-bromobenzophenone, diphenylmethane, Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(dppf)Cl<sub>2</sub>, Pd(OAc)<sub>2</sub>, Ph(*t*-Bu)<sub>3</sub>, sodium tert-butoxide, 4-iodoaniline, 4-(diphenylamino)benzaldehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 2-bromobenzaldehyde, 2-aminothiophenol, tributyltin chloride, potassium carbonate, potassium acetate, sodium carbanote, Bis(pinacolato) diboron, phenothiazine, iodopropane, bromine, glacial acetic acid, hydrobromic acid, p-Toluenesulfonic acid, sodium borohydride, Rhodamine-6G, 9,10-diphenylanthracene, quinine sulphate, tetrabutylammonium hexafluorophosphate (TBAF<sub>6</sub>) and were procured from Aldrich chemicals USA.

Silica gel (100–200 mesh and 230–400 mesh) were purchased from Rankem chemicals, India. TLC pre-coated silica gel plates (Kieselgel 60F254, Merck) were purchased from Merck, India and Spectrochem, India.

Dry solvents dichloromethane, 1,2-dichloroethane, chloroform, tetrahydrofuran (THF), 1,2-dichlorobenzene, 1,4-dioxane, ethanol, N,N-dimethylformamide and methanol were obtained from Spectrochem India and S. D. Fine chem. Ltd. All the oxygen or moisture sensitive reactions

were performed under nitrogen/argon atmosphere using standard schlenk method.

## **2.3. Spectroscopic measurements**

### **2.3.1. Mass spectrometry**

High resolution mass spectra (HRMS) were recorded on Bruker-Daltonics, micrOTOF-Q II mass spectrometer using positive and negative mode electrospray ionizations.

### **2.3.2. NMR spectroscopy**

$^1\text{H}$  NMR (400 MHz),  $^1\text{H}$  NMR (500 MHz), and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using  $\text{CDCl}_3$  and acetone- $d_6$  as solvent. Chemical shifts in  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra were reported in parts per million (ppm). In  $^1\text{H}$  NMR chemical shifts are reported relative to the residual solvent peak ( $\text{CDCl}_3$ , 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants  $J$ , are given in Hz.  $^{13}\text{C}$  NMR chemical shifts are reported relative to the solvent residual peak ( $\text{CDCl}_3$ , 77.16 ppm).

### **2.3.3. UV-Vis spectroscopy**

UV-Vis absorption spectra were recorded using a Varian Cary100 Bio UV-Vis and Perkin Elmer LAMBDA 35 UV/Vis spectrophotometer.

### **2.3.4. Fluorescence spectroscopy**

Fluorescence emission spectra were recorded upon specific excitation wavelength on a Horiba Scientific Fluoromax-4 spectrophotometer. The measurements were performed at 25 °C and path length of 1 cm quartz cuvette. The 2.0 mL volume of luminogen solutions were used for study. The solid state fluorescence measurements were performed on glass slide and front face sample holder accessory were used in fluorimeter. The quantum yields in the solid state were measured using a K-sphere integrating sphere. The excitation and emission slits were 2/2 nm for the emission measurements and 3/3 for solid quantum yield measurements.

### ***The fluorescence quantum yields ( $\phi_F$ )***

The fluorescence quantum yields ( $\phi_F$ ) of compounds were calculated by the steady-state comparative method using following equation,

$$\phi_F = \phi_{st} \times S_u/S_{st} \times A_{st} / A_u \times \eta_u^2/\eta_{st}^2 \dots\dots\dots (Eq. 1)$$

Where  $\phi_F$  is the emission quantum yield of the sample,  $\phi_{st}$  is the emission quantum yield of the standard,  $A_{st}$  and  $A_u$  represent the absorbance of the standard and sample at the excitation wavelength, respectively, while  $S_{st}$  and  $S_u$  are the integrated emission band areas of the standard and sample, respectively, and  $\eta_{st}$  and  $\eta_u$  the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

### **2.4. Electrochemical studies**

Cyclic voltamograms (CVs) were recorded on CHI620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was 100 mVs<sup>-1</sup>. A solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M) was employed as the supporting electrolyte.

### **2.5. Single crystal X-ray diffraction studies**

Single crystal X-ray diffraction studies were performed on SUPER NOVA diffractometer, BRUKER KAPPA APEX II CCD Duo with graphite monochromatic Mo Ka radiation (0.71073 Å), on Xcalibur, Eos, Gemini diffractometer and on Bruker D8 VENTURE diffractometer equipped with a CMOS Photon 100 detector and MoKa (λ = 0.71073 Å) radiation was used. The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F<sup>2</sup>.1. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with

isotropic temperature factors, generally  $1.2U_{eq}$  of their parent atoms. The CCDC numbers contain the respective supplementary crystallographic data. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic 42 Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## **2.6. Powder XRD (PXRD)**

Powder X-ray Diffraction (PXRD) analyses were performed on the Rigaku SmartLab, Automated Multipurpose x-ray Diffractometer.

## **2.7. Computational calculations**

The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G\*\* level for C, N, S, H, and Lan12DZ level for Fe in the Gaussian 09 program.<sup>[2]</sup>

## **2.8. Scanning electron microscopy (SEM)**

The SEM images were collected on Carl Zeiss supra 55 and Field emission JSM-7001F (JEOL) operated at 15 kV after sputtering with gold. The samples for SEM were prepared by drop casting AIE solution of luminogens.

## **2.9. Thermogravimetric analysis (TGA)**

Thermogravimetric analyses were performed on the Metler Toledo thermal analysis system. The measurements were done at heating rate of 10 °C/minute and heated upto 800 °C.

## **2.10. Dynamic light scattering (DLS)**

The dynamic light scattering (DLS) studies were done on a Micromeritics Nanoplus 3 instrument. The samples for DLS study was used as it is AIE solution of luminogens.

## **2.11. Mechanochromism study**

The mechanochromic properties were studied mainly by grinding, fuming and annealing. The grinded samples were prepared by taking the pristine/synthesized sample into a mortar and grinding it for approximately 10 minutes by using a pestle. Annealing was done by heating the grinded

samples in oven in open atmosphere at respective temperatures. In order to perform fumigation, the grinded samples were taken on a glass plate. The glass plate was further placed in a solvent chamber saturated with the vapors of the particular solvent

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## Chapter 3

# T-shaped donor-acceptor-donor type symmetrical quinoxaline derivatives: aggregation-induced emission and mechanochromism

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### 3.1. Introduction

In recent years, materials with high solid-state emission have gained significant attention due to their application in mechanofluorochromism and optoelectronic devices.<sup>[1]</sup> The mechanofluorochromic materials have a wide range of potential applications in mechanosensors, photo modulation, security inks, memory chips, luminescent switches, data storage and fluorescent probes.<sup>[2]</sup> This class of smart materials undergo reversible solid-state emission in response to external stimuli. High solid-state emission is one of the most important requirements for mechanofluorochromic materials and can be achieved by structural modifications and design strategies altering the molecular arrangement.<sup>[3]</sup> The factors governing solid state emission of organic materials are effective planarity, conjugation length, incorporation of different substituents (alkyl, aryl, halogen) and their interactions with the surrounding environment.<sup>[3,4]</sup> However, the use of traditional fluorophores is limited in mechanofluorochromic material as they are non-emissive in solid state due to aggregation caused quenching (ACQ).<sup>[5]</sup> Tang *et al* have designed a family of molecules which are emissive in solid state and have termed as aggregation-induced emission (AIE) which is contradictory to ACQ.<sup>[6]</sup> The use of AIE active fluorophores has been proved to be an effective approach to increase the solid state emission and hence the mechanochromic property. The propeller shaped structure of tetraphenylethylene (TPE) fulfils the requirement of restricted intramolecular rotations (RIR) thereby making it a well-known AIE active molecule which has been employed in various applications such as organic light emitting diodes (OLEDs), bioimaging, mechanochromic materials,

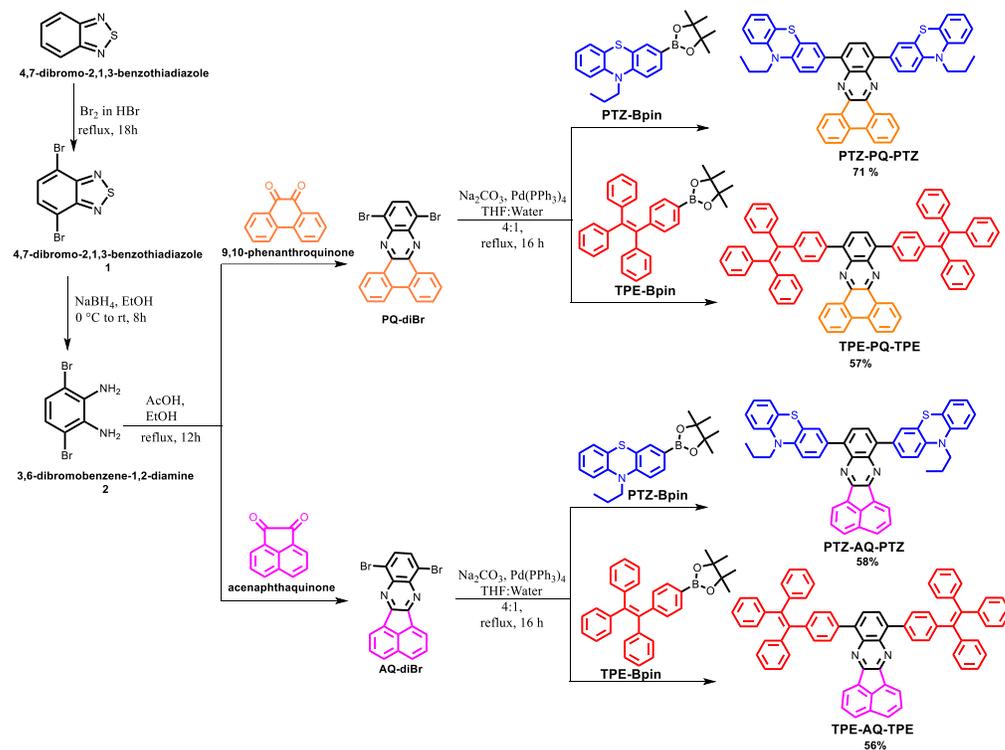
sensors and many more.<sup>[7]</sup> In recent years, heterocyclic donor phenothiazine (PTZ) has emerged as an effective AIEgen and has been utilized to develop a range of stimuli-responsive materials, TADF materials, room-temperature phosphorescent (RTP) materials and optoelectronic devices such as OLEDs, organic solar cells (OSCs) and perovskite solar cells (PSCs).<sup>[8]</sup>

The molecules having a donor (D) and acceptor (A) type (D-A-D) architecture are promising candidates for stimuli responsive materials and other optoelectronic properties.<sup>[9]</sup> The D-A-D structured luminogens enable us to attain tunable electronic states due to their intramolecular charge transfer (ICT) characteristic, which endows them with unique optoelectronic properties.<sup>[10]</sup> The use of typical AIEgens as donors in combination fusion with different acceptor units can produce efficient stimuli-responsive solid-state emissive materials. The TPE being a weak donor on combination with an electron acceptor generates a donor-acceptor type architecture which can be further utilized to develop good mechanochromic material as well as highly efficient solid-state emitters with exceptional stability. On the other hand, PTZ has a stronger electron-donating ability as compared to TPE and can result in distinct solid-state emission properties on fusion with an electron acceptor. Quinoxaline has outstanding electron accepting ability because of a strong electronegativity of two N atoms and stable quinoid structure leading to remarkable photophysical properties such as unique absorption and emission and high charge-carrier mobility.<sup>[11]</sup> Quinoxaline and its derivatives have been explored in opto-electronic devices like light-emitting diodes (LEDs), organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), organic field-effect transistors (OFETs), nonlinear optics, and fluorescent chemosensors owing to the facile synthesis and versatility.<sup>[12]</sup> The electron acceptor nature, highly fused structure and extended conjugation length of quinoxaline motivated us to choose phenanthrene-quinoxaline and acenaphthene-quinoxaline as an acceptor. Keeping all this in view, we have synthesized T-shaped symmetrical donor-acceptor-donor type

phenanthrene-quinoxaline **PQ** (A) and acenaphthene-quinoxaline **AQ** (A') based symmetrical derivatives **TPE-PQ-TPE**, **TPE-AQ-TPE** and **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ** functionalized with tetraphenylethylene (TPE) as donor (D) and phenothiazine (PTZ) as donor D' respectively and investigated their photophysical, AIE and stimuli-responsive properties. All the symmetrical quinoxaline derivatives show reversible mechanochromic behaviour and are good solid-state emitters.

### 3.2. Results and discussion

#### Synthesis



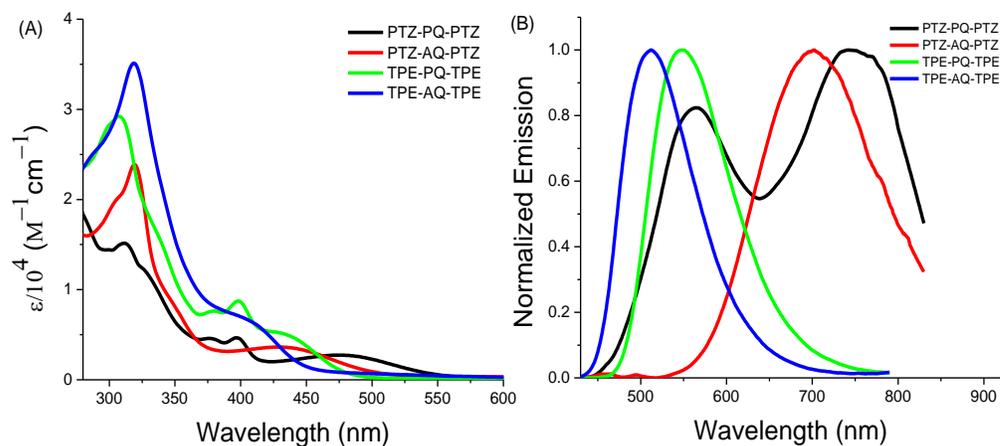
**Scheme 3.1.** Synthesis of symmetrical PTZ and TPE substituted PQ and AQ derivatives.

A straight-forward three step approach was proposed for the synthesis of the T-shaped symmetrical luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** and (Scheme 3.1.). The reduction of 4,7-dibromo-2,1,3-benzothiadiazole **1** was carried out by a reported

procedure using NaBH<sub>4</sub> in ethanol which resulted in 3,6-dibromobenzene-1,2-diamine **2**.<sup>[13]</sup> The intermediate **2** was further condensed with 9,10-phenanthroquinone and acenaphthaquinone yielding 10,13-dibromodibenzo[a,c]phenazine (**PQ-diBr**) and 8,11-dibromoacenaphtho[1,2-b]quinoxaline (**AQdi-Br**) respectively.<sup>[14]</sup> The symmetrical derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** consists of phenothiazine (PTZ) moiety as donor (D) whereas **TPE-PQ-TPE** and **TPE-AQ-TPE** utilize tetraphenylethylene (TPE) as donor (D'). The Suzuki cross-coupling reaction of **PQdi-Br** and **AQdi-Br** with PTZ-Bpin using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst afforded symmetrical di-substituted PTZ quinoxaline derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** in 71% and 58% yields respectively. The symmetrical derivatives **TPE-PQ-TPE** and **TPE-AQ-TPE** were obtained by a Suzuki cross-coupling reaction of **PQ-diBr** and **AQdi-Br** with TPE-Bpin using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst in argon atmosphere respectively. The **TPE-PQ-TPE** and **TPE-AQ-TPE** were obtained in 57% and 56% yields respectively. The PTZ and TPE substituted quinoxaline derivatives were purified using column chromatography. The symmetrical quinoxaline derivatives were well characterized by NMR and high-resolution mass spectrometry (HRMS) techniques.

### 3.3. Photophysical properties

The photophysical properties of the symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** were studied using UV-visible and fluorescence spectroscopy. The electronic absorption and fluorescence spectra were recorded in tetrahydrofuran solution (Figure 3.1.) and the data are compiled in Table 3.1. The symmetrical quinoxaline derivatives **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** displays absorption bands in the region of 300–400 nm corresponding to  $\pi \rightarrow \pi^*$  transitions of the PTZ, TPE and the quinoxaline units.<sup>[15]</sup>



**Figure 3.1.** (A) Electronic absorption spectra and (B) normalized fluorescence spectra of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** recorded in THF (concentration =  $2 \times 10^{-5}$  M).

The symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** also display an absorption band in the higher wavelength region at 485 nm, 440 nm, 440 nm and 414 nm respectively which could be originating from the intramolecular charge transfer (ICT) transition occurring from the donor (PTZ or TPE) to the acceptor quinoxaline units (**PQ** or **AQ**).<sup>[15]</sup> The phenanthrene-quinoxaline derivatives **PTZ-PQ-PTZ** and **TPE-PQ-TPE** have multiple strong absorption bands (300–400 nm) associated to the  $\pi-\pi^*$  transitions which could be due to the highly conjugated phenanthrene ring. Further, the ICT absorption bands for PTZ substituted quinoxaline derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** derivatives are red shifted as compared to the TPE-substituted quinoxaline derivatives **TPE-PQ-TPE** and **TPE-AQ-TPE** owing to the higher electron-donating ability of PTZ as compared to TPE which could result in a stronger ICT. The emission spectra of symmetrical derivative **PTZ-PQ-PTZ** shows an emission maximum at 750 nm which could be ascribed to the ICT emission, accompanied with an emission peak at 567 nm which could be due to a localized excited (LE) emission. The molecule **PTZ-AQ-PTZ** exhibits emission maximum at 700 nm which could be corresponding to the ICT emission. The emission spectra of the

luminophores **TPE-PQ-TPE** and **TPE-AQ-TPE** show emission maxima at 548 nm and 511 nm respectively.

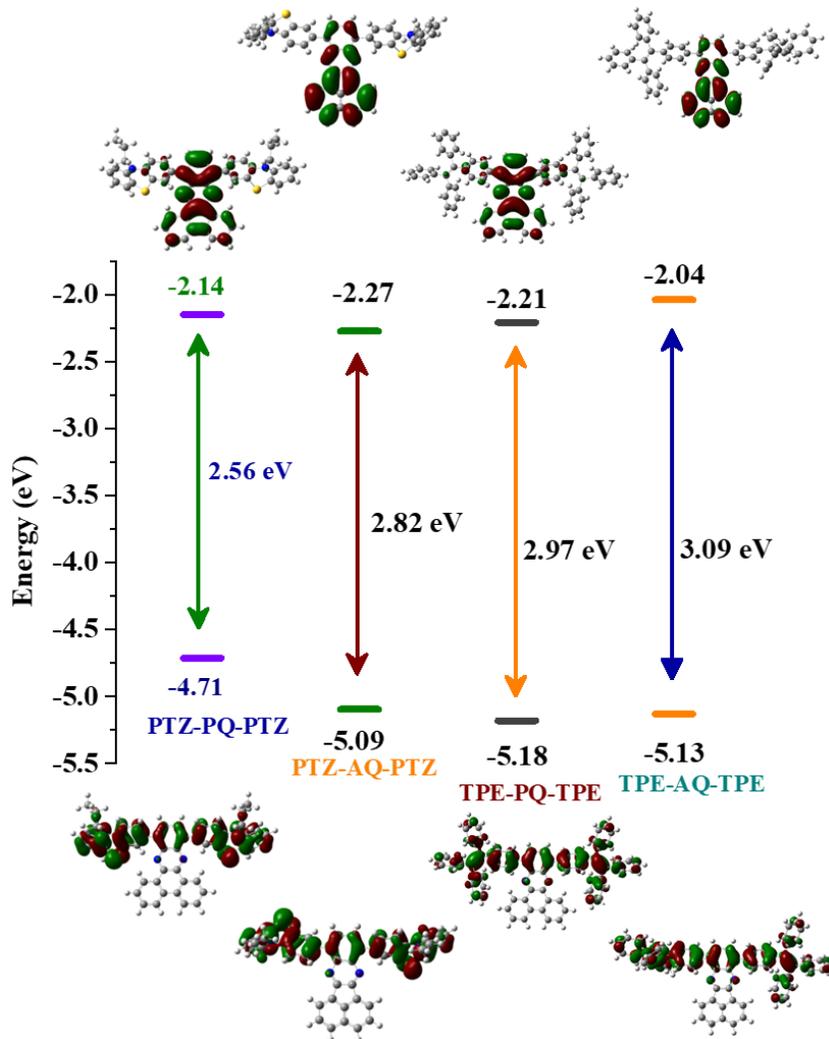
**Table 3.1.** Photophysical and thermal properties of **1** and **2**.

Compounds	$\lambda_{ab}[\text{nm}]$ ( $\epsilon[\text{Lmol}^{-1}\text{cm}^{-1}]$ ) <sup>a</sup>	$\lambda_{em.}$ (nm) <sup>b</sup>
<b>PTZ-PQ-PTZ</b>	312 (15138), 376 (4584), 397 (4660), 485 (2660)	567, 750
<b>PTZ-AQ-PTZ</b>	319 (23869), 440 (3516)	702
<b>TPE-PQ-TPE</b>	307 (29223), 378 (7598), 397 (8700), 440 (4690)	548
<b>TPE-AQ-TPE</b>	318 (35118), 414 (5896)	511

<sup>a,b</sup> Measured in tetrahydrofuran

### 3.4. Theoretical calculations

In order to gain an insight of the electronic structures of the symmetrical quinoxaline luminophores (**PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE**), the density functional theory (DFT) calculation was performed at the B3LYP/6-31G(d,p) level.<sup>[16]</sup> The calculated frontier molecular orbitals of the symmetrical quinoxaline derivatives are shown in Figure 3.2. and the values are tabulated in Table 3.2. The D-A-D symmetrical quinoxaline derivatives **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** possess non-planar architecture due to the incorporation of PTZ and TPE units at end capping positions which have a butterfly shape and a propeller structure respectively.



**Figure 3.2.** Correlation diagram showing the HOMO, and LUMO wave functions and energies of symmetrical quinoxaline derivatives as determined at the B3LYP/6-31G(d,p) level.

In the case of **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ**, the electron density of HOMO is mainly spread over both the PTZ unit and the benzene ring of the quinoxaline unit due to the C-substitution of the PTZ unit on the quinoxaline unit. The HOMOs for luminophores **TPE-PQ-TPE** and **TPE-AQ-TPE** are localized on the TPE unit extended to the central benzene of the quinoxaline unit. Further, the LUMOs for **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** are completely localized on central quinoxaline unit **PQ** and **AQ** suggesting the electron-accepting ability of the quinoxaline

unit in the D-A-D system. It is apparent from the DFT studies that the HOMO and LUMO for both the luminophores are well separated on the two  $\pi$  conjugated arms. This leads to stronger ICT transitions between the electron donor and acceptor. The estimated HOMO-LUMO gaps for **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** are 2.56 eV, 2.82 eV, 2.97 eV and 3.09 eV respectively.

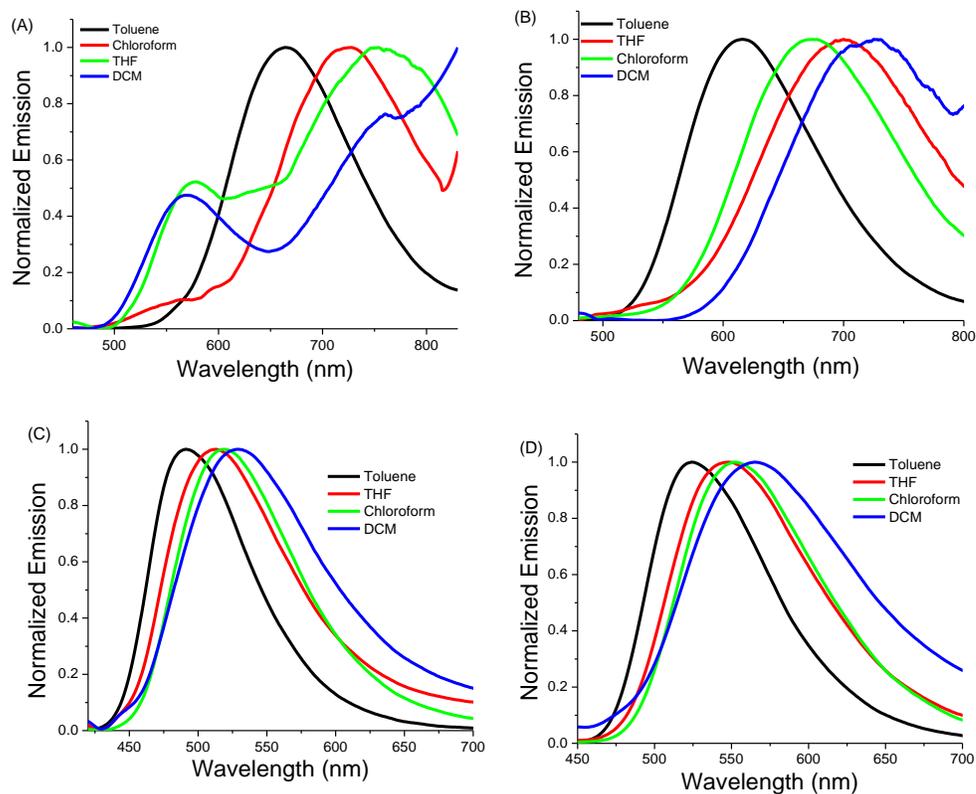
**Table 3.2.** Theoretical calculations of symmetrical quinoxaline derivatives

Compounds	HOMO <sup>a</sup> eV	LUMO <sup>a</sup> eV	HOMO-LUMO gap eV
<b>PTZ-PQ-PTZ</b>	-4.71	-2.14	2.56
<b>PTZ-AQ-PTZ</b>	-5.09	-2.27	2.82
<b>TPE-PQ-TPE</b>	-5.18	-2.21	2.97
<b>TPE-AQ-TPE</b>	-5.13	-2.04	3.09

<sup>a</sup> Calculated from CV: Reference electrode- Ag/AgCl.

### 3.5. Solvatochromism

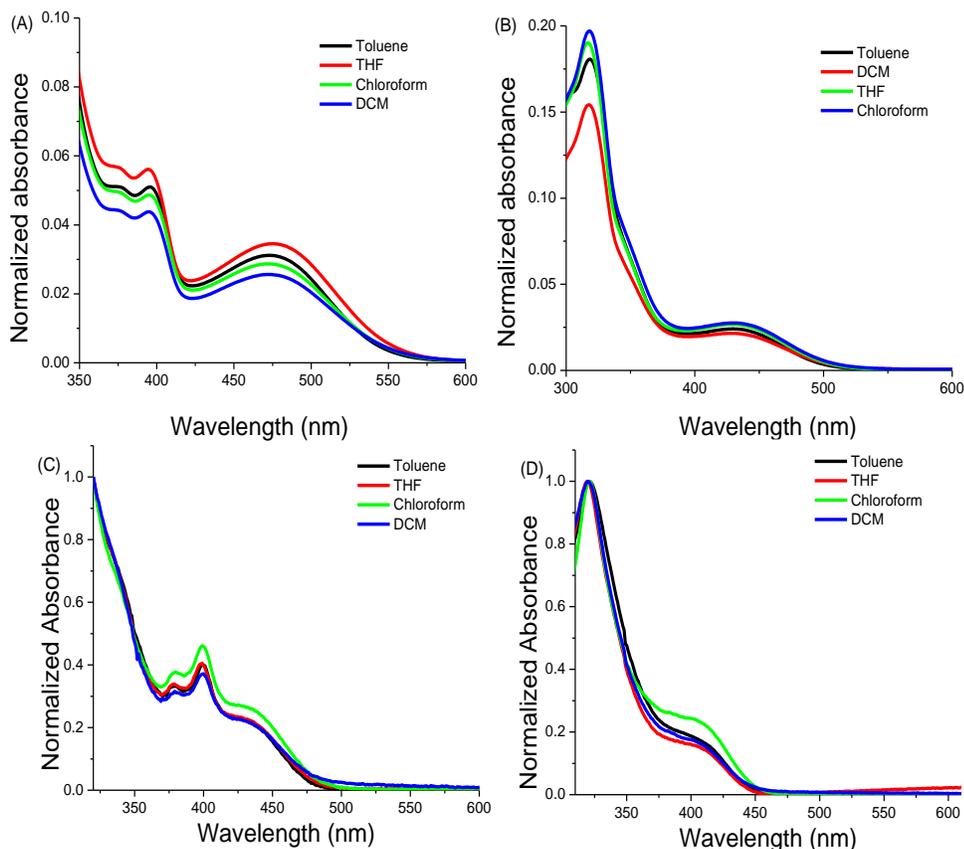
The symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** display an intramolecular charge transfer peak (ICT) owing to their D-A-D structure. The ICT transitions are highly sensitive to solvent polarity; hence the solvatochromic studies were performed on the target quinoxaline luminophores.<sup>[17]</sup> The solvatochromic effect was investigated by recording the emission (Figure 3.3) and the absorption spectra (Figure 3.4.) of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** in solvents of varying polarities (toluene, tetrahydrofuran, chloroform and dichloromethane).



**Figure 3.3.** (A) Fluorescence spectra of (A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** in different solvents of varying polarities. ( $\lambda_{exc} = 370$  nm-**TPE-PQ-TPE**, **TPE-AQ-TPE**,  $\lambda_{exc} = 420$  nm-**PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**).

The absorption spectra (Figure 3.4.) of quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** are less sensitive to change in solvent polarity as compared to the emission spectra. The weak solvatochromism in the absorption spectra suggest that the ground state electronic structures are independent of change in solvent polarity. On the other hand, a notable solvatochromism in the emission spectra (Figure 3.3.) is attributed to the more polarized excited states. The symmetrical luminophore **PTZ-PQ-PTZ** in toluene exhibits emission maxima due to charge transfer (CT) state at 564 nm which bathochromically shifts to 728 nm in chloroform and up to 753 nm in THF. A shoulder peak arises in the region of 550-580 nm for THF and

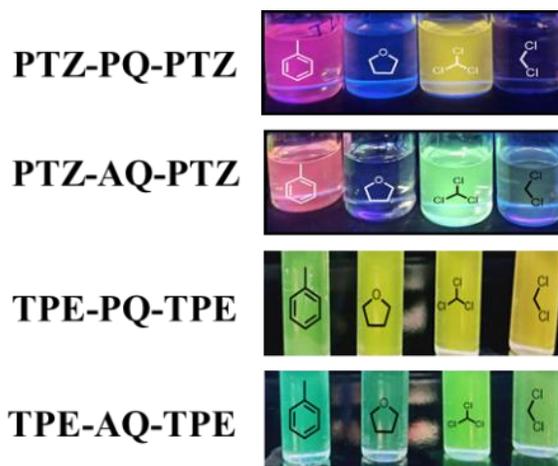
chloroform which could be due to the LE emissions. In DCM, the luminophore **PTZ-PQ-PTZ** shows a strong LE emission at 570 nm although the CT emission becomes distorted due to decrease in intensity and appears as a shoulder around 760 nm.



**Figure 3.4.** Electronic absorption spectra of ((A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** in solvents of different polarity.

The **AQ** based symmetrical derivative **PTZ-AQ-PTZ** has an emission maximum at 616 nm in toluene which shifts bathochromically in chloroform, THF and DCM to 675 nm, 700 nm and 725 nm respectively. A bathochromic shift of almost 180 nm and 109 nm occurs for **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** respectively on moving from toluene to DCM. The emission spectra of **TPE-PQ-TPE** and **TPE-AQ-TPE** also shows a bathochromic shift on increasing the solvent polarity. The symmetrical **PQ**

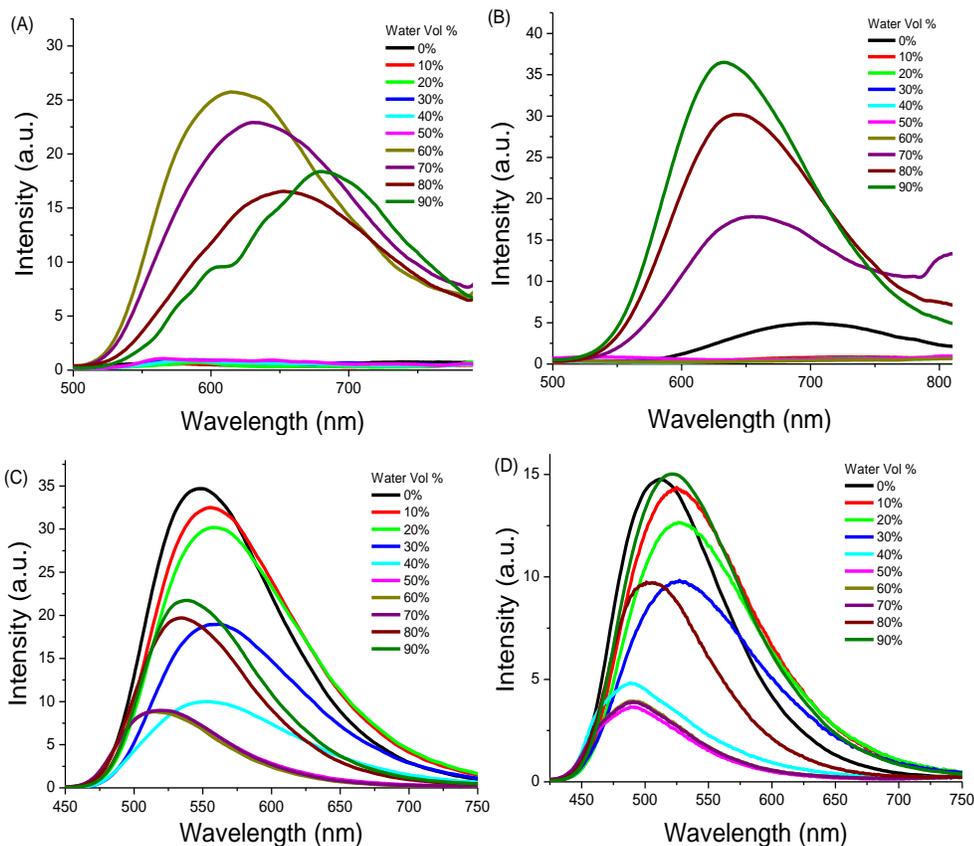
based luminophore **TPE-PQ-TPE** in toluene emitted green fluorescence at 524 nm and yellow fluorescence in dichloromethane at 565 nm with a red shift of 41 nm. Similarly, the luminophore **TPE-AQ-TPE** emitted sky-blue fluorescence in toluene at 490 nm and a green fluorescence in dichloromethane at 529 nm which was red shifted by 39 nm.



**Figure 3.5.** Photographs of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** in solvents of different polarity taken under 365nm UV illumination. (From left to right- toluene, THF, chloroform, DCM).

The PTZ substituted symmetrical quinoxaline derivatives **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** show higher bathochromic shifts on varying the polarity as compared to the TPE substituted derivatives **TPE-PQ-TPE** and **TPE-AQ-TPE**. Hence the PTZ substituted symmetrical quinoxaline derivatives exhibit an increased charge transfer character due inclusion of strong electron donating PTZ unit as compared to the weak donor TPE. The charge transfer transition leads to larger charge separation and a higher dipole moment in the excited state. The reorientation of solvent molecules stabilizes the enhanced dipole moment of excited state by accommodating the higher dipole moment thereby decreasing the energy of the system consequently leading to a bathochromic shift. The photographs for solvatochromism of the symmetrical quinoxaline derivatives under UV illumination are shown in Figure 3.5.

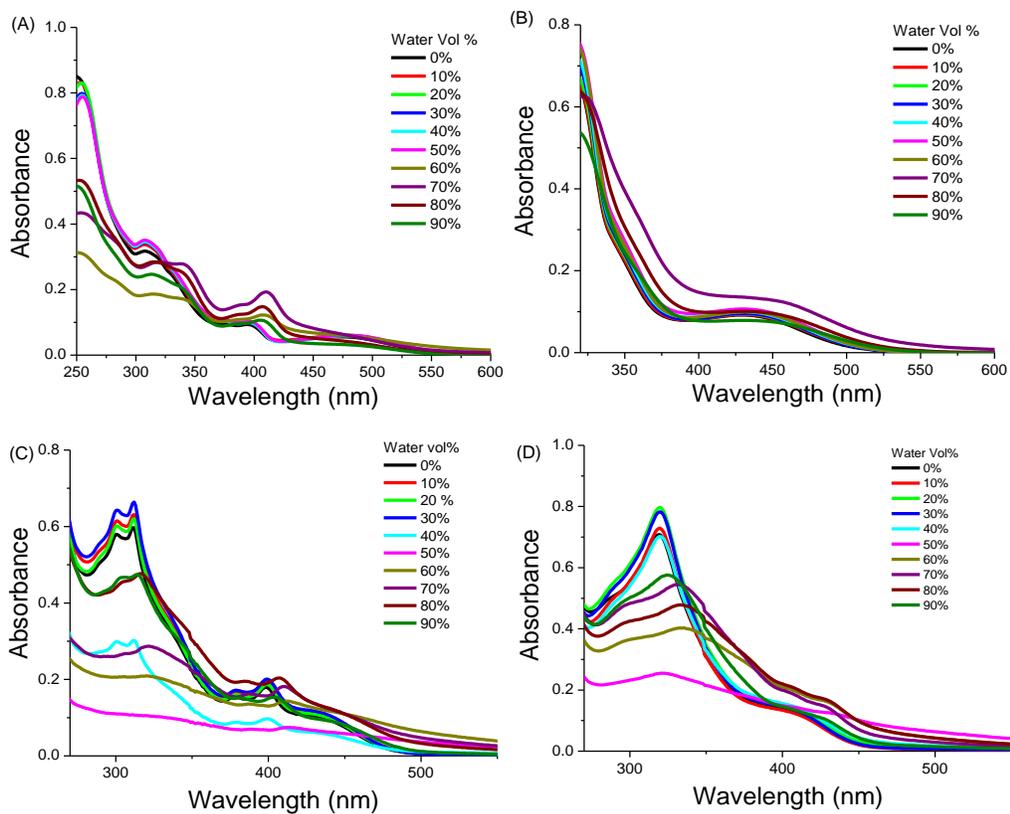
### 3.6. Aggregation-induced emission (AIE) studies



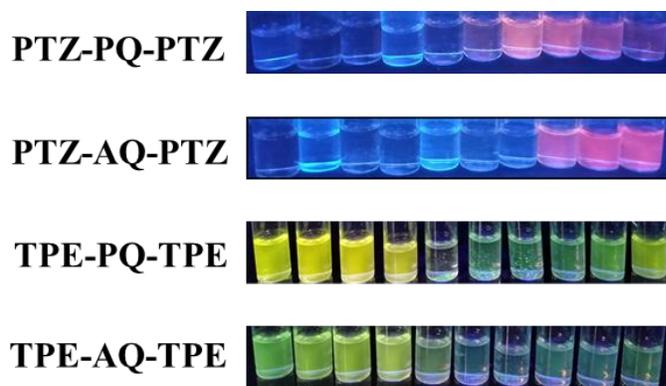
**Figure 3.6.** Emission spectra of (A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** in THF-water mixtures with increasing water fractions. (conc.  $2 \times 10^{-5}$  M).

The symmetrical luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** contain PTZ and TPE unit which are AIE active and hence the AIE properties for the symmetrical luminophores were investigated using fluorescence spectroscopy (Figure 3.6.). All the symmetrical quinoxaline luminophores are highly soluble in THF but poorly soluble in water. Using this idea, we prepared nanoaggregates by increasing percentage of water in THF solution. The AIE property was examined by preparing aggregates with gradual increase of water percentage in  $10\mu\text{M}$  THF solution. The PTZ substituted symmetrical quinoxaline molecules **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** in pure THF

exhibit less intense emissions around 700-750 nm due to the polarized ICT state which are not much altered up to  $f_w$  40-50%. A high intensity emission peak for **PTZ-PQ-PTZ** is observed at 615 nm for  $f_w$  60% which is due to the formation of aggregates in the solution. The molecule **PTZ-PQ-PTZ** at higher water percentage (70-90%) shows slight reduction in emission intensity (630 nm-680 nm) due to presence of large sized aggregates. Similarly, **PTZ-AQ-PTZ** exhibits increased emission at 654 nm for  $f_w$  60% due to aggregation and the emission is enhanced twice in intensity up to  $f_w$  90% and blue shifts to 630 nm. The TPE based symmetrical luminophores **TPE-PQ-TPE** and **TPE-AQ-TPE** are highly fluorescent in solution due to the intramolecular charge transfer from the weak donor (TPE) to the acceptor moiety as compared to the PTZ based symmetrical quinoxaline luminophores which have low intensity emissions in pure THF due to higher stabilization of their ICT emission. The luminophores are highly fluorescent at high water percentage owing to formation of aggregates. The **PQ** based luminophore **TPE-PQ-TPE** emits bright yellow fluorescence at 547 nm whereas the **AQ** based luminophore **TPE-AQ-TPE** emits yellowish green fluorescence in pure THF solution at 510nm. The addition of water up to 50% ( $f_w$ ) causes decrease in fluorescence intensity for **TPE-PQ-TPE** and **TPE-AQ-TPE**. This can be attributed to ICT bands and stabilization of charge transfer on increasing solvent polarity, also known as solvatochromism.



**Figure 3.7.** Electronic absorption spectra of (A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** in different THF-water mixtures with increasing water percentage. (conc.  $2 \times 10^{-5}$  M).



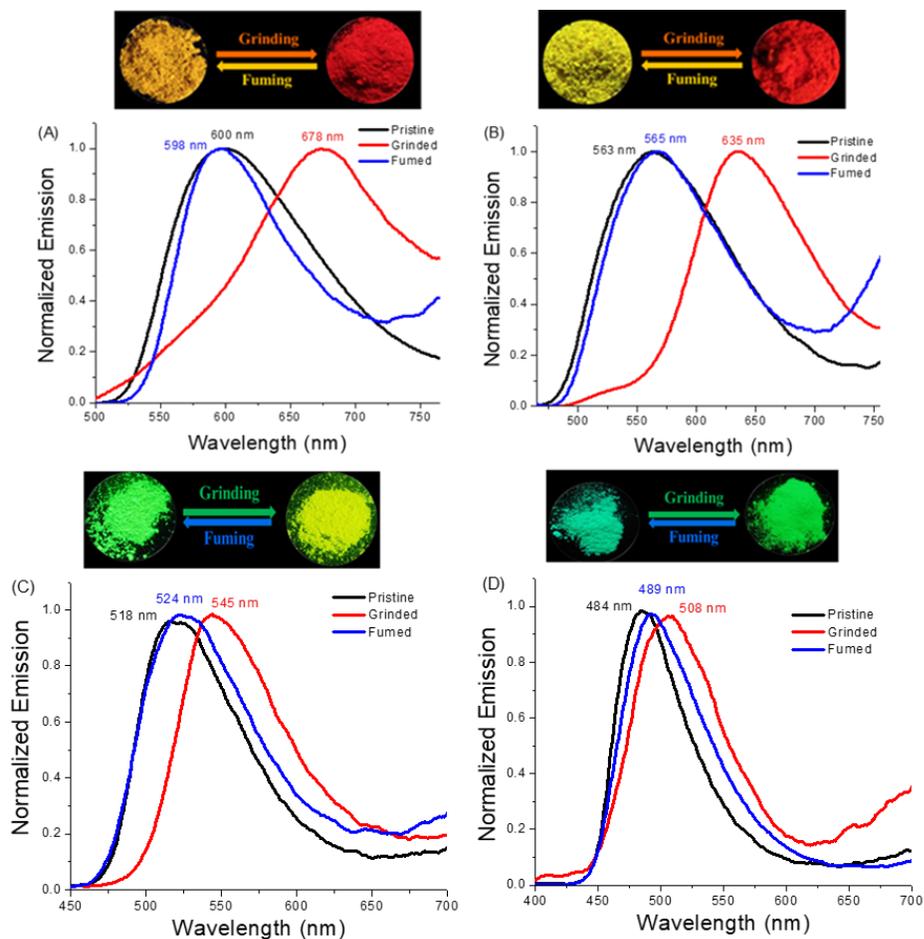
**Figure 3.8.** Photographs of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** in different THF-water mixtures taken under 365nm UV illumination. (From left to right 0% -90% water volume fraction)

The solvatochromic effect is dominant upto 50% ( $f_w$ ) water percentage for **TPE-PQ-TPE** and **TPE-AQ-TPE**. The formation of aggregates for **TPE-PQ-TPE** and **TPE-AQ-TPE** was initiated after 50% ( $f_w$ ) which was confirmed by consequent increase in fluorescence intensity upto 90% ( $f_w$ ). It was thus concluded that the AIE effect dominates solvatochromism after 50% ( $f_w$ ) for **TPE-PQ-TPE** and **TPE-AQ-TPE**. The AIE behaviour of the symmetrical quinoxaline luminophores was further explored using absorption spectra (Figure 3.7.). The formation of nanoaggregates in the suspension leads to scattering of light for **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** above  $f_w$  60% and above  $f_w$  50% for **TPE-PQ-TPE** and **TPE-AQ-TPE** which further confirms aggregate formation. The photographs of the THF-water mixtures of the symmetrical quinoxaline derivatives (Figure 3.8.) under UV illumination further confirm the AIE behaviour.

### 3.7. Mechanochromism

The mechanochromic behaviour of the symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** was studied using solid state emission spectra (Figure 3.9.) and the corresponding data are compiled in Table 3.3. The pristine solid of **PTZ-PQ-PTZ** displays light orange emission at 600 nm which on mechanical grinding is bathochromically shifted to bright red emission at 678 nm. The grinded powder of **PTZ-PQ-PTZ** on fuming with a mixture of DCM-hexane vapors returns to the pristine form with emission at 598 nm. The pristine solid of **PTZ-AQ-PTZ** has a yellow emission at 563 nm which on mechanical grinding exhibits red-shifted dark orange emission at 635 nm and reverts to its original form on fuming with an emission at 565 nm. The luminophore **TPE-PQ-TPE** in its pristine form shows green emission at 518 nm which on mechanical grinding exhibits a yellow emission at 545 nm. On the other hand, the luminophore **TPE-AQ-TPE** exhibits bluish green emission at 484 nm in its pristine form and upon mechanical grinding in a mortar pestle a green emission at 508 nm was observed. The grinded

forms of **TPE-PQ-TPE** and **TPE-AQ-TPE** revert to its original form on fuming with dichloromethane (DCM) and exhibit emission at 524 nm and 489 nm respectively. The grinding induced spectral shift for **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** was 80 nm, 72 nm, 27 nm and 24 nm respectively.



**Figure 3.9.** Emission spectra of (A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** as pristine, ground, and fumed solids and photograph taken under 365 nm UV illuminations.

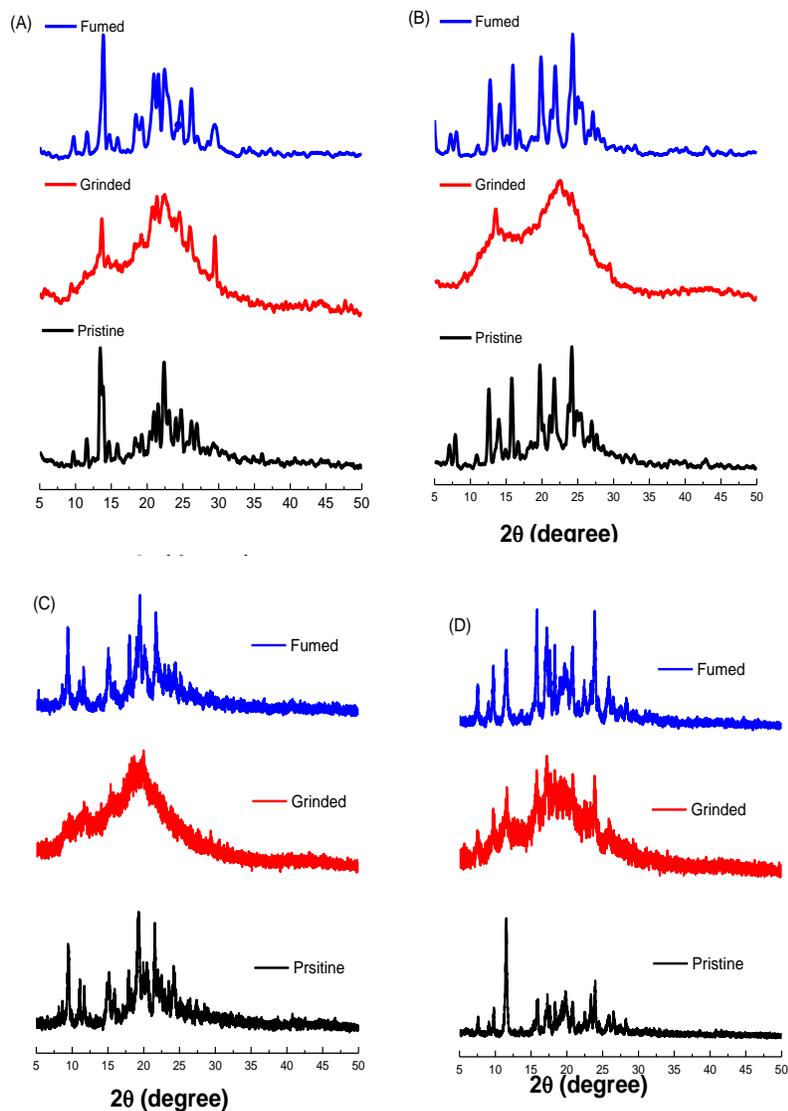
**Table 3.3.** Peak emission wavelengths ( $\lambda$ , in nm) of **1** and **2** under various external stimuli.

<b>Emission</b>				
<b>Compounds</b>	$\lambda_{\text{pristine}}$ (nm)	$\lambda_{\text{ground}}$ (nm)	$\lambda_{\text{fumed}}$ (nm)	$\Delta\lambda^a$ (nm)
<b>PTZ-PQ-PTZ</b>	600	678	598	80
<b>PTZ-AQ-PTZ</b>	563	635	565	72
<b>TPE-PQ-TPE</b>	518	545	524	27
<b>TPE-AQ-TPE</b>	484	508	489	24

<sup>a</sup> Grinding-induced spectral shift,  $\Delta\lambda = \lambda_{\text{ground}} - \lambda_{\text{original}}$ .

### 3.8. Powder X-ray diffraction studies

For a deeper understanding about mechanochromism, powder X-ray diffraction (PXRD) (Figure 3.10.) study was conducted for pristine, grinded and fumed samples of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE**. The symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** in their pristine form displayed multiple intense sharp peaks indicating its crystalline nature. The diffraction pattern upon grinding of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** shows broad and diffused peaks suggesting its amorphous nature. The crystalline state of the luminophores was destroyed upon grinding. The grinded samples of **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE** after fuming again exhibit sharp diffraction patterns indicating conversion to crystalline state and thus proving reversible mechanochromic behaviour.



**Figure 3.10.** PXRD curves of (A) **PTZ-PQ-PTZ**, (B) **PTZ-AQ-PTZ**, (C) **TPE-PQ-TPE** and (D) **TPE-AQ-TPE** in pristine, ground, and fumed forms.

### 3.9. Experimental section

#### General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere.  $^1\text{H}$  NMR (400 MHz) spectra were recorded on the Bruker Avance (III) 400 MHz instrument by using  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts

are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, *J*, are given in Hz. Thermogravimetric analyses were performed on the Metler Toledo Thermal Analysis system. UV visible absorption spectra were recorded on a Carry 100 Bio UV visible Spectrophotometer. Emission spectra were taken in a fluoromax4p fluorimeter from HoribaYovin (model: FM-100). The excitation and emission slits were 2/2 nm for the emission measurements. All of the measurements were done at 25°C. HRMS was recorded on Bruker Daltonics, micrOTOF Q II mass spectrometer. The density functional theory (DFT) calculation was carried out at the B3LYP/6 31G (d, p) level in the Gaussian 09 program.

#### **Synthesis and Characterization of PTZ-PQ-PTZ:**

A mixture of **PQ-diBr** (1.0 mmol) and 10-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**PTZ-Bpin**) (2.2 mmol), was dissolved in THF/water (4/1, v/v) and then sodium carbonate (6.6 mmol) was added. After degassing the reaction mixture for 10 minutes, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 mmol) was added and the reaction mixture was heated to reflux for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and then worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (40:60) as the eluent. An orange solid of PTZ-PQ-PTZ was obtained in 71 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ 9.19 (d, *J* = 8 Hz, 2H), 8.56 (d, *J* = 8 Hz, 2H), 7.93 (s, 2H), 7.85-7.69 (m, 9H), 7.20 (t, *J* = 8 Hz, 3H), 7.10 (d, *J* = 8 Hz, 2H), 6.96 (t, *J* = 8 Hz, 4H), 3.97 (t, *J* = 6 Hz, 4H), 2.03-1.95 (m, 4H), 1.11 (t, *J* = 8 Hz, 6H). HRMS (ESI): Calcd. for [M + H]<sup>+</sup>: 759.2611. Found: 759.2168.

### Synthesis and Characterization of PTZ-AQ-PTZ:

A mixture of **AQ-diBr** (1.0 mmol) and 10-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**PTZ-Bpin**) (2.2 mmol) was dissolved in THF/ water (4/1 v/v) and then Sodium carbonate (6.6 mmol) was added. After degassing the reaction mixture for 10 min, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 mmol) was added and the reaction mixture was heated to reflux for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (65:35) as the eluent. A yellow solid of PTZ-AQ-PTZ was obtained in 56% yield. ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25<sup>o</sup>C): δ 8.35 (d, *J* = 5 Hz, 2H), 8.08 (d, *J* = 10 Hz, 2H), 7.82-7.79 (m, 4H), 7.71-7.69 (m, 4H), 7.20-7.17 (m, 4H), 7.05 (d, *J* = 10 Hz, 2H), 6.96-6.92 (m, 4H), 3.94 (t, *J* = 5 Hz, 4H), 1.99-1.92 (m, 4H), 1.09 (t, *J* = 7.5 Hz, 6H). HRMS (ESI): Calcd. for [M]<sup>+</sup>: 732.2376. Found: 732.2399.

### Synthesis and characterization of TPE-PQ-TPE:

Pd(PPh<sub>3</sub>)<sub>4</sub> (0.026 mmol) was added to a well degassed mixture of dibromo compound (**PQ-diBr**) (0.2 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester (**TPE-Bpin**) (0.5 mmol) and sodium carbonate (1.61 mmol) in THF (40 mL) and water (10 mL). The mixture was stirred and refluxed overnight at 80 <sup>o</sup>C under nitrogen atmosphere. The completion of reaction was monitored with thin layer chromatography. The mixture was evaporated to dryness under reduced pressure and the resulting residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to obtain TPE-PQ-TPE. Yield: 57%, as a yellowish green solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 <sup>o</sup>C): δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.79–7.84 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.08-7.23 (m, 34H). HRMS (ESI): Calcd. for [M + H]<sup>+</sup>: 915.3770. Found: 915.3734.

### Synthesis and characterization of TPE-AQ-TPE:

Pd(PPh<sub>3</sub>)<sub>4</sub> (0.026 mmol) was added to a well degassed mixture of dibromo compound (**AQ-diBr**) (0.2 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester (**TPE-Bpin**) (0.5 mmol) and sodium carbonate (1.61 mmol) in THF (40 mL) and water (10 mL). The mixture was stirred and refluxed overnight at 80 °C under nitrogen atmosphere. The completion of reaction was monitored with thin layer chromatography. The mixture was evaporated to dryness under reduced pressure and the resulting residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to obtain TPE-AQ-TPE. Yield: 56%, as a yellowish green solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.94 (d, *J* = 8.0 Hz, 2H), 8.54 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 4H), 7.65-7.79 (m, 8H), 7.09-7.24 (m, 34H). HRMS (ESI): Calcd. for [M + H]<sup>+</sup>: 941.3837. Found: 941.3890.

### 3.10. Conclusion

In conclusion, we have synthesized novel T-shaped donor-acceptor-donor type phenanthrene-quinoxaline (**PQ**)-A and acenaphthene-quinoxaline (**AQ**)-A' functionalized symmetrical luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ** and **TPE-PQ-TPE**, **TPE-AQ-TPE** employing phenothiazine (PTZ)-D and tetraphenylethylene (TPE)-D' respectively by utilizing a Suzuki cross-coupling reaction. The D-A-D structured symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE**, **TPE-AQ-TPE** generates intramolecular charge transfer (ICT) transitions which is confirmed by solvatochromism. The PTZ based symmetrical luminophores **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** manifest higher donor-acceptor character as compared to the TPE substituted luminophores owing to the higher donor character of PTZ in comparison to TPE. All the symmetrical quinoxaline luminophores exhibit AIE characteristics due to the incorporation of AIEgens PTZ and TPE which makes them suitable solid-state emitters. The AIE properties for

luminophores **TPE-PQ-TPE** and **TPE-AQ-TPE** reveal that AIE dominates the emission at higher water percentage; whereas at low water percentage emission is dependent on solvent polarity. The symmetrical quinoxaline luminophores **PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE**, **TPE-AQ-TPE** display reversible emission changes in response to mechanical stimuli with a good color contrast. The PTZ substituted luminophores **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** shows a color change from yellow to red with higher grinding induced spectral shift upto 80 nm. The TPE substituted quinoxaline luminophores **TPE-PQ-TPE** and **TPE-AQ-TPE** shows a color change from green to yellow. The AIEgen PTZ exhibits better stimuli-responsive behavior as compared to AIEgen TPE owing to the better conformational flexibility of butterfly shaped PTZ unit. The mechanochromic behavior was further studied using powder XRD which suggests that a morphological change from crystalline to amorphous is responsible for mechanochromism. The DFT calculations reveal that HOMO and LUMO for both the luminophores are well separated on the two  $\pi$  conjugated arms which supports the strong ICT transitions. The PTZ and TPE based symmetrical quinoxaline derivatives behave as good solid-state emitters and the distinct donor acceptor interaction between the two moieties can be further exploited to employ these materials in various optoelectronic devices. The attachment of AIEgens PTZ and TPE to quinoxaline adds to the wide applications of quinoxaline and provides a novel approach to synthesis of mechanochromic materials.

### 3.11. References

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## Chapter 4

### Effect of different donors on mechanochromism of AIE active unsymmetrical D-A-D' type quinoxaline derivatives

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#### 4.1. Introduction

Solid-state emissive organic small molecules have acquired noteworthy importance of the scientific community due to their promising applications in optoelectronic devices, solid-state lasers, stimuli-responsive materials, bioimaging, sensors and many more.<sup>[1]</sup> In particular, stimuli-responsive solid-state organic emitters that display variation in their emission as a response to various external stimuli (mechanical pressure, pH, temperature, light) have gained considerable interest of researchers in recent times.<sup>[2]</sup> Mechanochromic materials which show reversible changes in emission on application of mechanical stimuli (rubbing, crushing, grinding, scratching) are termed as *smart* stimuli-responsive materials,<sup>[3]</sup> owing to their potential usage in optoelectronic devices, pressure sensors, anticounterfeiting applications, security inks and optical storage devices.<sup>[4]</sup> The changes in emission of organic molecules stimulated by mechanical pressure are attainable only in their solid state, hence adequate emission in solid state is vital for organic molecules to be employed as mechanochromic materials.<sup>[5]</sup> However, most of the typical organic chromophores are highly emissive in their solution although experience quenching of emission in their aggregated or solid state due to the phenomenon of aggregation caused quenching (ACQ).<sup>[6]</sup> This drawback of organic chromophores has been successfully controlled after the introduction of aggregation-induced emission (AIE) by Tang *et al.* in 2001 which alternatively takes advantage of aggregation to result in increased emission. The idea of AIE is to construct non-planar luminogens which show enhanced emission on aggregation or in the solid state by eliminating the  $\pi$ - $\pi$  stacking interactions as an outcome of restriction of intramolecular rotations (RIR).<sup>[7]</sup>

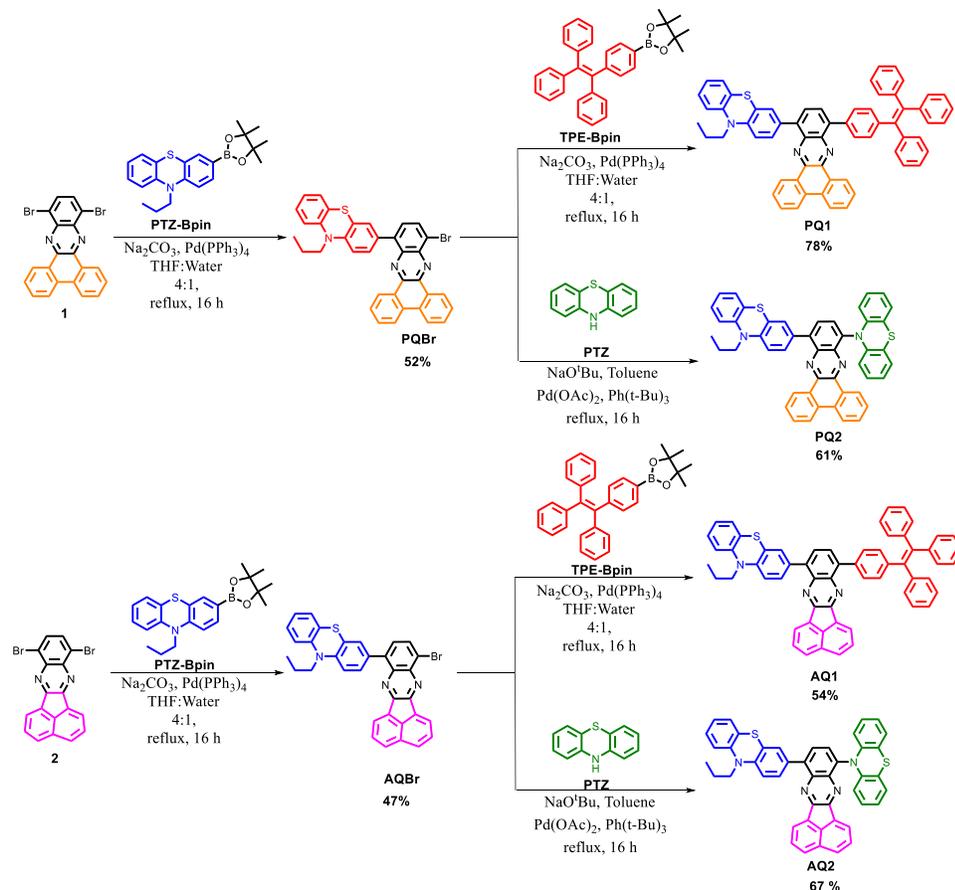
Tetraphenylethylene (TPE) is an ideal and most widely employed AIEgen owing to its distinct propeller type structure which endows the core with high solid-state emission.<sup>[8]</sup> Over the past few years, TPE and its derivatives have been widely used in developing efficient organic solid-state emitters which find numerous applications in mechanochromic materials, OLEDs, bioimaging, fluorescent probes and sensors.<sup>[9]</sup> Recently, phenothiazine (PTZ) has been exploited as a heterocyclic AIEgen by many researchers due to its butterfly shaped non-planar structure which empowers the moiety with improved solid-state emission. Furthermore, PTZ based emitters have been used in OLEDs, organic solar cells (OSCs), room-temperature phosphorescent (RTP) materials, thermally activated delayed fluorescence (TADF) materials, stimuli-responsive materials, perovskite solar cells and many more.<sup>[10]</sup>

Mechanochromic emission switching is usually achieved through modifications in the physical structure or through phase transitions, hence it heavily depends on the molecular packing modes and various intermolecular interactions occurring in the solid state.<sup>[11]</sup> Accordingly, the solid-state emission can be modulated by minor structural alterations such as inclusion of heteroatoms, incorporation of alkyl or aryl substituents, use of different halogen or heavy atoms, changes in the conjugation length and torsional angles, regio-isomerism *etc.*<sup>[12]</sup> Organic molecules comprising of various electron donor and electron acceptor units in different manners such as D-A, D-A-D, D-A-A', D- $\pi$ -A allow modulating the solid-state emission properties and hence are a good choice for developing highly emissive mechanochromic materials.<sup>[13]</sup> The utilization of heterocyclic acceptor units and AIE active donor units will not only alter the intermolecular interactions and molecular packing in the solid state but also help in generating favorable emission switching properties.<sup>[14]</sup> Quinoxaline has been widely explored in optoelectronic devices and various biological and material applications owing to its electron accepting nature induced by presence of two N atoms, outstanding chemical and thermal stability due to its largely

fused structure and favorable photophysical and electronic properties.<sup>[15]</sup> Inspired by this, we have utilized quinoxaline as acceptor in designing donor-acceptor-donor target molecules to attain tunable solid-state emission. We have developed phenanthrene-quinoxaline (PQ) and acenaphthene-quinoxaline (AQ) derivatives with unsymmetrical substitution of AIE active donors PTZ (D), TPE (D') and have exploited different attaching position of PTZ (N-position) and used N-PTZ as one of the donors (D''). In the Chapter 3, we have explored D-A-D phenanthrene-quinoxaline PQ (A) and acenaphthene-quinoxaline AQ (A') derivatives with symmetrically substituted TPE and PTZ (**PTZ-PQ-PTZ**, **PTZ-AQ-PTZ**, **TPE-PQ-TPE** and **TPE-AQ-TPE**) which exhibit admirable AIE and mechanochromic properties.<sup>[16]</sup> In this work, we have designed and synthesized D-A-D'/D-A'-D'' structured unsymmetrical phenanthrene-quinoxaline (PQ)-A and acenaphthene-quinoxaline (AQ)-A' derivatives where phenothiazine (PTZ) unit is utilized as donor (D) in combination with tetraphenylethylene (TPE) as donor (D') (**PQ1** and **AQ1**) and N-substituted phenothiazine (N-PTZ) moiety as donor (D'') (**PQ2** and **AQ2**) respectively. The unsymmetrical substitution of strong donor PTZ in combination with donors TPE and N-PTZ can perturb the donor-acceptor character and thereby exert effect on the photophysical, solvatochromic, AIE and mechanochromic properties have been investigated. The unsymmetrical derivatives show contrasting solvatochromic behaviors with highly emissive intramolecular charge transfer (ICT) state in **PQ1** and **AQ1** and quenched twisted intramolecular charge transfer (TICT) state in **PQ2** and **AQ2** respectively. The unsymmetrical derivatives **PQ1** and **AQ1** containing TPE and PTZ units exhibit AIE and mechanochromic characteristics whereas **PQ2** and **AQ2** are non-emissive in the solid state although mechanochromic in nature. The following work in-depth contributes to understanding the impact of different donor-acceptor structures on the AIE and mechanochromic characteristics.

## 4.2. Results and discussion

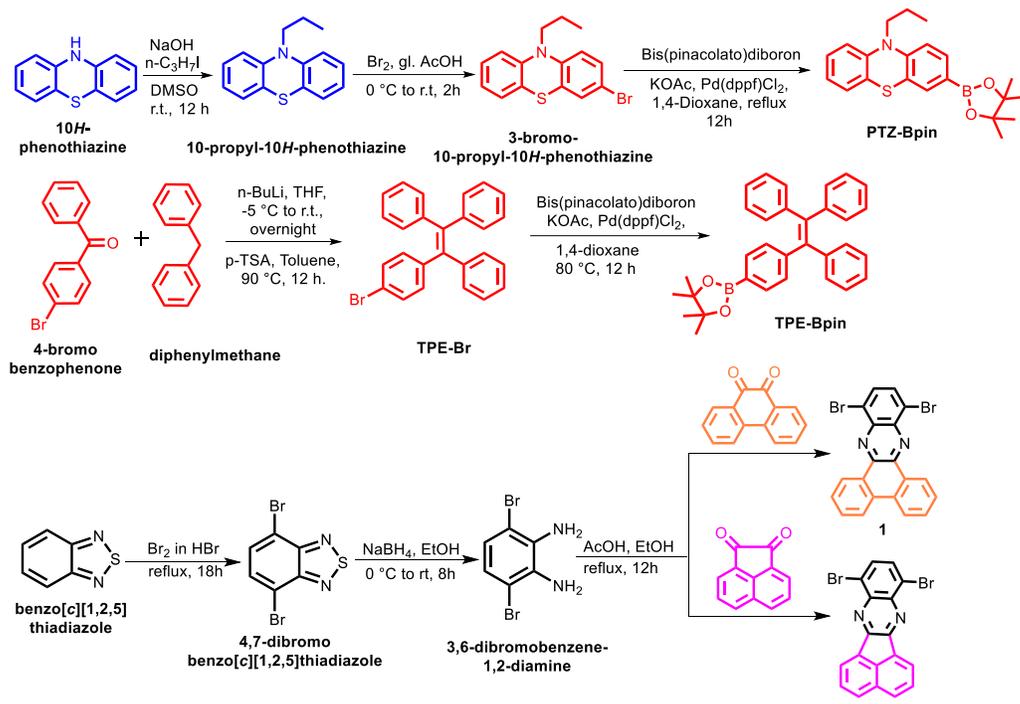
### Synthesis



**Scheme 4.1.** Synthesis of unsymmetrical phenanthrene-quinoxaline (**PQ**) and acenaphthene-quinoxaline (**AQ**) derivatives.

The unsymmetrical donor-acceptor-donor structured quinoxaline derivatives (**PQ1**, **PQ2**, **AQ1** and **AQ2**) using phenanthrene-quinoxaline (**PQ**) and acenaphthene-quinoxaline (**AQ**) as central acceptor units A and A' respectively were synthesized as shown in Scheme 4.1. Phenothiazine (PTZ) moiety was fixed as one of the terminal donors (D) unit in all the unsymmetrical quinoxaline derivatives owing to its favorable solid-state emission switching properties whereas the remaining bromo substitution of the quinoxaline unit was exploited with donors of different strengths and geometries. The unsymmetrical D-A-D'/D-A'-D' derivatives **PQ1** and **AQ1**

utilize tetraphenylethylene (TPE) as donor (D'), in addition to phenothiazine (PTZ) as donor (D). Similarly, the other set of unsymmetrical D-A-D'' and D-A'-D'' derivatives **PQ2** and **AQ2** use the N-substituted phenothiazine (N-PTZ) moiety as donor (D'') along with (PTZ) as donor (D).



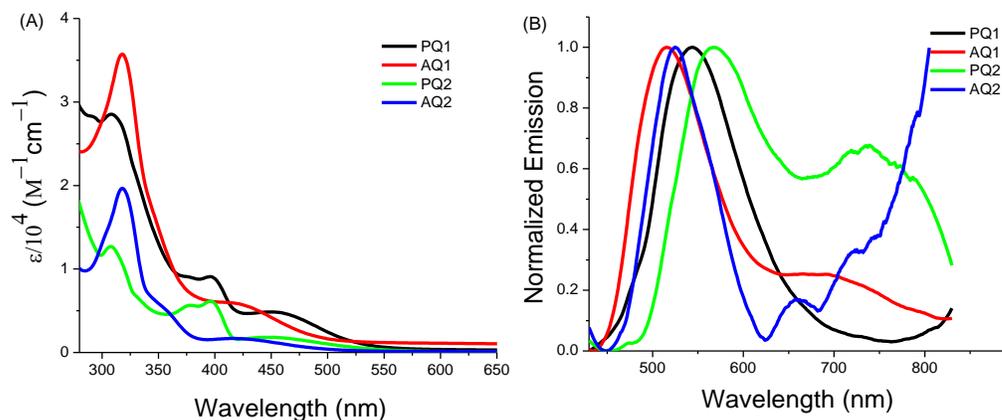
**Scheme 4.2.** Synthetic scheme for intermediates **PTZ-Bpin**, **TPE-Bpin**, **1** and **2**.

The intermediates **TPE-Bpin** and **PTZ-Bpin** were synthesized using reported procedure by Miyaura Borylation reaction<sup>[17]</sup> The dibromo phenanthrene-quinoxaline **1** and acenaphthene-quinoxaline **2** were obtained from the reported condensation reaction of 3,6-dibromobenzene-1,2-diamine with 9,10-phenanthroquinone and acenaphthoquinone respectively.<sup>[18]</sup> The detailed synthesis of the intermediates is compiled in Scheme 4.2. The Suzuki cross-coupling reaction of **1** and **2** with 0.8 equivalent and 0.5 equivalent of PTZ-Bpin in THF:water as solvent and Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst results in mono-substituted PTZ bromo intermediates **PQBr** and **AQBr** in 52% and 47% yields respectively. Further, the

unsymmetrical quinoxaline derivatives **PQ1** and **AQ1** were synthesized by the Suzuki cross-coupling reaction of **PQBr** and **AQBr** with **TPEBpin** using  $\text{Pd}(\text{PPh}_3)_4$  as catalyst in 78% and 54% yield respectively. The unsymmetrical quinoxaline derivatives **PQ1** and **AQ1** were obtained by the Suzuki cross coupling with **PTZ** on one side and **TPE** on the other side. The intermediates **PQBr** and **AQBr** were further subjected to the Pd-catalyzed Buchwald-Hartwig coupling reaction with **PTZ** to form unsymmetrical quinoxaline derivatives **PQ2** and **AQ2** in 61% and 67% yields respectively. The unsymmetrical substitution in **PQ2** and **AQ2** was achieved by the Pd-catalyzed C-C cross coupling of **PTZ** on one side and the Pd-catalyzed C-N coupling reaction of **PTZ** on other side of the central quinoxaline acceptor unit. All the quinoxaline derivatives are readily soluble in tetrahydrofuran (THF), dichloromethane (DCM), chloroform, toluene, ethyl-acetate and the structures of quinoxaline derivatives (**PQ1**, **PQ2**, **AQ1** and **AQ2**) were confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HMRS techniques.

### 4.3. Photophysical Properties

The photophysical properties of the quinoxaline derivatives were evaluated by recording the electronic absorption spectra and the emission spectra of the derivatives in ( $2 \times 10^{-5}$  M) THF solution as shown in Figure 4.1. and the related data are listed in Table 4.1. The phenanthrene-quinoxaline derivatives **PQ1** and **PQ2** display multiple strong absorption bands between 300–400 nm associated to the various  $\pi-\pi^*$  transitions originating either from the donor moieties or from the phenanthrene ring.



**Figure 4.1.** Electronic absorption spectra (A) and normalized emission spectra (B) of unsymmetrical quinoxaline derivatives **PQ1**, **PQ2**, **AQ1** and **AQ2** measured in THF ( $2 \times 10^{-5}$  M).

Alternatively, the acenaphthene-quinoxaline derivatives **AQ1** and **AQ2** possess only one absorption band in this region (300–400 nm) at 319 nm and 318 nm respectively owing to the  $\pi-\pi^*$  transitions. The presence of multiple  $\pi-\pi^*$  bands in **PQ** derivatives could be due to the highly conjugated phenanthrene ring. The quinoxaline derivatives **PQ1**, **PQ2**, **AQ1**, and **AQ2** also possess an absorption band in the higher wavelength region at 458 nm, 428 nm, 456 nm and 431 nm, respectively which may have originated from the intramolecular charge transfer (ICT) transition occurring from the donor to acceptor quinoxaline units which was further validated using solvatochromism studies. The absorption bands associated to the ICT transition for **PQ** derivatives were red shifted as compared the **AQ** derivatives. Furthermore, the phenanthrene-quinoxaline **PQ** and acenaphthene-quinoxaline **AQ** derivatives having symmetrical substitution of PTZ on both sides (**PTZ-PQ-PTZ** and **PTZ-AQ-PTZ**, Chapter 3, Figure 3.2.) exhibit bathochromically shifted ICT absorption band as compared to the unsymmetrical quinoxaline **PQ1**, **PQ2**, **AQ1** and **AQ2** derivatives which either possess only one PTZ donor or a weak donor TPE. The bathochromic shift in the ICT absorption band for the symmetrical quinoxaline **PQ** and **AQ** derivatives as compared to the unsymmetrical

derivatives could be ascribed to the higher electron-donating ability of PTZ and the presence of two PTZ donors which could result in a stronger D-A character. The emission spectra for **PQ1** shows emission maximum at 544nm which was similar to the emission of symmetrical TPE substituted **PQ** derivative (**TPE-PQ-TPE**) (Figure 3.2. Chapter 3). Similarly, the unsymmetrical derivative **AQ1** shows an emission maximum at 516 nm comparable to the emission of the symmetrical TPE substituted **AQ** derivative (**TPE-AQ-TPE**) accompanied with a shoulder emission at 694 nm. The molecule **PQ2** has an emission maximum at 567 nm along with a low intensity emission peak at 738 nm. The emission peak at 567 nm in **PQ2** could be due to the localized excited (LE) emission whereas the emission peak in the range of 700–800 nm could be ascribed to the ICT emission. The molecule **AQ2** shows an emission maximum at 525 nm which could be due to the LE emission along with a shoulder peak at 660 nm which could be due to the ICT emission. The quinoxaline **PQ** and **AQ** derivatives with symmetrical substitution of PTZ (**PTZ-PQ-PTZ** and **PTZ-AQ-PTZ**, Chapter 3, Figure 3.2.) have red-shifted emissions as compared to the unsymmetrical derivatives due to the presence of two PTZ donor units in conjugation with the quinoxaline moiety.

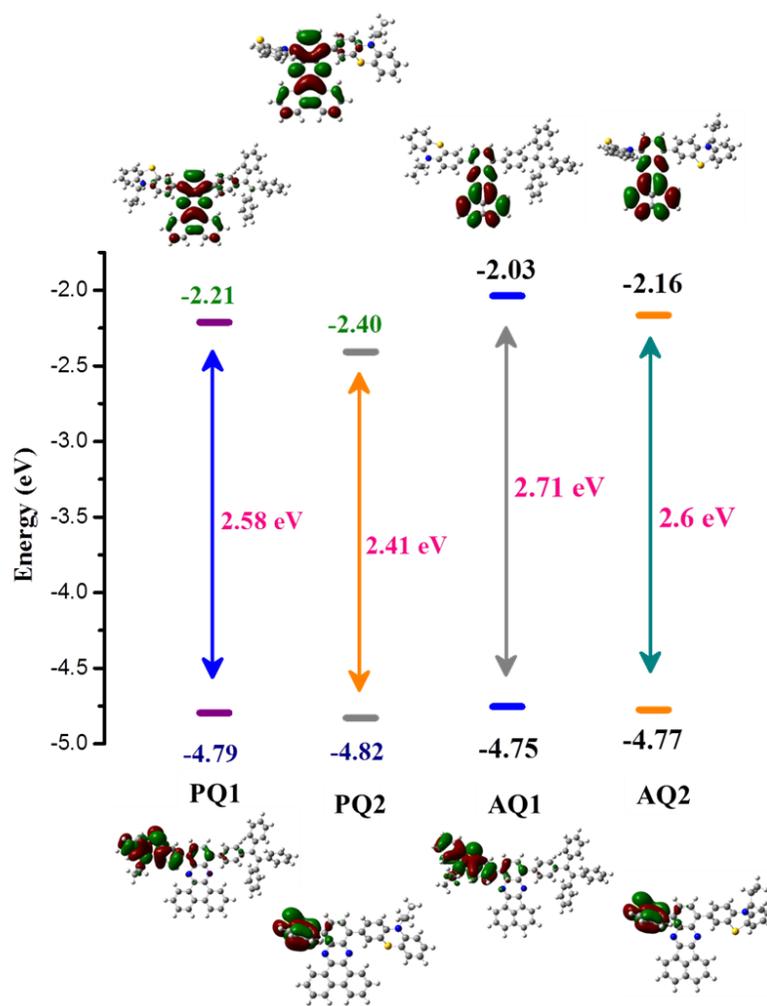
**Table 4.1.** Photophysical properties of **PQ1**, **PQ2**, **AQ1**, and **AQ2**.

<b>Compounds</b>	$\lambda_{ab}[\text{nm}] (\epsilon[\text{Lmol}^{-1}\text{cm}^{-1}])^a$	$\lambda_{em} .(\text{nm})^b$	$\Phi_f^c$
<b>PQ1</b>	288 (28356), 309 (28520), 396 (9077), 458 (4776)	544	0.05
<b>PQ2</b>	307 (12669), 378 (5643) 398 (6065), 456 (1787)	567, 738	0.01
<b>AQ1</b>	318 (35737), 425 (5701)	516, 694	0.06
<b>AQ2</b>	318 (19667), 431 (1581)	525, 660	0.02

<sup>a,b</sup> Measured in tetrahydrofuran, <sup>c</sup> The fluorescence quantum yields were recorded using Rhodamine 6G as a standard in ethanol solution

#### 4.4. Theoretical studies

The density functional theory (DFT) calculations for the unsymmetrical quinoxaline derivatives **PQ1**, **PQ2**, **AQ1** and **AQ2** were carried out to analyze the electronic structures and the distribution of frontier molecular orbitals (FMO) on the molecules by using B3LYP/631-G+(d,p) basis set.<sup>[19]</sup> The calculated frontier molecular orbitals for **PQ1**, **PQ2**, **AQ1** and **AQ2** are depicted in Figure 4.2. and the values are tabulated in Table 4.2.



**Figure 4.2.** Energy level diagram illustrating the HOMO and LUMO energy levels of **PQ1**, **PQ2**, **AQ1** and **AQ2** determined at the B3LYP/6-31G+(d,p) level.

The unsymmetrical quinoxaline derivatives **PQ1**, **PQ2**, **AQ1** and **AQ2** exhibit non-planar structure due to the presence of PTZ and TPE units at the end capping positions which have a butterfly type structure and a propeller type structure respectively. In the case of **PQ1** and **AQ1**, the HOMO energy levels were mainly localized on the PTZ unit, due to the presence of TPE unit which acts as a weak electron donating unit. However, the HOMO energy levels of **PQ2** and **AQ2** are mainly concentrated over the N-substituted PTZ unit rather than the C-substituted PTZ unit due to its extremely twisted structure upon substitution of PTZ through -N position on the quinoxaline unit.<sup>[20]</sup> The LUMO energy level was mainly concentrated on the phenanthrene-quinoxaline unit and the acenaphthene-quinoxaline respectively in the quinoxaline derivatives **PQ1**, **PQ2**, **AQ1** and **AQ2**, indicating that the quinoxaline unit is a strong acceptor unit in the donor-acceptor-donor system. The computed HOMO-LUMO gaps for **PQ1**, **PQ2**, **AQ1**, and **AQ2** are 2.58 eV, 2.41 eV, 2.71 eV and 2.60 eV respectively.

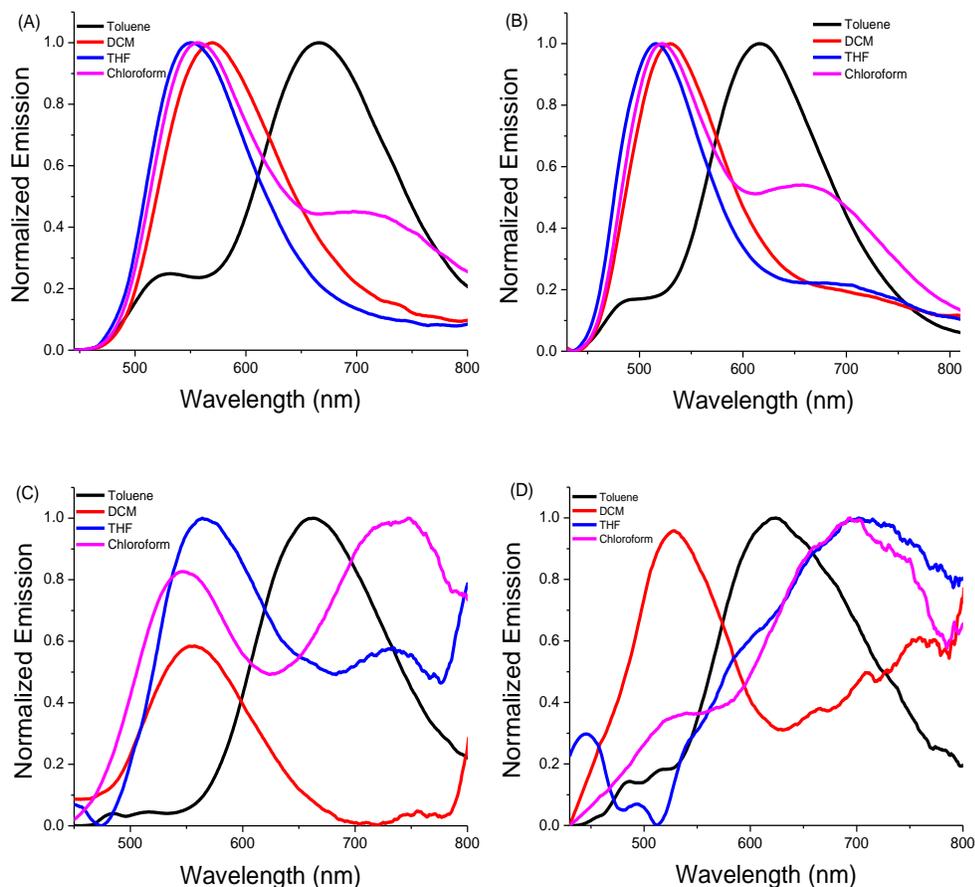
**Table 4.2.** DFT calculations of unsymmetrical PQ and AQ derivatives.

<b>Compounds</b>	<b>HOMO<sup>a</sup> eV</b>	<b>LUMO<sup>a</sup> eV</b>	<b>HOMO-LUMO gap eV</b>
<b>PQ1</b>	-4.79	-2.21	2.58
<b>PQ2</b>	-4.82	-2.40	2.41
<b>AQ1</b>	-4.75	-2.03	2.71
<b>AQ2</b>	-4.77	-2.16	2.60

<sup>a</sup>Theoretical values calculated at B3LYP/631-G+(d,p)

#### 4.5. Solvatochromism

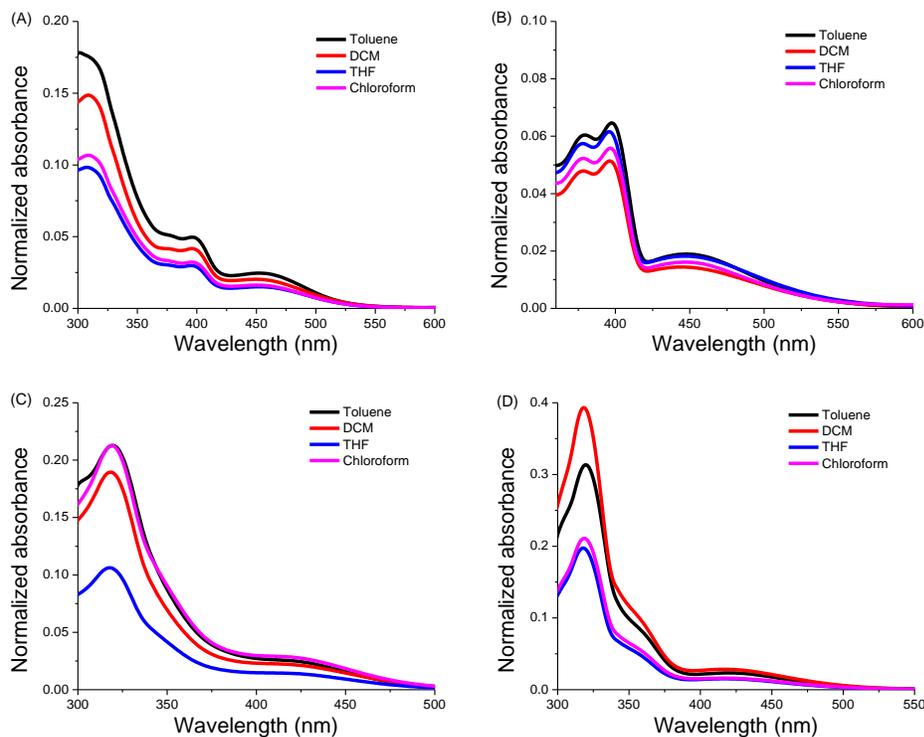
The donor-acceptor-donor based quinoxaline molecules are presumed of demonstrating intramolecular charge transfer (ICT) transition from the donor unit to the acceptor unit which can be easily affected by changes in the solvent polarity. Hence, the variations in the ICT transition with the use of different solvents from non-polar to polar (Toluene, THF, DCM and chloroform) were studied by emission (Figure 4.3.) and absorption spectroscopy (Figure 4.4.). The unsymmetrical PTZ-TPE based **PQ** derivative, **PQ1** in toluene has an emission maximum at 666 nm along with a shoulder peak around 526 nm. The shoulder peak in toluene (526 nm) lies at the same position as the emission maximum of TPE-based symmetrical **PQ** derivative (**TPE-PQ-TPE**) reported in Chapter 3 (Figure 3.3.). It can be concluded that the emission maximum at 666 nm in **PQ1** could be arising due to the ICT from PTZ donor to **PQ** acceptor and the shoulder at 526 nm could be the ICT emission from TPE donor to **PQ** acceptor.<sup>[16]</sup>



**Figure 4.3.** Emission spectra of (A) **PQ1**, (B) **AQ1**, (C) **PQ2** and (D) **AQ2** in solvents of different polarity. ( $\lambda_{exc} = 420\text{nm}$ ).

The molecule **PQ1** exhibits emission maxima at 550 nm, 556 nm and 568 nm in THF, chloroform and DCM respectively similar to the TPE based symmetrical **PQ** derivative (**TPE-PQ-TPE**) (Figure 3.3, Chapter 3). In THF and DCM, single emission peaks without shoulder emissions were observed for **PQ1** although **PQ1** in chloroform displays a shoulder peak at 721 nm which could be due to the ICT from PTZ to **PQ**. Similarly, the TPE substituted unsymmetrical derivative **AQ1** in toluene has an emission maximum at 616 nm along with shoulder peak at 486 nm. The emission of **AQ1** in toluene at 486 nm was similar to the emission of symmetrical TPE-substituted AQ molecule (**TPE-AQ-TPE**) reported in (Chapter 3, Figure 3.3) and hence the emission at 616 nm could be assigned to the ICT from PTZ to AQ. In THF, chloroform and DCM; **AQ1** shows emission maxima

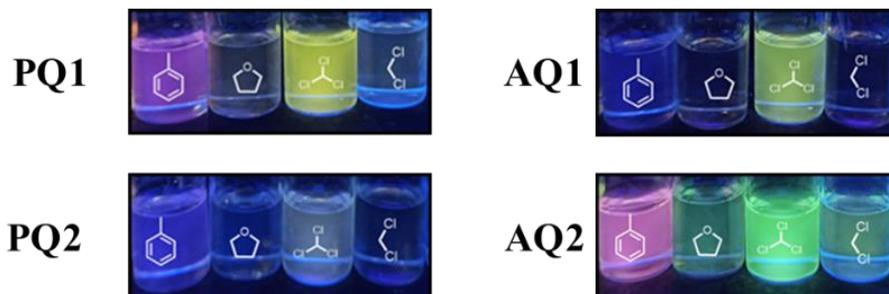
at 516 nm, 522 nm and 530 nm respectively which could be ascribed to the ICT from TPE to **AQ**.<sup>[16]</sup> The molecule **AQ1** also displays shoulder peaks in THF, chloroform and DCM at 705 nm, 672 nm and 710 nm respectively which could be due to the ICT from PTZ to **AQ**. Both the unsymmetrical derivatives **PQ1** and **AQ1** display dual ICT emission occurring from the two respective donor TPE and PTZ. The ICT emission corresponding to PTZ donor has reduced intensity in polar solvents as compared to the TPE corresponding ICT emission as PTZ acts as a strong donor compared to TPE which is a weak donor. The unsymmetrical molecule **PQ2** in toluene has a charge transfer (CT) based emission maximum at 663 nm which in chloroform was red shifted to 747 nm accompanied by a LE based emission at 547 nm. In THF, the emission due to CT state appearing at 734 nm has reduced intensity whereas in DCM the CT based emission was almost quenched and appears as a small hump around 747 nm. Emission in the region of 540-560 nm associated to LE state was observed in THF and DCM for the molecule **PQ2**. A total redshift of 89 nm occurs for **PQ2** on moving from non-polar to polar solvents. The unsymmetrical molecule **AQ2** emits at 624 nm in toluene with shoulder peaks in the region of 450–530 nm ascribed to LE emissions. The emission for **AQ2** was bathochromically shifted to 696 nm and 705 nm in chloroform and THF respectively with shoulder peaks related to LE state in the region of 520–590 nm. In DCM, **AQ2** has a strong LE emission at 524 nm and the CT emission appears as a broad shoulder with reduced intensity. The unsymmetrical quinoxaline derivatives **PQ2** and **AQ2** possess N-PTZ substitution which is assumed to be almost perpendicular to the acceptor moiety which could result in formation of a twisted intramolecular charge transfer (TICT) state resulting in reduced or quenched CT emissions in polar solvents.<sup>[21]</sup> Thus, the N-PTZ unit can act as strong donor and enhance the D-A character but also results in quenched emissions in polar solvents as compared to the C-substituted PTZ unit.



**Figure 4.4.** Electronic absorption spectra of (A) **PQ1**, (B) **PQ2**, (C) **AQ1**, (D) **AQ2** in solvents of different polarity.

The symmetrical quinoxaline derivatives using PTZ donor **PTZ-PQ-PTZ** and **PTZ-AQ-PTZ** reported in (Chapter 3, Figure 3.3) exhibit an increased charge transfer character due inclusion of strong electron donating PTZ unit on both sides as compared to the unsymmetrical quinoxaline derivatives. A polarized excited state is created on charge transfer from donor to acceptor and the reorganization of the solvent dipoles around the polarized excited state results in stabilization of the excited state which lowers the energy of the excited state thereby resulting in a bathochromic shift on increasing the polarity.<sup>[22]</sup> The solvatochromism of the unsymmetrical quinoxaline derivatives was also explored by absorption spectroscopy (Figure 4.4.) which shows negligible changes on varying the solvent polarity concluding that the ground states are less polarized compared to the excited states.<sup>[22]</sup>

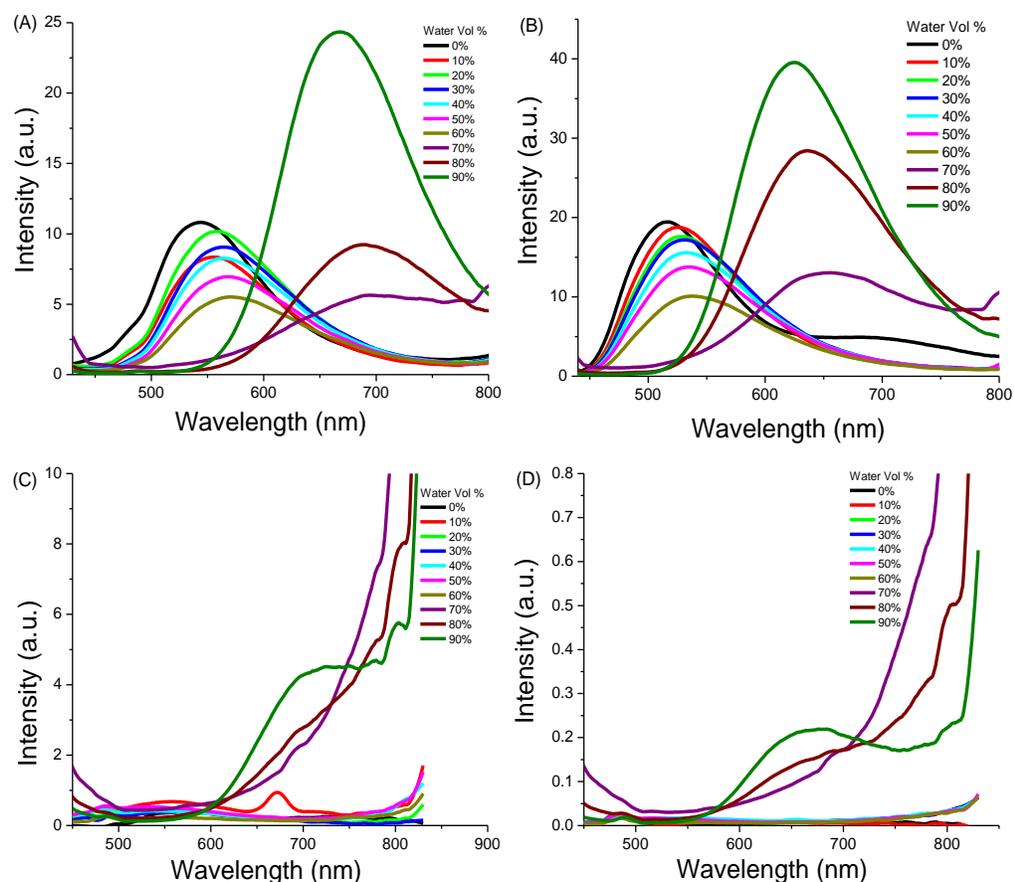
The pictures of quinoxaline derivatives in different solvents are given in Figure 4.5.



**Figure 4.5.** Photographs of **PQ1**, **PQ2**, **AQ1** and **AQ2** in solvents of different polarity taken under 365nm UV illumination. (From left to right-toluene, THF, chloroform, DCM).

#### 4.6. Aggregation-induced emission studies

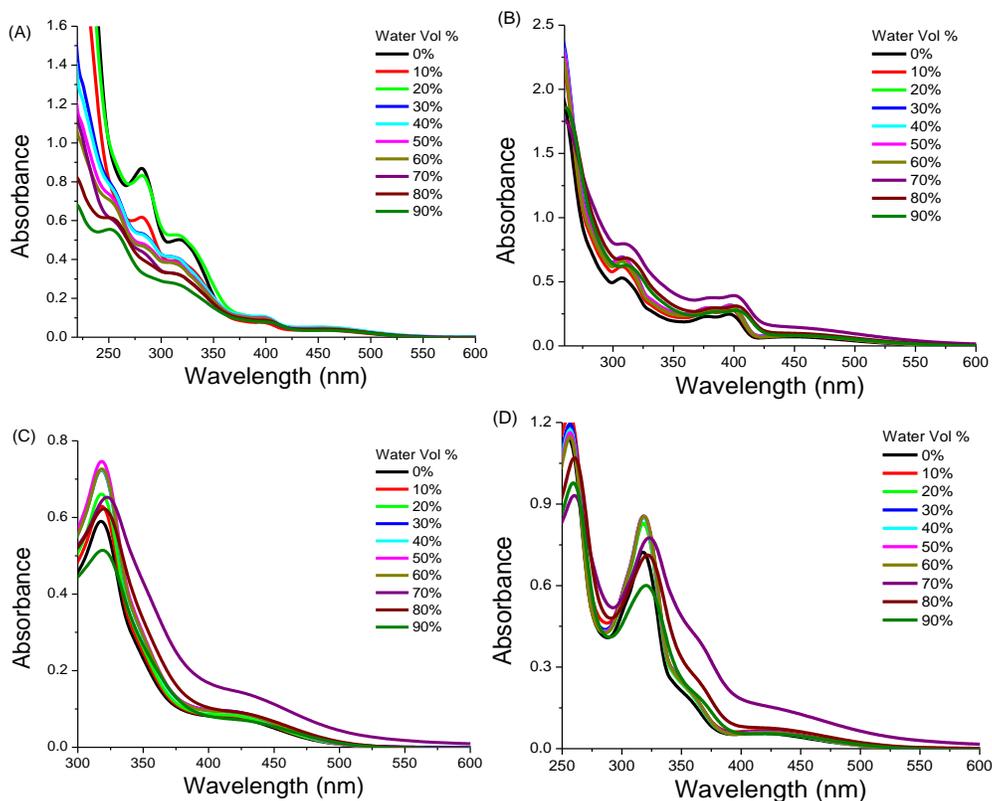
The unsymmetrical quinoxaline derivatives incorporate non-planar PTZ and TPE moieties which could endow the D-A-D molecules with twisted geometries resulting in improved emission in the aggregated state. Considering the above aspects, the aggregation-induced emission (AIE) properties of the unsymmetrical quinoxaline derivatives were explored using emission (Figure 4.6.) and absorption spectroscopy (Figure 4.7.). The nanoaggregates were generated by gradual increment of water fraction ( $f_w=0-90\%$ ) in ( $2 \times 10^{-5}$  M) THF solution of the quinoxaline molecules. The addition of water in THF produces nano-aggregates as the quinoxaline molecules are readily soluble in THF but are insoluble in water.



**Figure 4.6.** Emission spectra of (A) **PQ1**, (B), **AQ1**, (C) **PQ2** and (D) **AQ2** in THF-water mixtures with increasing water fractions. (conc.  $2 \times 10^{-5}$  M).

In contrast to the usual AIE behavior, the unsymmetrical TPE based quinoxaline derivatives show emission both in solution and in aggregated state. The molecules **PQ1** and **AQ1** show ICT emission in THF at 543 nm and 514 nm respectively which was red shifted with a drop in intensity on increasing the water percentage upto  $f_w$  60% attributed to the stabilization of the polarized ICT state due to increase in polarity with increasing  $f_w$ . A distinct emission peak was generated at 697 nm and 653 nm for **PQ1** and **AQ1** respectively at  $f_w$  70% owing to the nano-aggregation formation. The emission intensity increases three-fold for **PQ1** and **AQ1** due to aggregation on increasing the water fraction to 90% and the emission maximum was observed at 669 nm and 621 nm respectively. The TPE based unsymmetrical derivatives **PQ1** and **AQ1** exhibit ICT dependent emission

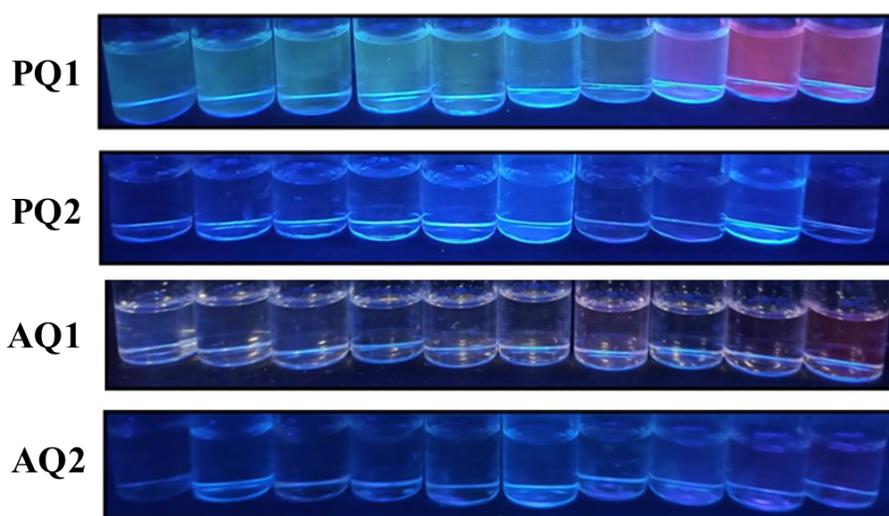
at lower  $f_w$  (0-60%) and at higher  $f_w$  (70-90%) the emission was influenced by the generation of nanoaggregates.<sup>[23]</sup>



**Figure 4.7.** Electronic absorption spectra of (A) **PQ1**, (B) **PQ2**, (C) **AQ1**, and (D) **AQ2** in different THF-water mixtures with increasing water percentage.

The unsymmetrical molecules **PQ2** and **AQ2** containing N-PTZ are AIE inactive and show no significant emission on aggregation possibly due to the N-substituted PTZ which stays perpendicular to the quinoxaline moiety and could engage in intermolecular  $\pi$ - $\pi$  stacking interactions with other N-PTZ unit in their aggregated state which could result in non-radiative emission. The PTZ donor attached by C-C coupling has lower torsional angle with the quinoxaline unit as compared to N-PTZ and retains its non-

planar butterfly framework which interrupts the  $\pi$ - $\pi$  stacking in the solid state which could allow the molecule to be emissive on aggregation. Hence, the unsymmetrical quinoxaline derivatives **PQ1** and **AQ1** which have the C-substituted PTZ moiety and TPE as donor show significant AIE character compared to **PQ2** and **AQ2** which are AIE inactive due to the dominant effect of N-PTZ donor. The absorption spectra of the quinoxaline derivatives display Mie scattering effect due to aggregates present in the solution above  $f_w$  60%.<sup>[23]</sup> The pictures of the THF-water mixtures of the quinoxaline molecules are given in Figure 4.8.

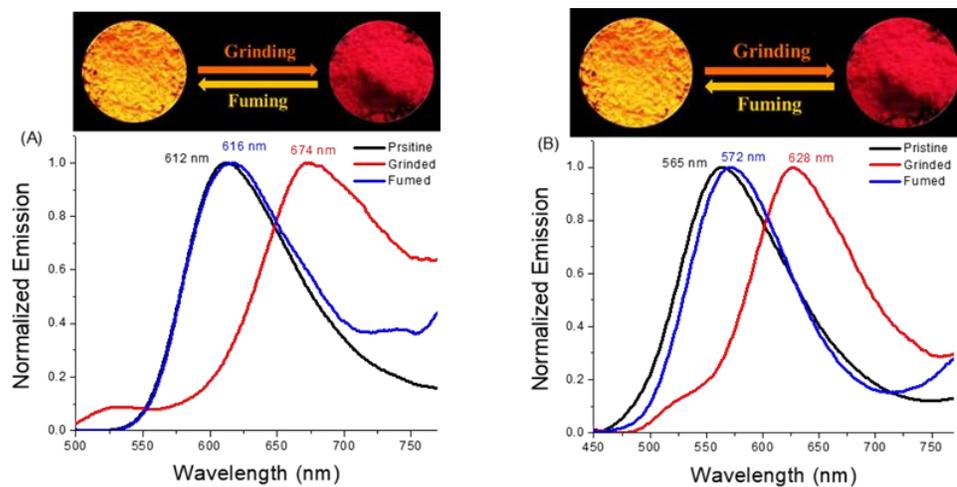


**Figure 4.8.** Photographs of **PQ1**, **PQ2**, **AQ1**, and **AQ2** in different THF-water mixtures taken under 365nm UV illumination. (From left to right-0%-90% water volume fraction.)

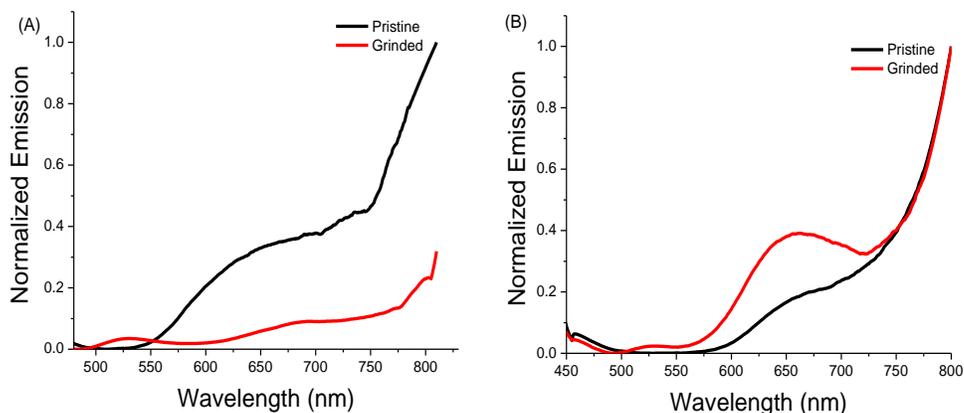
#### 4.7. Mechanochromism

The D-A-D **PQ** and **AQ** quinoxaline molecules exploit typical AIEgens PTZ and TPE as donors and possess twisted structures which enables these molecules with efficient solid-state emission which is sensitive to mechanical stimuli. Taking into consideration the following aspects, the mechanochromic properties of **PQ** and **AQ** quinoxaline derivatives were investigated by grinding the powders of the synthesized molecules in a

mortar-pestle and the response was recorded using emission spectroscopy (Figure 4.9.–Figure 4.11.).



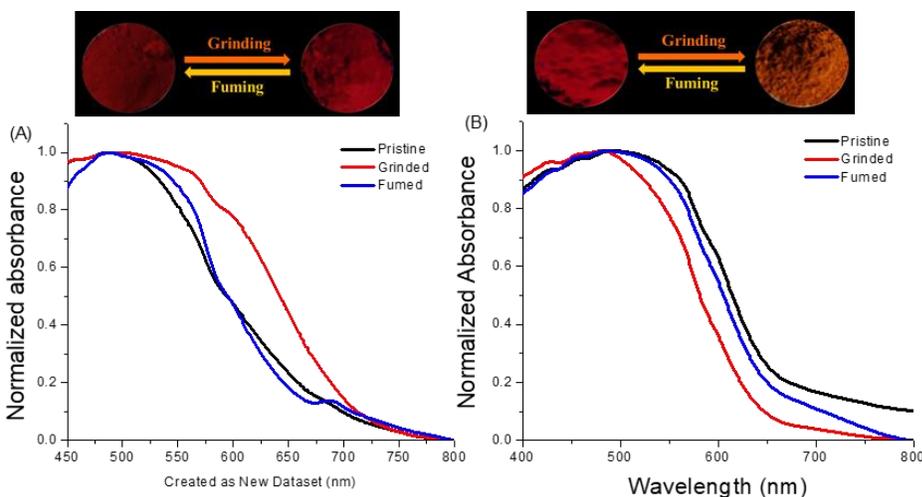
**Figure 4.9.** Solid-state emission spectra of the pristine, grinded and fumed forms of (A) **PQ1** and (B) **AQ1**. ( $\lambda_{exc}=420$  nm).



**Figure 4.10.** Solid-state emission spectra of pristine and grinded forms of (A) **PQ2** and (B) **AQ2**. ( $\lambda_{exc}=420$  nm).

The TPE based unsymmetrical derivative **PQ1** in its pristine state has a bright orange emission at 612 nm which on grinding bathochromically shifts to 674 nm and appears as a red powder. The fumigation of grinded solid of **PQ1** with DCM-Hexane (1:1) (3 minutes) allows it to return to its

pristine state emitting at 616 nm. The pristine solid of TPE based unsymmetrical derivate **AQ1** exhibits yellow emission at 565 nm which on grinding displays orange emission at 628 nm. The grinded solid of **AQ1** requires longer fuming time up to 15 minutes and reverts to its original state with an emission at 572 nm having a difference of 8 nm as compared to the pristine form. The molecule **AQ1** does not completely revert to its pristine form on fuming and hence has a lower reversibility on fuming as compared to the other quinoxaline molecules. The spectral shifted induced by grinding in **PQ1** and **AQ1** is 62 nm and 63 nm respectively which is high in comparison to other reported mechanochromic materials. The emission of **PQ** derivatives is red shifted than **AQ** derivatives suggesting higher degree of conjugation in phenanthrene ring as compared to acenaphthene ring.



**Figure 4.11.** Solid-state absorption spectra of (A) **PQ2** and (B) **AQ2** in its pristine, grinded and fumed forms.

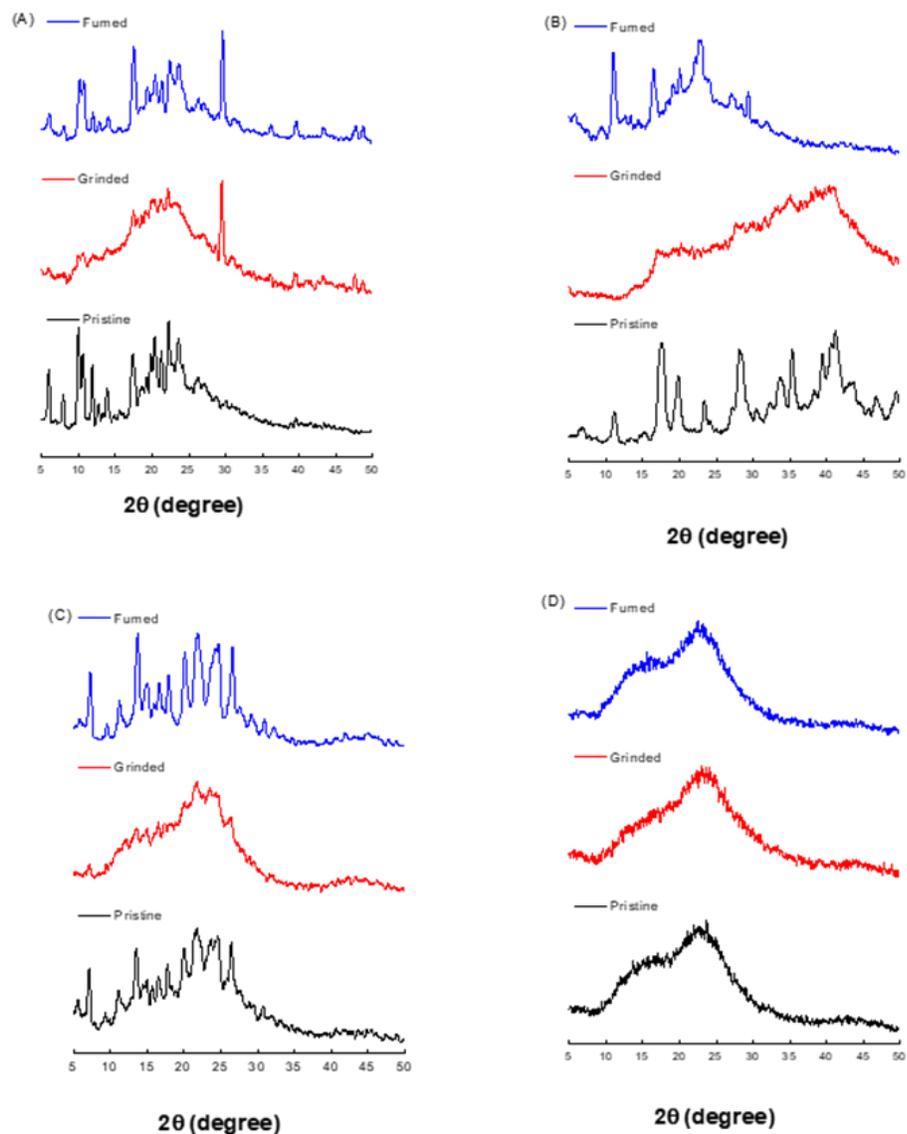
In contrast to the PTZ-TPE substituted unsymmetrical quinoxaline derivatives, the N-PTZ substituted quinoxaline derivatives **PQ2** and **AQ2** have quenched emissions in the solid state due to the perpendicular lying N-PTZ unit (Figure 4.10.) which was also confirmed by their AIE studies. The molecules **PQ2** and **AQ2** are completely non-emissive in their pristine form; although the grinding of pristine powders shows visual color change that can be easily observed with naked eye and returns to its original color

on fuming. The solid-state absorption spectra of the pristine, grinded and fumed solids were recorded to further confirm the mechanochromic behavior of the non-emissive **PQ2** and **AQ2** molecules (Figure 4.11.). The orange pristine powder of **PQ2** exhibits an absorption band around 520 nm which on grinding displays a red shift in the absorption band around to 560 nm and possesses a deep red color. The fumed solid of **PQ2** shows absorption around 518 nm similar to the pristine powder. Surprisingly, the orange color pristine powder of **AQ2** with absorption band around 545 nm on grinding gets converted to a yellow powder and shows a hypsochromically shifted absorption band at 488 nm. On fuming, the grinded solid of **AQ2** shows absorption band around 539 nm which was close to the absorption of the pristine powder. The emissions of molecules **PQ2** and **AQ2** were quenched in the solid state possibly be due to the planarity of N-PTZ unit which could result in  $\pi$ - $\pi$  stacking increasing the possibility of non-radiative decay of the excited state. However, the molecules **PQ2** and **AQ2** also possess C-substituted PTZ as donor on one side which has a unique non-planar butterfly architecture which could change its confirmation on grinding thereby displaying reversible color change.

#### **4.8. Powder X-ray diffraction studies.**

The mechanochromic behavior in the quinoxaline derivatives was expected to be arising from physical structure alterations which was examined by powder X-ray diffraction (PXRD) technique (Figure 4.12.). Sharp peaks depicting crystalline nature are detected for the pristine powders of **PQ1** and **AQ1**. The sharp peaks are diminished to a certain extent on grinding the powders of **PQ1** and **AQ1** and a broad diffused pattern was observed for the grinded solids which proves their amorphous nature. The crystalline peaks are completely regained for **PQ1** and **AQ1** on fumigation validating the reversible nature of the stimuli-responsive molecules. The crystalline peaks for **AQ1** were somewhat recovered on fuming similar to its emission

profile which was not fully reversed on fumigation. This shows that **AQ1** has lower reversibility from grinded to pristine form on fuming as compared to the other molecules.



**Figure 4.12.** PXRD patterns of pristine, grinded and fumed solids of (A) **PQ1**, (B) **PQ2**, (C) **AQ1** and (D) **AQ2**.

The quinoxaline derivative **AQ2** exhibits amorphous nature with broad diffused bands in all the three forms pristine, grinded and fumed. It can be

thus concluded that the color change on grinding is associated with a morphological transformation from crystalline to amorphous state.

## 4.9. Experimental section

### General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under a nitrogen/argon atmosphere.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker Avance III instrument by using  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ( $\text{CDCl}_3$ , 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet), and the coupling constants,  $J$ , are given in hertz.  $^{13}\text{C}$  NMR chemical shifts are reported relative to the solvent residual peak ( $\text{CDCl}_3$ , 77.0 ppm). UV-visible absorption spectra were recorded on a PerkinElmer Lambda 35 UV-visible spectrophotometer. Emission spectra were recorded using a Fluoromax-4C, S/n.1579D-1417-FM fluorescence software Ver 3.8.0.60. The relative quantum yields in solution were calculated using Rhodamine 6G in ethanol solution as a standard. The excitation and emission slits were 2/2 nm for the emission measurements. All the measurements were done at 25 °C. HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. The PXRD studies were done using powdered samples on a Rigaku SmartLab automated multipurpose X-ray diffractometer, equipped with a high-accuracy theta-theta goniometer featuring a horizontal sample mount.

### Synthesis and Characterization of PQBr

A mixture of **1** (1.0 mmol) and 10-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**PTZ-Bpin**) was dissolved in THF/water (4/1 v/v) and then Sodium carbonate (3.3 mmol) was added. After degassing the reaction mixture for 10 min,  $\text{Pd}(\text{PPh}_3)_4$  (0.1 mmol) was added and the reaction mixture was heated to reflux for 16 h under a nitrogen

atmosphere. The reaction mixture was cooled to room temperature and then worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (60:40) as the eluent. An orange solid of PQBr was obtained in 52% yield. ;  $^1\text{H}$  NMR( 400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  9.53 (d,  $J = 8$  Hz, 1H), 9.14 (d,  $J = 8$  Hz, 1H), 8.57 (d,  $J = 8$  Hz, 2H), 8.21 (d,  $J = 8$  Hz, 1H), 7.85-7.78 (m, 4H), 7.75-7.69 (m, 3H), 7.21-7.19 (m, 2H), 7.08 (d,  $J = 8$  Hz, 1H), 7.00-6.94 (m, 2H), 3.96 (t,  $J = 16$  Hz, 2H), 2.01-1.92 (m, 2H), 1.10 (t,  $J = 8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  147.6, 145.0, 135.4, 132.8, 132.3, 132.2, 131.9, 130.8, 130.7, 130.5, 130.0, 130.0, 129.9, 129.8, 128.9, 128.2, 128.1, 127.6, 127.6, 127.5, 127.2, 126.9, 126.8, 123.0, 122.8, 122.5, 115.4, 114.8, 49.3, 30.2, 20.2, 11.4. HRMS (ESI): Calcd. for  $[\text{M}]^+$ : 597.0869. Found: 597.0862.

### Synthesis and Characterization of AQBr

A mixture of **2** (1.0 mmol) and 10-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**PTZ-Bpin**) (1 mmol) was dissolved in THF/ water (4/1 v/v) and Sodium carbonate (3.3 mmol) was added. After degassing the reaction mixture for 10min,  $\text{Pd}(\text{PPh}_3)_4$  ( 0.1 mmol) was added and the reaction mixture was heated to reflux for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (75:25) as the eluent. An orange solid of AQBr was obtained in 47% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  8.58-8.55 (m, 1H), 8.36-8.33 (m, 1H), 8.19-8.08 (m, 3H), 7.93-7.86 (m, 1H), 7.84-7.80 (m, 1H), 7.63-7.61 (m, 3H), 7.19 (d,  $J = 5$  Hz, 2H), 7.04 (d,  $J = 5$  Hz, 1H), 6.93 (d,  $J = 5$  Hz, 2H), 3.95-3.91 (m, 2H), 1.98-1.91 (m, 2H), 1.09 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  145.0, 140.0,

139.2, 136.9, 136.6, 132.5, 131.5, 131.5, 130.2, 130.1, 130.0, 129.9, 129.8, 129.6, 129.4, 128.7, 128.6, 128.5, 127.5, 127.2, 124.4, 123.5, 123.3, 122.8, 122.6, 122.4, 115.4, 114.7, 49.2, 20.2, 11.4. HRMS (ESI): Calcd. for [M + H]<sup>+</sup>: 573.0696. Found: 573.0738.

### Synthesis and Characterization of PQ1

A mixture of **PQBr** (1.0 mmol) and 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (**TPE-Bpin**) (1.1 mmol) was dissolved in THF/ water (4/1 v/v) and then Sodium carbonate (3.3 mmol) was added. After degassing the reaction mixture for 10 min, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 mmol) was added and the reaction mixture was heated to reflux for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (60:40) as the eluent. An orange solid of PQ1 was obtained in 76% yield. ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25<sup>o</sup>C): δ 9.18 (d, *J* = 5 Hz, 1H), 8.97 (d, *J* = 10 Hz, 1H), 8.56 (d, *J* = 5 Hz, 2H), 7.93 (s, 2H), 7.85 (s, 1H), 7.81-7.68 (m, 8H), 7.28 (s, 1H), 7.23-7.13 (m, 19H), 6.95 (s, 1H), 4.00- 3.96 (m, 2H), 2.02-1.91 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25<sup>o</sup> C) : δ 145.1, 144.7, 143.9, 143.8, 142.9, 141.2, 141.1, 140.1, 139.9, 139.2, 138.4, 136.6, 132.7, 132.2, 132.1, 131.6, 131.5, 131.4, 131.0, 130.6, 130.5, 130.4, 130.1, 130.1, 129.6, 128.0, 127.7, 127.6, 127.2, 126.7, 126.5, 126.5, 126.4, 124.7, 124.2, 122.8, 122.4, 115.4, 114.8, 49.3, 20.2, 11.4. HRMS (ESI): Calcd. for [M + K]<sup>+</sup>: 888.2809. Found: 888.2836.

### Synthesis and Characterization of AQ1

A mixture of **AQBr** (1.0 mmol) and 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (**TPE-Bpin**) (1.1 mmol) was dissolved in THF/ water (4/1 v/v) and Sodium carbonate (3.3 mmol) was added. After degassing the reaction mixture for 10 min, Pd(PPh<sub>3</sub>)<sub>4</sub> ( 0.1 mmol) was added and reaction mixture was heated to reflux for 16 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and worked up with dichloromethane. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane/dichloromethane (60:40) as the eluent. A yellow solid of AQ1 was obtained in 54 % yield ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25<sup>o</sup>C): δ 8.35-8.33 (m, 1H), 8.25-8.23 (m, 1H), 8.09-8.06 ( m, 2H), 7.83-7.77 (m, 4H), 7.70 (d, *J* = 5 Hz, 2H), 7.65 (d, *J* = 10 Hz, 2H), 7.23-7.10 (m, 19H), 7.05 (d, *J* = 5 Hz, 1H), 6.96-6.92 (m, 2H), 3.94 (t, *J* = 5 Hz, 2H), 1.99-1.92 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H) ); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25<sup>o</sup> C) : δ 153.0, 152.9, 145.1, 144.7, 143.9, 143.9, 143.8, 142.6, 141.1, 140.9, 139.8, 139.2, 139.1, 139.0, 136.8, 136.7, 133.0, 132.2, 132.2, 131.6, 131.5, 131.4, 130.9, 130.4, 130.1, 129.8, 129.2, 128.5, 128.4, 127.8, 127.6, 127.6, 127.5, 127.1, 126.4, 126.3, 124.8, 124.1, 122.3, 122.2, 121.9, 115.3, 114.7, 49.2, 20.2, 11.4. HRMS (ESI): Calcd. for [M ]<sup>+</sup>: 823.3016. Found: 823.3116.

### Synthesis and Characterization of PQ2

To a X mL round-bottom flask, **PQBr** (1 mmol) and **PTZ** (1 mmol) was dissolved in dry toluene(40 ml) and sodium tert-butoxide (0.1 mmol) was added. After degassing the reaction mixture for 10 min, Ph(t-Bu)<sub>3</sub> (0.05 mmol) and Pd(OAc)<sub>2</sub> (0.02 mmol) were added. The reaction mixture was heated to refluxed for 16 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and the solution was filtered to remove insoluble solids. The filtrate was concentrated in vacuum and purified by silica gel column chromatography by using hexane: dichloromethane (55:45) as eluent. A Orange solid of PQ2

was obtained in 61 % yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  9.18 (d,  $J=10$  Hz, 1H), 9.12 (d,  $J = 10$  Hz, 1H), 8.53 (d,  $J = 10$  Hz, 1H), 8.49 (d,  $J = 10$  Hz, 1H), 8.09-8.04 (m, 2H), 7.90 (d,  $J = 2$  Hz, 1H), 7.86-7.83 (m, 1H), 7.82-7.76 (m, 2H), 7.74-7.69 (m, 2H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.23-7.20 (m, 2H), 7.14-7.09 (m, 3H), 6.99-6.94 (m, 2H), 6.77 (t,  $J = 7.5$  Hz, 2H), 6.71-6.68 (m, 2H), 6.16 (d,  $J = 10$  Hz, 2H), 3.98 (t,  $J = 7.5$  Hz, 2H), (m, 2H), 1.12 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) :  $\delta$  145.1, 144.9, 144.7, 142.1, 142.0, 141.0, 140.5, 140.0, 137.7, , 130.0, 130.1, 130.1, 130.2, 130.2, 130.4, 130.5, 132.1, 132.2, 132.3, 132.9 , 126.7, 127.0, 127.2, 127.2, 127.5, 128.0, 128.0, 128.1, 129.0, 129.1, 129.6 , 120.5, 122.2, 122.4, 122.5, 122.2, 122.8, 122.9, 124.3, 124.6, 126.2, 126.5 : HRMS (ESI). , 11.4, 20.2, 49.3, 77.2, 114.7, 114.8, 115.4, 115.5, 116.5 . Calcd. for  $[\text{M}]^+$ : 716.2063. Found: 716.2091

### Synthesis and Characterization of AQ2

To a X mL round-bottom flask, **AQBr** (1 mmol) and **PTZ** (1 mmol) was dissolved in dry toluene and sodium tert-butoxide (5 mmol) was added. After degassing the reaction mixture for 10 min  $\text{Ph}(\text{t-Bu})_3$  (0.1 mmol) and  $\text{Pd}(\text{OAc})_2$  (0.2 mmol) were added. The reaction mixture was refluxed for 16 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and the solution was filtered to remove insoluble solids. The filtrate was concentrated in vacuum and purified by silica gel column chromatography by using hexane:dichloromethane (50:50) as eluent. A Orange solid of AQ2 was obtained in 67% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  8.37 (d,  $J = 8$  Hz, 1H), 8.33-8.28 (m, 1H), 8.07 (t,  $J = 8$  Hz, 3H), 7.92 (s, 1H), 7.83-7.75 (m, 3H), 7.21 (d,  $J = 4$  Hz, 1H), 7.09-7.04 (m, 3H), 6.95 (s, 2H), 6.81-6.71 (m, 5H), 6.15 (d,  $J = 8$  Hz, 1H), 6.09 (d,  $J = 4$  Hz, 1H), 3.96 (t,  $J =$  Hz, 2H), 2.00-1.94 (m, 2H), 1.11 (t,  $J = 8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) :  $\delta$  154.0, 153.8, 145.1, 145.0, 144.5, 144.4, 141.5, 141.2, 140.3, 140.2, 138.3, 136.9, 133.2, 132.4, 132.0, 131.8, 131.7, 130.2, 129.5, 128.5,

128.4, 127.5, 127.2, 126.7, 126.3, 124.7, 124.3, 123.0, 122.4, 122.1, 120.8, 120.2, 116.5, 115.4, 114.8, 49.3, 20.2, 11.4. HRMS (ESI): Calcd. for [M]<sup>+</sup>: 690.1906. Found: 690.1923.

#### 4.10. Conclusion

In this contribution, we have designed and synthesized a series of D-A-D'/D-A'-D' quinoxaline derivatives with two types of fused quinoxaline namely phenanthrene-quinoxaline (PQ) and acenaphthene-quinoxaline (AQ) as acceptors A and A' respectively. The D-A-D'/D-A'-D' quinoxaline derivatives were substituted with three different donors namely phenothiazine (PTZ), tetraphenylethylene (TPE) and N-substituted PTZ in an unsymmetrical fashion. The unsymmetrical derivatives **PQ1** and **AQ1** comprise of strong donor PTZ (D) in combination with weak donor TPE (D') whereas **PQ2** and **AQ2** contain C-substituted PTZ as donor (D) one side and N-substituted PTZ as donor (D'') on the other side. The PQ and AQ quinoxaline derivatives exhibit contrasting photophysical properties due to the unsymmetrical substitution of different donors which majorly affects the D-A character, structural geometries and intermolecular interactions in the solid state. The unsymmetrical derivative **PQ1** and **AQ1** having donors PTZ and TPE exhibit intense ICT emissions originating from both the TPE and PTZ donors which are highly solvent-dependent. The ICT emission corresponding to PTZ donor in **PQ1** and **AQ1** exhibit reduced intensity in polar solvents as compared to the TPE corresponding ICT emission due to the stronger donating ability of PTZ in comparison to TPE which could generate highly polarized ICT state. In contrast, the unsymmetrical quinoxaline derivatives **AQ2** and **PQ2** having N-PTZ substitution along with PTZ display reduced or quenched CT emissions in polar solvents owing to the formation of a twisted intramolecular charge transfer (TICT) state originating from the almost perpendicular positioned N-PTZ unit. The presence of AIEgens PTZ and TPE in **PQ1** and **AQ1** endow the derivatives with intense emission in the aggregated state; however the unsymmetrical

derivatives **PQ2** and **AQ2** display quenching of emission in their aggregated state. The derivative **PQ1** and **AQ1** display reversible emission switching on grinding with very high grinding induced spectral shift making them suitable stimuli-responsive materials and the mechanochromic performance is related to crystalline to amorphous phase change. The derivatives **PQ2** and **AQ2** also exhibit grinding induced color-switching which is validated using solid-state absorption spectroscopy owing to their non-fluorescent pristine solids. To summarize, the donors PTZ and TPE are favorable in developing AIE active stimuli-responsive materials as compared to N-PTZ donor. The current work gives a detailed analysis of utilizing donors with different strengths in unsymmetrical fashion with heterocyclic  $\pi$ -conjugated acceptor unit and its effect on the photophysical and electronic properties, solid-state emission and stimuli-responsive properties. This contribution provides insights on choosing suitable donor and acceptor units and their proper positioning to further produce effective donor-acceptor based AIE and mechanochromic systems.

#### 4.11. References

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## Chapter 5

# Stimuli responsive AIE active positional isomers of phenanthroimidazole

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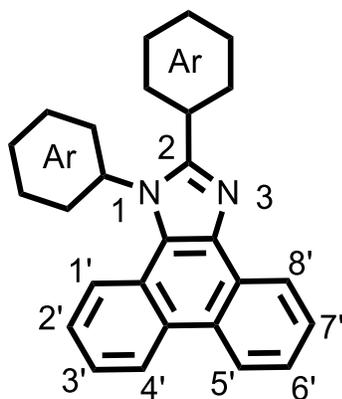
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### 5.1. Introduction

Organic materials with tunable solid-state emission are of broad and current interest owing to their promising applications in mechanical sensors, deformation detectors, security systems, memory devices, data storage, fluorescent probes and in various optoelectronic devices.<sup>[1, 2]</sup> Mechanochromic materials are a class of *smart* materials with reversible solid-state emission that can be altered on applying external stimuli.<sup>1(a), 1(e), [3]</sup> The variable emission in mechanochromic materials have been most commonly accomplished by phase transitions and alteration of the molecular packing modes.<sup>[4]</sup> A prerequisite for reversible mechanochromism is high solid-state emission<sup>[5]</sup> which mainly depends on the molecular arrangement and various factors such as planarity, effective conjugation and interaction with the surrounding environment.<sup>[6]</sup> The molecular system exhibiting aggregation-induced emission (AIE) are highly emissive in solid state<sup>[7]</sup> unlike the common organic fluorophores which are weakly emissive or non-emissive in solid state due to aggregation caused quenching (ACQ).<sup>[8]</sup> The fusion of AIE active fluorophores with the ACQ fluorophores is an effective technique for producing luminescent molecules in solid state with a wide variety of optoelectronic applications. Tetraphenylethylene (TPE) is highly emissive in solid state due to restriction of intramolecular rotations (RIR) due to the twisted propeller shaped structure and has been utilized for the development of AIE active mechanochromic materials.<sup>[9]</sup>

Recently, the development of organic light emitting diodes (OLEDs) has gained significant attention because of its applications in full colour flat

panel displays and solid state lighting.<sup>[10]</sup> The aggregation-induced emission (AIE) active materials have been effectively used in developing high performance organic light emitting diodes OLEDs.<sup>[11]</sup> The past years have witnessed use of phenanthroimidazole as a key building block in development of efficient solid state emitters due to its potential applications in sensing, bio-imaging, electrochemical luminescent cell, mechanochromic materials and organic light emitting diodes (OLEDs).<sup>[12]</sup> Phenanthroimidazole is a rigid, planar, aromatic heterocyclic compound comprising of a phenanthrene ring fused with an imidazole ring, possessing high thermal stability, good charge carrier mobility, wide band gap and excellent fluorescence quantum yield.<sup>[13]</sup> The two nitrogen atoms of the imidazole ring result in bipolar properties and easy functional modification at the N1 and C2 positions (Figure 5.1.) make phenanthroimidazole derivatives suitable to be employed in high performance organic light emitting diodes (OLEDs) and mechanochromic materials.<sup>[13]</sup>



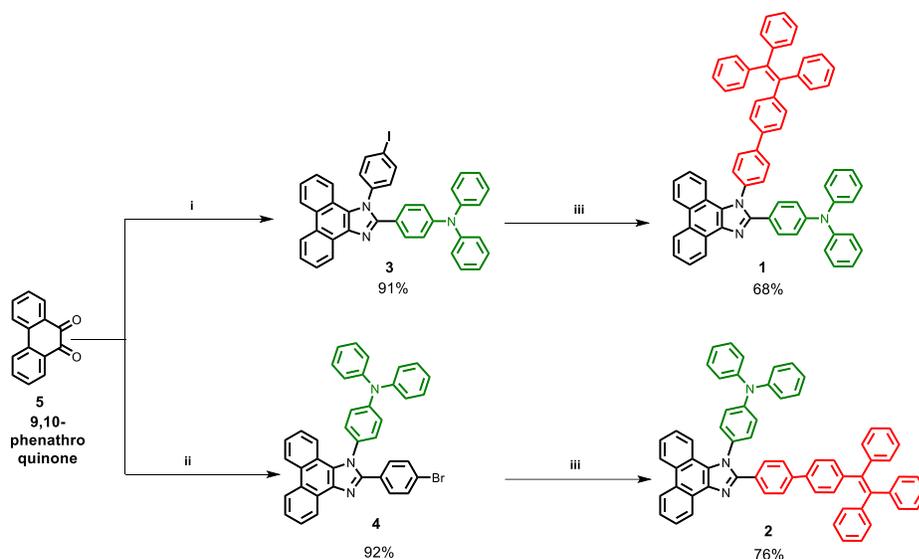
**Figure 5.1.** Chemical structure of phenanthroimidazole

The literature reveals reports on synthesis of phenanthroimidazole derivatives with reversible stimuli responsive solid state emission and efficient OLED properties.<sup>[14,15]</sup> The combination of phenanthroimidazole unit with a triphenylamine (TPA) and a tetraphenylethylene (TPE) unit simultaneously can produce materials with intriguing mechanochromic and organic light emitting diode (OLED) properties.

In this contribution we have synthesized phenanthroimidazole **1** and **2** incorporated with a triphenylamine (TPA) unit as well as a phenyl-TPE unit. The molecules are positional isomers and were synthesized with a view to study the effect of interchange of the TPA and phenyl-TPE unit on their photophysical and mechanochromic properties. Moreover, the TPA unit and the TPE unit differ in the donor strengths as well as effective conjugation which could further influence the properties. The aggregation-induced emission (AIE) and mechanochromic properties of phenanthroimidazole **1** and **2** are investigated. The phenanthroimidazoles show reversible mechanochromism between blue and green and are excellent solid-state emitters.

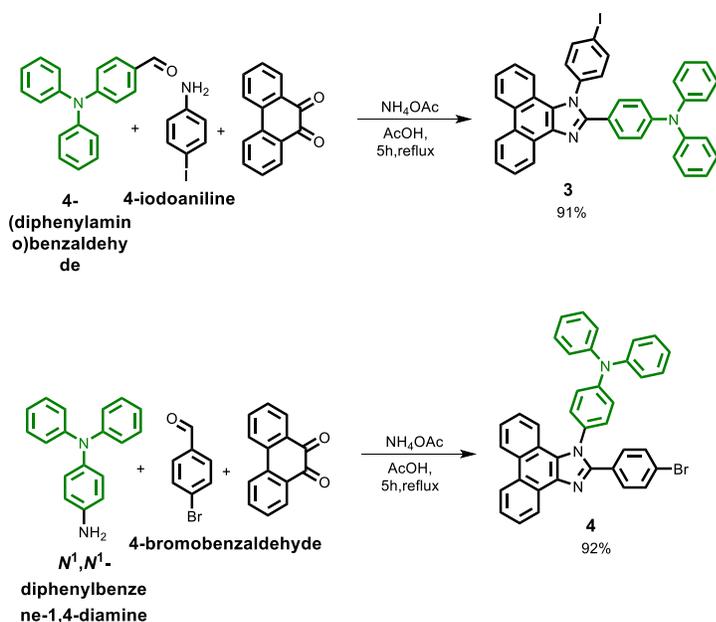
## 5.2. Results and discussions

The synthesis of phenanthroimidazoles **1** and **2** was carried out by a simple and efficient two step approach as illustrated in Scheme 5.1. The intermediates **3** and **4** were synthesized by a facile condensation reaction of 9,10-phenanthroquinone with corresponding aldehydes, amines and ammonium acetate in refluxing acetic acid. The intermediate **3** was obtained from 4-iodoaniline and 4-(diphenylamino) benzaldehyde in 91% yield, whereas the intermediate **4** was obtained from N',N'-diphenylbenzene-1,4-diamine and 4-bromobenzaldehyde in 92% yield. The aldehyde and amine intermediates of TPA were synthesized by reported procedures (Scheme 5.2.).<sup>[16]</sup> The Suzuki cross-coupling reaction of **3** and **4** with 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester<sup>[5(e)]</sup> in argon atmosphere using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst furnished the target phenanthroimidazoles **1** and **2** in 68% and 76% yields respectively. All the newly synthesized molecules were well characterized by NMR and HRMS techniques. The phenanthroimidazole **1** and intermediate **3,4** and were characterized by single crystal analysis.



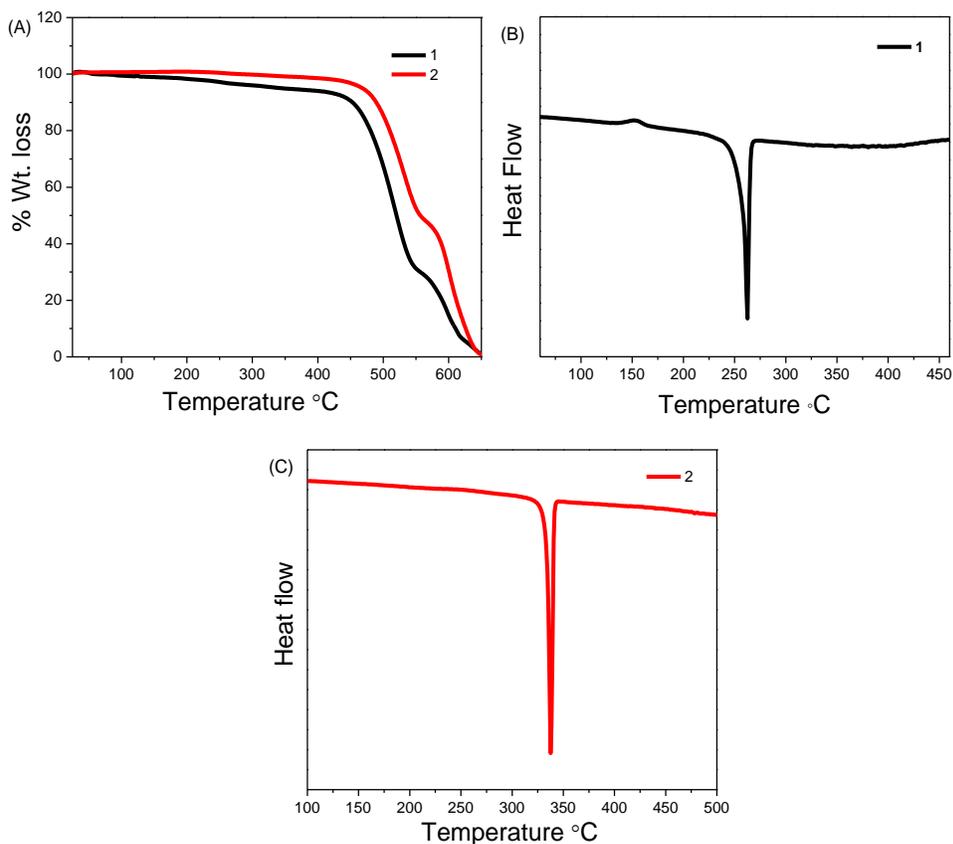
**Scheme 5.1.** Synthetic route for the phenanthroimidazoles **1** and **2**<sup>a</sup>

<sup>a</sup> (i) 4-iodoaniline, 4-(diphenylamino) benzaldehyde, acetic acid (AcOH) and ammonium acetate (NH<sub>4</sub>OAc), 5 hours, 120 °C (ii) N',N'-diphenylbenzene-1,4-diamine, 4-bromobenzaldehyde, acetic acid (AcOH) and ammonium acetate (NH<sub>4</sub>OAc), 5 hours, 120 °C (iii) 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene:ethanol:water (10.0 mL:4.0 mL:0.5 mL), 12 hours, 110 °C.



**Scheme 5.2.** Synthetic scheme for intermediates **3** and **4**

### 5.3. Thermal analysis

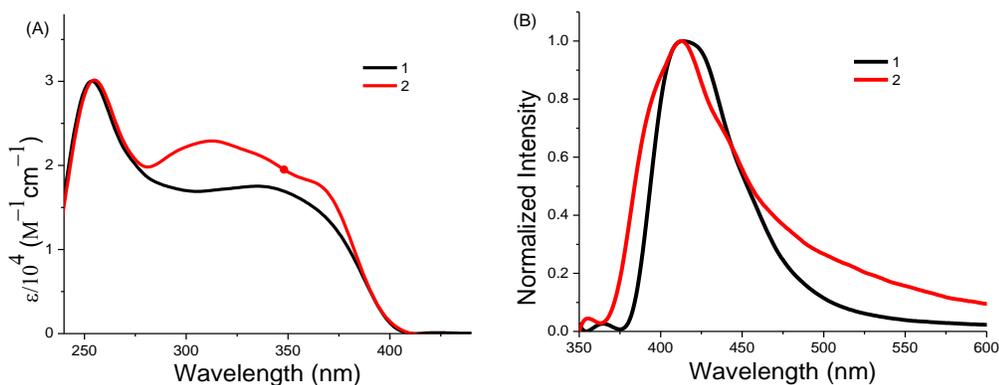


**Figure 5.2.** Thermogravimetric analysis (A) and differential scanning calorimetry curves of luminophores **1** (B) and **2** (C).

The fabrication of solid-state devices requires materials to withstand high temperatures and hence the materials should be stable at elevated temperatures. Hence, the thermal stability of phenanthroimidazoles **1** and **2** was checked by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 5.2.). The decomposition temperatures and melting temperatures are given in Table 5.1. The thermal decomposition temperatures ( $T_d$ ) for **1** and **2** are 422 °C and 432 °C respectively and correspond to 5% weight loss under a nitrogen atmosphere. The phenanthroimidazoles **1** and **2** are thermally stable above 400 °C and hence a suitable choice for material applications. The rigid structure of both the molecules leads to a high thermal stability, the phenanthroimidazole **2**

being more stable than **1**. The differential scanning calorimetry (DSC) curves reveal an endothermic process for **1** and **2** and a high melting temperature of 261 °C and 339 °C (Figure 5.2.).

#### 5.4. Photophysical properties



**Figure 5.3.** Electronic absorption spectra of **1** and **2** (A) and normalized fluorescence spectra of **1** and **2** (B) recorded in THF (concentration =  $2 \times 10^{-5}$  M).

**Table 5.1.** Photophysical and thermal properties of **1** and **2**.

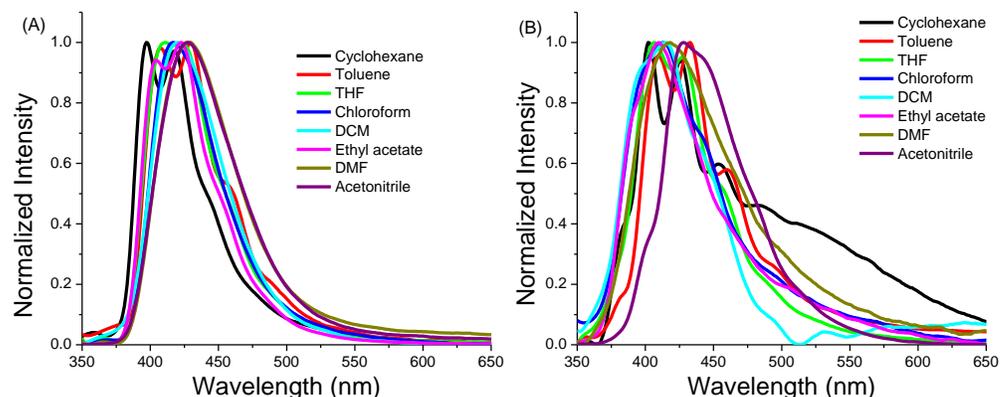
Compounds	$\lambda_{ab}$ [nm $1\text{cm}^{-1}$ ] <sup>a</sup>	$(\epsilon[\text{Lmol}^{-1}$	$\lambda_{em.}$ (nm) <sup>b</sup>	$\Phi_f^c$	$T_d$ (°C)	$T_m$ (°C)
<b>1</b>	253(30028), 342(17487)		413	0.032	422 °C	261 °C
<b>2</b>	255(30180), 355(18532)		413	0.031	432 °C	339 °C

<sup>a,b</sup> Recorded in tetrahydrofuran, <sup>c</sup> The fluorescence quantum yields were recorded using 9,10-diphenylanthracene as a standard in ethanol solution.

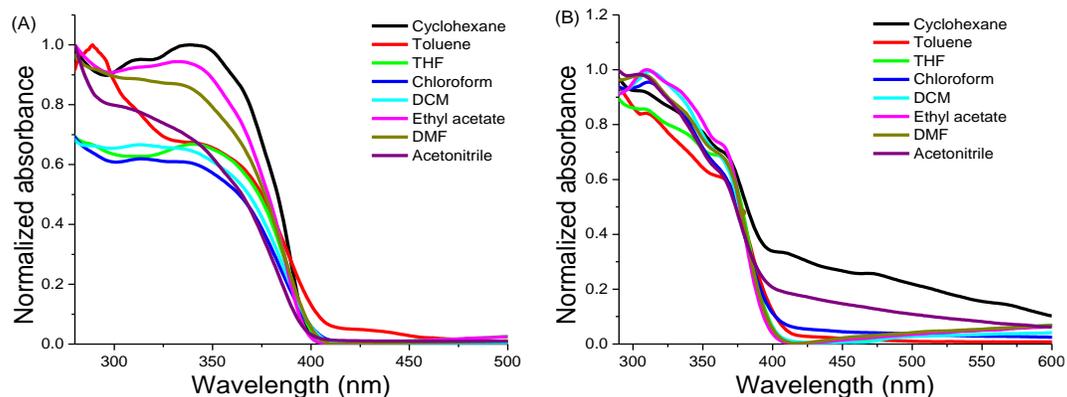
The phenanthroimidazoles **1** and **2** are soluble in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF), chloroform, and hexane but are poorly soluble in water, methanol and acetonitrile. The photophysical properties of **1** and **2** were studied in THF solution using electronic absorption and fluorescence spectroscopy (Figure 5.3.) and the data are listed in Table 5.1. The phenanthroimidazoles **1** and **2** display

absorption peaks at 250 nm and 260 nm respectively corresponding to the combined  $\pi$ - $\pi^*$  transitions of the aromatic segments. The absorption peaks between 340 to 360 nm arise from the delocalized  $\pi$ - $\pi^*$  transitions of the phenanthroimidazole unit.<sup>[17]</sup> The emission spectra reveal emission maximum at 413 nm for both the molecules.

### 5.5. Solvatochromism



**Figure 5.4.** (A) Fluorescence spectra of **1** (A) and **2** (B) in different solvents of varying polarities. (excitation wavelength or  $\lambda_{ex}$  = 340 nm).



**Figure 5.5.** UV-vis absorption spectra of **1** (A) and **2** (B) in different solvents of varying polarities.

The solvatochromism was examined by recording the fluorescence (Figure 5.4.) and absorption spectra (Figure 5.5.) of phenanthroimidazoles **1** and **2** in solvents of varying polarity (cyclohexane, toluene, tetrahydrofuran

(THF), chloroform, dichloromethane (DCM), ethyl acetate, dimethylformamide (DMF) and acetonitrile).

**Table 5.2.** Solvatochromic properties of luminophores **1** and **2**.

Comp.	Solvent	$\lambda_{ab}$ (nm)	$\lambda_{em}$ (nm)	Stokes shift (cm <sup>-1</sup> )	$\Phi_f^a$
<b>1</b>	Cyclohexane	337	397	4484.67	0.0187
	Toluene	340	407	4841.74	0.0438
	Chloroform	337	417	5782.38	0.0153
	DCM	336	420	5952.38	0.0207
	Ethyl acetate	333	422	6333.35	0.0193
	DMF	334	428	6575.63	0.0208
	Acetonitrile	310	428	8893.57	0.0115
<b>2</b>	Cyclohexane	367	402	2372.34	0.0081
	Toluene	361	409	3250.95	0.0276
	Chloroform	365	411	3451.82	0.0100
	DCM	363	415	3066.36	0.0111
	Ethyl acetate	363	409	3098.33	0.0059
	DMF	364	417	3491.71	0.0118
	Acetonitrile	365	428	4026.77	0.0284

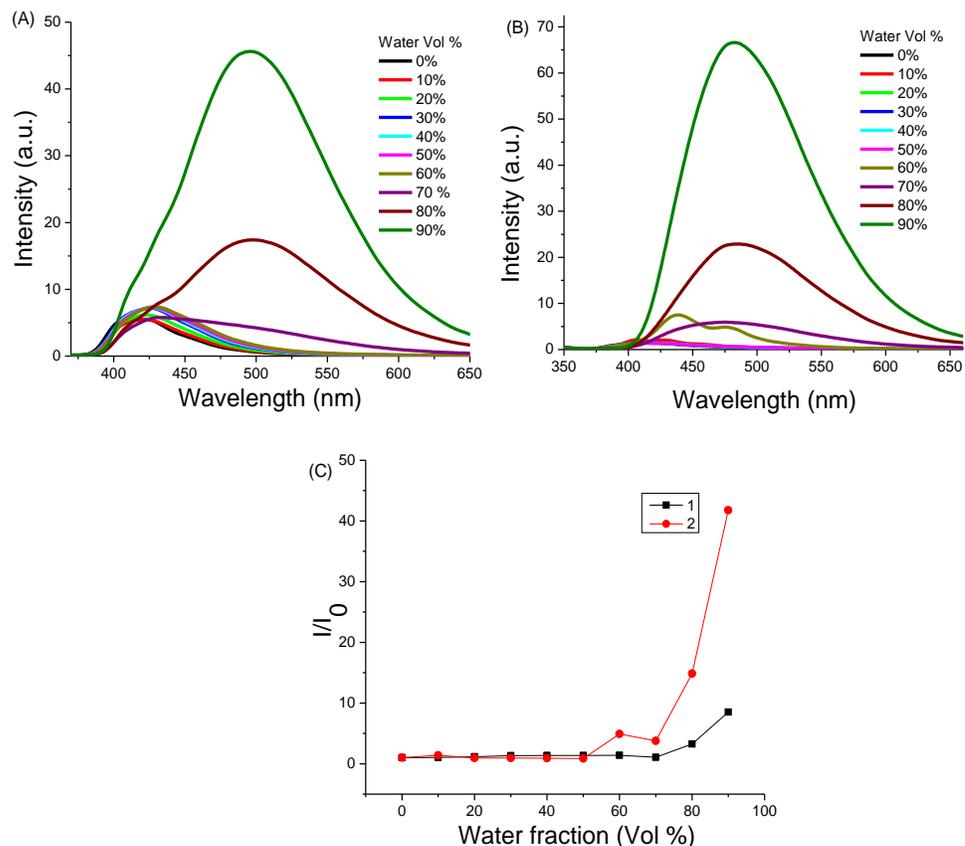
<sup>a</sup>The fluorescence quantum yields were recorded using 9,10-diphenylanthracene as a standard in ethanol solution.

The fluorescence spectra of phenanthroimidazoles **1** and **2** in the non-polar solvents display fine vibrational structure which vanishes in polar solvents; also, emission was red shifted in polar solvents. In non-polar solvent emission arises from the localised excited (LE) state whereas in polar solvents the emission is from charge transfer (CT) state. <sup>[14(b)]</sup> The solvatochromic properties have been compiled in Table 5.2.

### 5.6. Aggregation-induced emission

The TPE moiety is well established for its aggregation-induced emission (AIE) characteristics due to its inbuilt propeller shaped, following which fluorescence spectroscopy was used to study the aggregation-induced

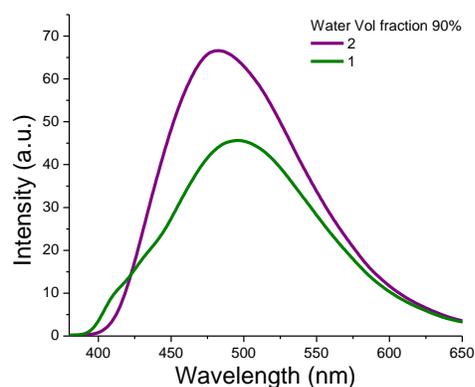
emission (AIE) properties of phenanthroimidazoles **1** and **2** (Figure 5.6.). The phenanthroimidazoles **1** and **2** exhibit good solubility in THF and poor solubility in water. The gradual increase of water percentage in THF solution consequently initiates the formation of nanoaggregates.



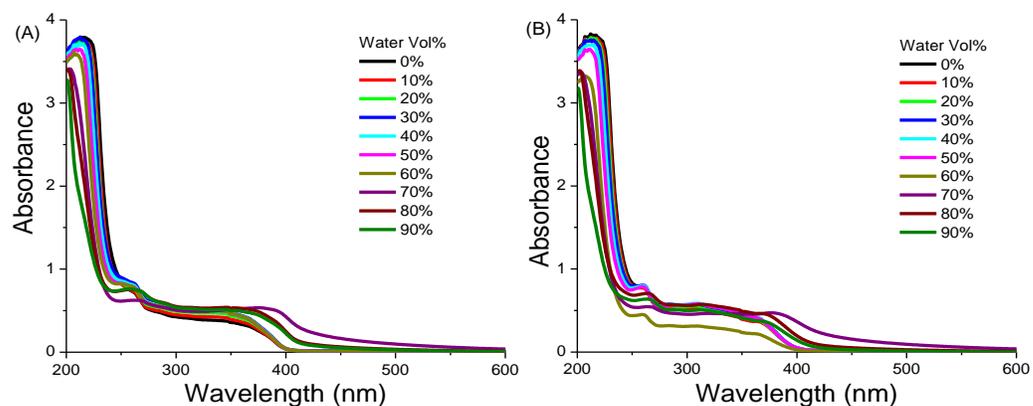
**Figure 5.6.** Fluorescence spectra of **1** (A) and **2** (B) in THF–water mixtures with different water fractions (10  $\mu$ M). (C) Plot of intensity vs % of water fraction ( $f_w$ ). Luminogen concentration: 10  $\mu$ M; intensity calculated at  $\lambda_{max}$ .

The phenanthroimidazoles **1** and **2** are weakly emissive at low water fraction. The relative PLQY at 0% water for **1** is 0.016 and for **2** is 0.005. The non-radiative energy loss of the excited state caused by the free rotation of phenyl rings of the TPE moiety in the solution state renders the solutions non-emissive. The formation of aggregates at higher water percentage restricts the free rotation of phenyl ring resulting in enhanced intensity and red shifted emission. The phenanthroimidazoles **1** and **2** exhibit increase in

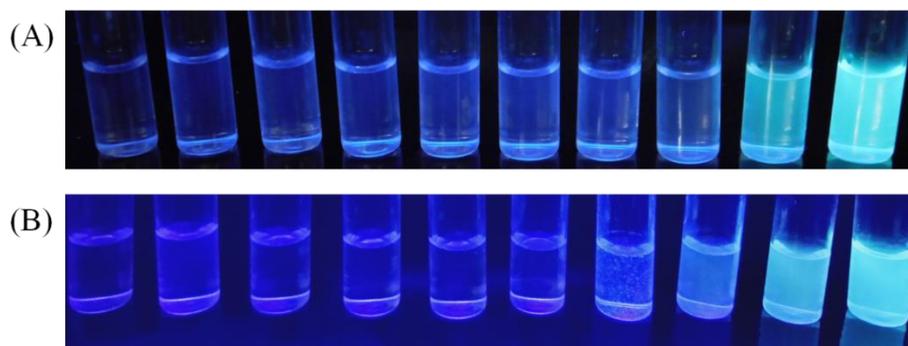
the emission with a bathochromic shift above 60% water fractions respectively due to aggregate formation. There is slight decrease of  $I/I_0$  value at 70% water for both **1** and **2**. The phenanthroimidazole **2** has higher degree of enhancement in intensity as compared to phenanthroimidazole **1** which could be due to the positional effect. The superposition of the emission spectra of **1** and **2** (Figure 5.7.) at 90% water fraction gives a clear idea about the intensity enhancement. The aggregation-induced emission (AIE) behaviour was also studied using absorption spectroscopy (Figure 5.8.). The absorption spectra for phenanthroimidazoles **1** and **2** reveal similar trend of the absorption bands upto 60% water fraction, above which there is scattering of light or Mie effect observed due to formation of nanoaggregates. The aggregation-induced emission (AIE) behaviour of **1** and **2** is shown in photographs (Figure 5.9.) under UV illumination.



**Figure 5.7.** Emission spectra of **1** and **2** at 90% THF-water mixture.



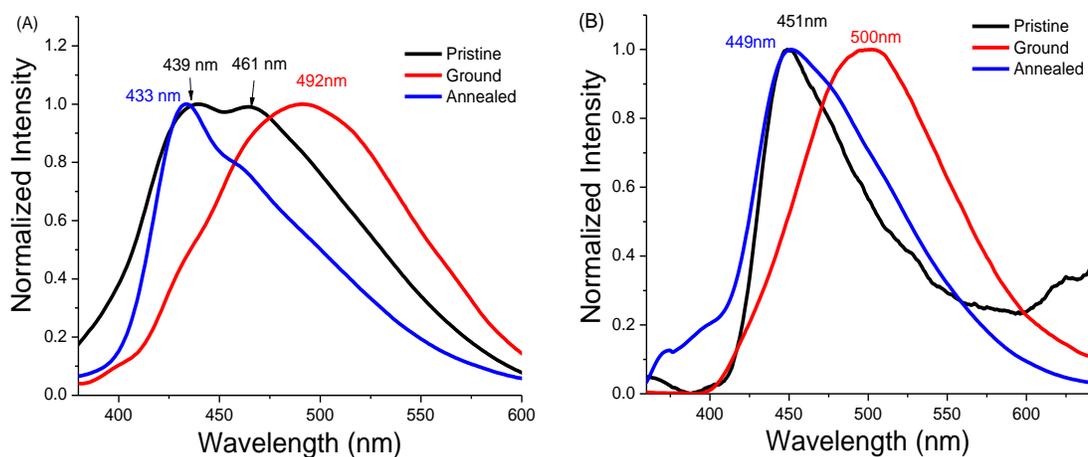
**Figure 5.8.** UV-vis absorption spectra of **1** (A) and **2** (B) in THF–water mixtures with different water fractions.



**Figure 5.9.** Photograph of **1** (A) and **2** (B) in THF–water mixtures with different water fractions (10  $\mu$ M) under 365 nm UV illumination (0% to 90% water fraction from left to right).

### 5.7. Mechanochromism

The phenanthroimidazoles **1** and **2** were presumed to display reversible mechanochromic behaviour on account of the twisted structure of the TPE moiety. The mechanochromic behaviour was studied using the fluorescence spectroscopy (Figure 5.10.) and the data are listed in Table 5.3.



**Figure 5.10.** Emission spectra of **1** (A) and **2** (B) as pristine, ground, and annealed solids.

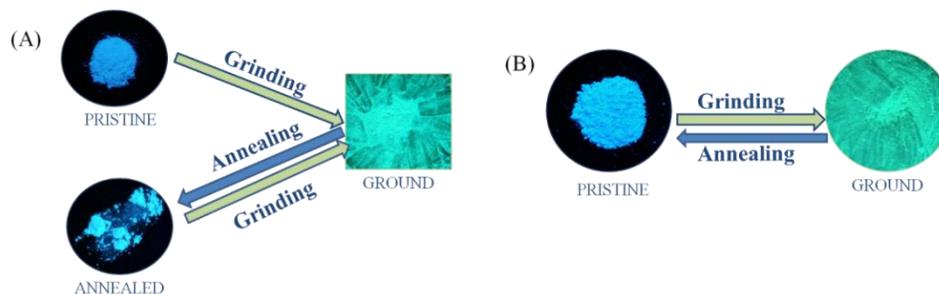
**Table 5.3.** Peak emission wavelengths ( $\lambda$ , in nm) of **1** and **2** as pristine, grinded and annealed solids.

Emission				
Compounds	$\lambda_{\text{pristine}}$ (nm)	$\lambda_{\text{ground}}$ (nm)	$\lambda_{\text{annealed}}$ (nm)	$\Delta\lambda^a$ (nm)
<b>1</b>	461	492	433	59
<b>2</b>	449	500	451	49

<sup>a</sup> Grinding-induced spectral shift,  $\Delta\lambda = \lambda_{\text{ground}} - \lambda_{\text{annealed}}$

The phenanthroimidazoles **1** and **2** were mechanically grinded with the aid of a mortar and pestle. The phenanthroimidazole **1** in its pristine form emits at 439 nm and a lower intensity peak at 461 nm with a bright sky-blue fluorescence, which was red shifted to 492 nm on grinding emitting a bright green fluorescence. In order to check the reversibility of the colour switching, the phenanthroimidazole **1** was annealed at 230 °C for five minutes which resulted in a same blue fluorescence as the pristine sample and with a higher blue shift in the emission wavelength upto 433 nm. The peak at 461 nm could be ascribed to intermediate species which arise from the gentle grinding of the pristine sample. However, a strong grinding results in 492 nm emission band. The results reflect a highly sensitive nature

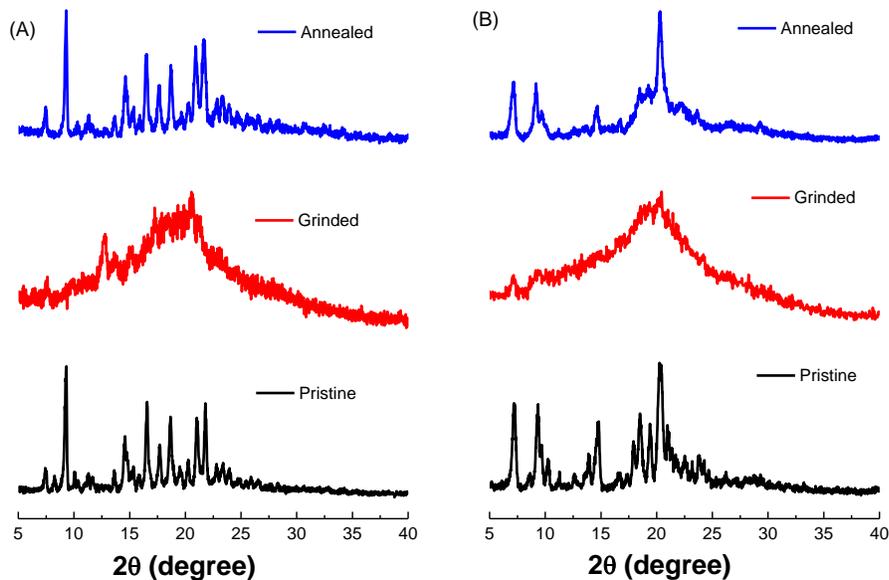
of phenanthroimidazole **1** towards mechanical stimuli. The high sensitivity of phenanthroimidazole **1** could be due to the position of TPA and phenyl-TPE with phenyl-TPE directly attached to N atom of the imidazole ring. The phenanthroimidazole **2** similarly emitted a bright blue fluorescence at 449 nm which was red shifted on grinding to emit a bright green fluorescence at 500 nm reverting to its original form on annealing at 200 °C for five minutes. The absolute quantum yields for phenanthroimidazole **1** in their pristine, grinded and annealed forms are 34.04%, 32.85% and 51.34% respectively. The absolute quantum yields for phenanthroimidazole **2** in their pristine, grinded and annealed forms are 68.09%, 74.07% and 74.00% respectively.



**Figure 5.11.** Photograph of **1** (A) and **2** (B) as pristine, ground, and annealed solids taken under 365 nm UV illumination.

The photographs of pristine, grinded and annealed solids taken under UV illumination are displayed in Figure 5.11. The phenanthroimidazoles **1** and **2** exhibited a grinding induced spectral shift of 59 nm and 49 nm respectively.

## 5.8. Powder X-ray diffraction studies

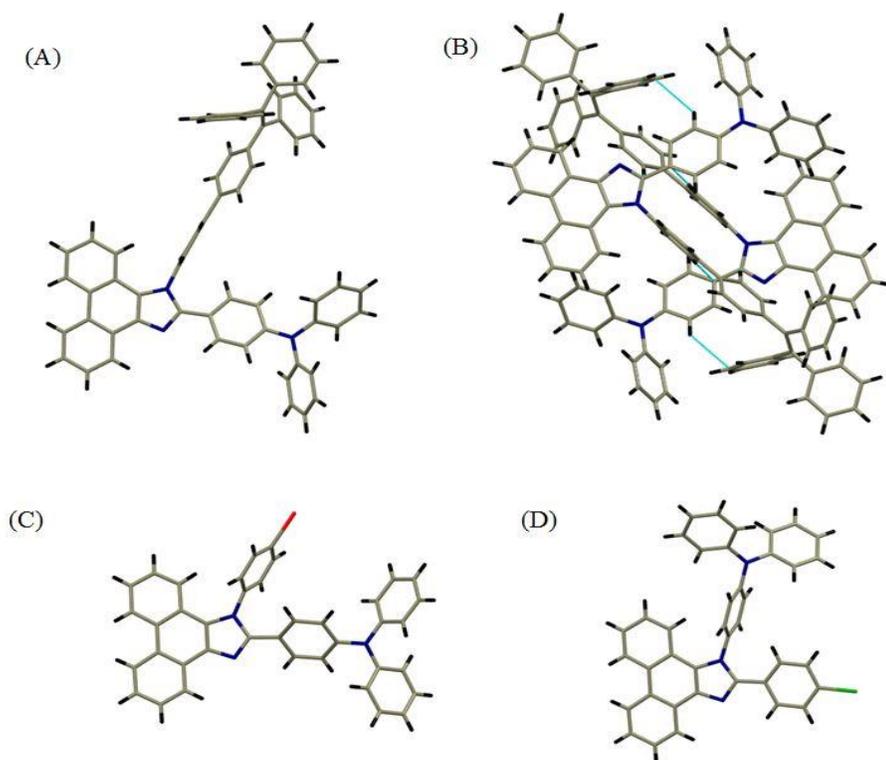


**Figure 5.12.** Powder X-ray diffraction curves of **1** (A) and **2** (B) in pristine, grinded and annealed forms.

The powder X-ray diffraction studies (PXRD) studies (Figure 5.12.) were performed to gain an insight about the morphological change which could be a possible reason associated with the reversible mechanochromic behaviour. The phenanthroimidazoles **1** and **2** in their pristine form displayed sharp and intense diffraction peaks which can be attributed to crystalline structures. The sharp diffraction peaks disappear on grinding giving a broad band indicating the morphological change from crystalline state to amorphous state caused due to grinding. The crystallinity of the phenanthroimidazoles is resumed on annealing which is clearly seen by the sharp diffraction peaks.

## 5.9. Single crystal X-ray analysis

The single crystal of **1**, **3** and **4** were obtained by slow diffusion of ethanol in DCM solution of the compounds. The single crystal of phenanthroimidazole **1** was beneficial in further understanding its mechanochromic and AIE behaviour.



**Figure 5.13.** (A) Crystal structure of phenanthroimidazole **1**. (B) Packing diagram of phenanthroimidazole **1**. (C) Crystal structure of intermediate **3**. (D) Crystal structure of intermediate **4**.

The single crystal of **1** (Figure 5.13.(A)) shows that the TPA and phenyl-TPE unit adopt twisted conformations. In aggregated state, the twisted conformation brings a restraint on the  $\pi$ - $\pi$  stacking interaction resulting in intensified emissions. The crystal packing diagram reveals only C-H interactions and no H-bonding or  $\pi$ - $\pi$  interactions which make it loosely packed making it sensitive to grinding thereby allowing mechanochromism. The single crystal of intermediate **3** (Figure 5.13.(C)) and **4** (Figure 5.13.(D)) reveal a propeller orientation of the TPA unit. The TPA unit and the iodo-substituted phenyl ring in intermediate **3** are not in plane of the phenanthroimidazole unit and exhibit highly twisted geometry. Similarly, the TPA unit in intermediate **4** has a highly twisted geometry. However, the bromo-substituted phenyl ring is coplanar to the phenanthroimidazole unit with a slight twisting. The data for the crystals are summarized in Table 5.4.

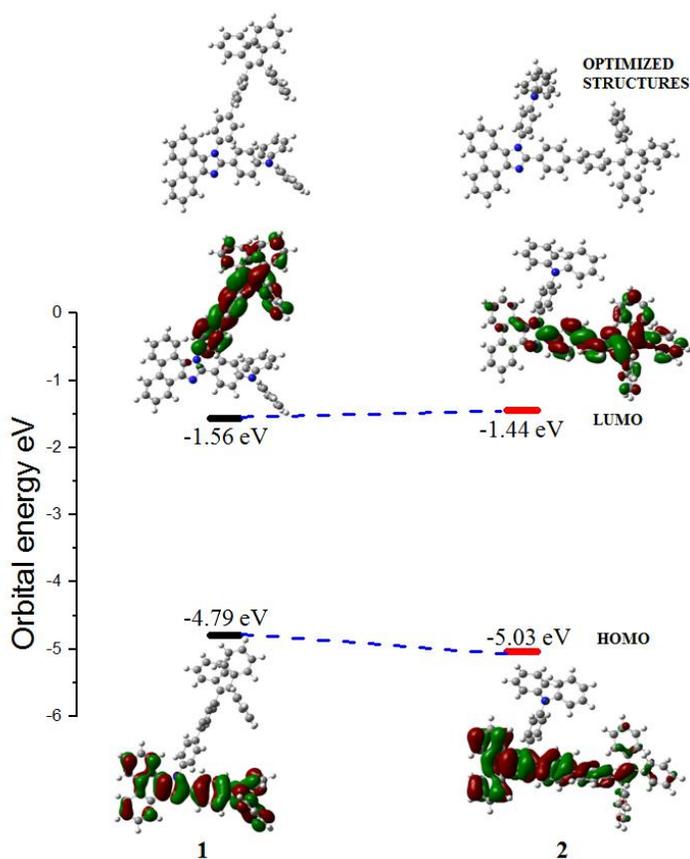
**Table 5.4.** Crystal data and structure refinement for **1**, **3** and **4**.

Identification code		rm230	rm193
Empirical formula	C <sub>65</sub> H <sub>45</sub> N <sub>3</sub>	C <sub>39</sub> H <sub>27</sub> I N <sub>3</sub>	C <sub>39</sub> H <sub>26</sub> BrN <sub>3</sub>
Formula weight	868.04	664.53	616.54
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	1.54184 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P -1	Triclinic, P -1	Monoclinic, P21/n
a/(Å)	11.0325(4)	8.1689(12) Å	16.0838(5)
b/(Å)	13.8922(5)	11.2594(9) Å	6.9446(2)
c/(Å)	17.6967(8)	17.439(2) Å	26.8363(7)
Alpha/(°)	100.024(4)	96.245(9)	90
Beta/(°)	94.455(4)	91.993(13)	91.926(3)
Gamma/(°)	109.496(4)	101.903(10)	90
Volume	2490.68(18) Å <sup>3</sup>	1557.4(3) Å <sup>3</sup>	2995.80(15) Å <sup>3</sup>
Z, Calculated density	2, 1.157 mg/m <sup>-3</sup>	2, 1.417 mg/m <sup>-3</sup>	4, 1.367 Mg/m <sup>-3</sup>
Absorption coefficient	0.513 mm <sup>-1</sup>	1.060 mm <sup>-1</sup>	1.405 mm <sup>-1</sup>
F(000)	912	670	1264
Crystal size	0.230 x 0.180 x 0.120 mm	0.230 x 0.180 x 0.130 mm	0.260 x 0.210 x 0.180 mm
Θ range for data collection/(°)	3.454 to 71.472	3.032 to 28.846	2.911 to 32.252
Reflections collected / unique	16838 / 9463 [R(int) = 0.0683]	13182 / 7155 [R(int) = 0.0921]	37707 / 9935 [R(int) = 0.0923]
Completeness to theta	Θ = 67.684 99.8 %	Θ = 25.242 99.8 %	Θ = 25.242 99.9 %

Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.70721	1.00000 and 0.48753	1.00000 and 0.78417
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9463 / 630 / 669	7155 / 0 / 389	9935 / 0 / 389
Goodness-of-fit on F <sup>2</sup>	1.072	1.316	1.005
Final R indices [I > 2σ(I)]	R1 = 0.0780, wR2 = 0.2241	R1 = 0.1382, wR2 = 0.3736	R1 = 0.0630, wR2 = 0.1208
R indices (all data)	R1 = 0.0889, wR2 = 0.2348	R1 = 0.1809, wR2 = 0.4207	R1 = 0.1815, wR2 = 0.1661
Extinction coefficient	n/a	0.072(10)	0.0014(3)
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.348 and -0.387	1.848 and -1.929	0.351 and -0.531

## 5.10. Theoretical calculations

In order to get a clear understanding about the geometry and electronic structures of phenanthroimidazoles **1** and **2**, the density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level.<sup>[18]</sup> The optimized structures, calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for phenanthroimidazoles **1** and **2** are as shown in Figure 5.14. and the data are compiled in Table 5.5.



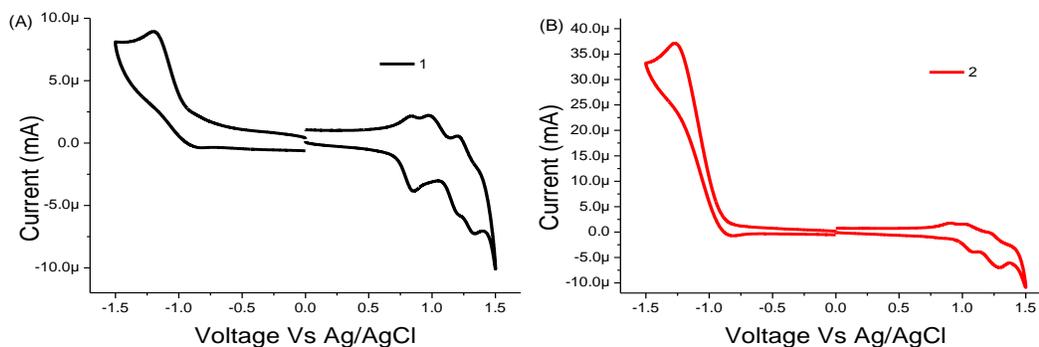
**Figure 5.14.** Correlation diagram showing the optimized structures, HOMO and LUMO wave functions and energies of **1** (left) and **2** (right), as determined at the B3LYP/6-31G(d,p) level.

The optimized structures of phenanthroimidazoles **1** and **2** reveal a twisted geometry of the TPE and TPA unit. The HOMO and LUMO are well

separated in phenanthroimidazole **1**, the HOMO mainly localized on the phenanthroimidazole and the TPA unit whereas the LUMO is localized on the TPE unit. However, in phenanthroimidazole **2** the HOMO and LUMO are not well separated and mainly localized on the TPE and imidazole unit. The attachment of the TPE unit through the N atom of the phenanthroimidazole in **1** causes a disruption in the extended conjugation resulting in a better separation of the molecular orbitals. In phenanthroimidazole **2**, the TPE unit is attached by the carbon atom of the imidazole ring producing a highly extended conjugation allowing the molecular orbitals to be delocalized on the whole molecule. The theoretical HOMO–LUMO gap of phenanthroimidazole **1** and **2** are 3.23 eV and 3.59 eV respectively.

### 5.11. Electrochemical studies

The electrochemical properties and the energy levels of the phenanthroimidazoles **1** and **2** were examined by performing the cyclic voltammetry experiment in dichloromethane (DCM) using tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte. The cyclic voltamograms (Figure 5.15.) of phenanthroimidazole **1** and **2** reveal quasi-reversible oxidation and reduction waves. The energies for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by applying the equation  $\text{HOMO/LUMO} = - (E_{\text{onset}} + 4.4) \text{ eV}$ , where  $E_{\text{onset}}$  is value of onset of oxidation or reduction wave<sup>[19]</sup> The energy values for HOMO of phenanthroimidazole **1** and **2** are -5.12 eV and -5.36 eV respectively, whereas the energy values for LUMO of **1** and **2** are -3.48 eV and -3.54 eV respectively.



**Figure 5.15.** Cyclic voltammetry (CV) plots of **1**(A) and **2**(B).

The resulting electrochemical HOMO-LUMO gap for phenanthroimidazoles **1** and **2** are 1.64 eV and 1.82 eV respectively. The electrochemical HOMO-LUMO gap and theoretical HOMO-LUMO gap follow the same trend and are higher for the phenanthroimidazole **2**. The data of electrochemical studies are compiled in Table 5.5.

**Table 5.5.** Electrochemical and theoretical properties of **1** and **2**.

No.	Electrochemical properties		Theoretical properties			
	HOMO <sup>a</sup> eV	LUMO <sup>a</sup> eV	HOMO- LUMO gap eV	HOMO <sup>b</sup> eV	LUMO <sup>b</sup> eV	HOMO- LUMO gap Ev
<b>1</b>	-5.12	-3.48	1.64	-4.79	-1.56	3.23
<b>2</b>	-5.36	-3.54	1.82	-5.03	-1.44	3.59

<sup>a</sup> Calculated from CV: Reference electrode- Ag/AgCl <sup>b</sup> Theoretical values at B3LYP/6-31g(d,p) level.++iop v+.

## 5.12. Experimental details

### General Methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were

recorded on a Bruker Avance III instrument by using CDCl<sub>3</sub>. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet), and the coupling constants, *J*, are given in hertz. <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). Thermogravimetric analyses were performed on the Mettler Toledo thermal analysis system. UV–visible absorption spectra were recorded on a Cary-100 Bio UV–visible spectrophotometer. Emission spectra were taken in a The Fluoromax-4C, S/n.1579D-1417-FM Fluorescence software Ver 3.8.0.60. The excitation and emission slits were 2/2 nm for the emission measurements. All of the measurements were done at 25 °C. HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. The voltammograms were recorded on a CHI620D electrochemical analyzer in dichloromethane solvent and 0.1 M TBAF<sub>6</sub> as the supporting electrolyte. The electrodes used were glassy carbon as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode. Single-crystal X-ray structural studies of **1** and **4** were performed on a CCD equipped SUPERNOVA diffractometer from Agilent Technologies with Oxford Instruments low-temperature attachment under argon/nitrogen using standard Schlenk and vacuum-line techniques.

### **Synthesis and characterization of intermediates 3 and 4:**

**3:** A mixture of 9,10-phenanthrenequinone (2.54 mmol), 4-(diphenylamino)benzaldehyde (2.80 mmol), 4-iodoaniline (3.04 mmol) and ammonium acetate (25.4 mmol) was refluxed in glacial acetic acid (10 mL) were for 4 h under an argon atmosphere. The reaction was cooled to room temperature and was added to a methanol solution with continuous stirring. The resulting solid was filtered, washed with 30 mL water and dried to obtain intermediate **3** as a pale yellow solid. Yield: 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.86 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H),

8.70 (d,  $J = 8.0$  Hz, 1H), 7.94 (d,  $J = 8.0$  Hz, 2H), 7.73 (t,  $J = 8.0$  Hz, 1H), 7.65 (t,  $J = 8.0$  Hz, 1H), 7.52 (t,  $J = 8.0$  Hz, 1H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.26–7.34 (m, 7H), 7.19 (d,  $J = 8.0$  Hz, 1H), 7.05–7.11 (m, 6H), 6.97 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  150.7, 148.6, 147.1, 139.4, 138.7, 131.0, 130.1, 129.4, 129.2, 128.2, 127.7, 127.3, 127.0, 126.4, 125.7, 125.1, 124.9, 124.2, 123.6, 123.1, 122.8, 121.8, 120.6, 0.0 ppm. HRMS (ESI): Calcd. for  $[\text{M} + \text{H}]^+$ : 664.128. Found: 664.1244.

**4:** A mixture of 9,10-phenanthrenequinone (3.60 mmol), 4-bromobenzaldehyde (3.96 mmol),  $\text{N}'\text{,N}'$ -diphenylbenzene-1,4-diamine (4.32 mmol) and ammonium acetate (36.0 mmol) was refluxed in glacial acetic acid (15 mL) were for 4 h under an argon atmosphere. The reaction was cooled to room temperature and was poured in methanol solution with continuous stirring. The resulting solid was filtered, washed with 30 mL water and dried to give intermediate **4** as a grey coloured solid. Yield: 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.84 (d,  $J = 8.0$  Hz, 1H), 8.76 (d,  $J = 8.0$  Hz, 1H), 8.70 (d,  $J = 8.0$  Hz, 1H), 7.74 (t,  $J = 8.0$  Hz, 1H), 7.65 (t,  $J = 8.0$  Hz, 1H), 7.46–7.58 (m, 6H), 7.35–7.42 (m, 5H), 7.27–7.30 (m, 2H), 7.20–7.24 (m, 6H), 7.14 (t,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  149.8, 149.1, 146.9, 137.2, 131.3, 131.1, 130.8, 129.6, 129.6, 129.5, 129.3, 128.4, 128.2, 127.3, 127.1, 126.2, 125.6, 125.3, 125.0, 124.2, 124.1, 123.3, 123.1, 123.0, 122.7, 122.6, 120.9, 0.0 ppm. HRMS (ESI): Calcd. for  $[\text{M} + \text{H}]^+$ : 616.1363. Found: 616.1383.

### **Synthesis and characterization of phenanthroimidazoles **1** and **2**:**

General procedure for synthesis of phenanthroimidazole **1** and **2**.  $\text{Pd}(\text{PPh}_3)_4$  (0.04 mmol) was added to a well degassed solution of intermediate **3** (0.4 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester (0.52 mmol),  $\text{K}_2\text{CO}_3$  (2.0 mmol) in a mixture of toluene (24.0 mL)/ethanol (8.0 mL)/ $\text{H}_2\text{O}$  (4.0 mL). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue subjected to column chromatography on silica (Hexane–

DCM 50:50 in vol) to yield the desired product **1** as a white powder. The same procedure was employed using intermediate **4** to obtain the desired product **2** as a white powder.

**1.** Yield: 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.87 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.47–7.57 (m, 7H), 7.23–7.27 (m, 8H), 7.02–7.20 (m, 22H), 6.95 (d, *J* = 8.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ 147.2, 143.9, 143.6, 143.6, 141.8, 141.5, 140.2, 137.0, 132.1, 131.4, 131.3, 130.1, 129.4, 129.3, 129.1, 128.3, 127.9, 127.8, 127.7, 126.6, 126.6, 126.3, 125.0, 124.1, 123.5, 123.1, 121.9, 124.1, 120.9, 0.0 ppm. HRMS(ESI): Calcd. for [M + H]<sup>+</sup>: 868.3687. Found: 868.3686.

**2.** Yield: 76%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.87 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.0 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 7.72–7.76 (m, 3H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.53–7.57 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.32–7.41 (m, 9H), 7.20–7.23 (m, 7H), 7.04–7.13 (m, 19H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ 150.8, 149.0, 147.0, 143.7, 143.7, 143.2, 141.3, 140.7, 140.7, 140.4, 137.9, 137.4, 131.9, 131.6, 131.4, 131.3, 131.3, 129.7, 129.7, 129.6, 129.4, 129.3, 128.4, 128.2, 127.8, 127.7, 127.6, 127.3, 127.2, 126.5, 126.5, 126.5, 126.2, 126.1, 125.5, 125.2, 124.8, 124.1, 124.0, 123.2, 123.1, 122.8, 122.7, 0.0 ppm. HRMS(ESI): Calcd. for [M + H]<sup>+</sup>: 868.3701. Found: 868.3686.

### 5.13. Conclusion

In conclusion, we have designed and synthesized positional isomers of phenanthroimidazole comprising of a phenyl-TPE and TPA unit, using a Suzuki cross-coupling reaction. The phenanthroimidazole **1** and **2** exhibit high thermal stability making them suitable for practical applications. The single crystal of phenanthroimidazole **1** reveals a propeller orientation of the TPA unit and TPE unit which is well in accordance with the theoretically optimized structure. The phenanthroimidazole **1** and **2** display strong aggregation-induced emission (AIE) characteristics and are excellent solid-

state emitters. The phenanthroimidazole **1** and **2** display reversible emission changes in response to mechanical stimuli with a good colour contrast. The positional change results in the high sensitivity of phenanthroimidazole **1** towards mechanical stimuli as compared to **2**. The PXRD studies show that a morphological change from amorphous state to crystalline state is associated with the color change. The DFT studies reveal better separation of HOMO and LUMO in phenanthroimidazole **1** compared to phenanthroimidazole **2** which is an attribute of the positions. The inclusion of TPA and TPE on the phenanthroimidazole unit provides a new approach for the development of stimuli responsive solid-state emitters. The combination of phenanthroimidazole, TPA and TPE synergistically result in the high solid-state emission which can be further employed in optoelectronic applications.

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## Chapter 6

### Stimuli-responsive phenothiazine-based donor-acceptor isomers:

#### AIE, mechanochromism and polymorphism

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##### 6.1. Introduction

The development of emissive organic molecules responsive to external stimuli (pressure, temperature, heat, acid *etc.*)<sup>[1]</sup> has advanced the production of organic light emitting diodes (OLEDs), memory and data storage devices, sensors, security inks, fluorescent probes and switches, pressure sensors and other optoelectronic devices.<sup>[2]</sup> Mechanofluorochromic (MFC) have emerged as *smart* stimuli-responsive materials, which have their solid-state emission profiles reversibly responsive to mechanical grinding.<sup>[3]</sup> Considerable emission in solid state is essential for construction of MFC materials.<sup>[4]</sup> Typical organic fluorophores like pyrene, anthracene have substantial amount of  $\pi$ - $\pi$  stacking in their aggregated state owing to which they dissipate their excited state energy non-radiatively which is well known as aggregation caused quenching (ACQ).<sup>[5]</sup> This drawback has been successfully addressed by Tang *et al.* by establishing the idea of aggregation-induced emission (AIE). The non-planar framework of AIEgens minimize the  $\pi$ - $\pi$  stacking and as a consequence of restriction of intramolecular rotation (RIR) result in enhancement of emission in aggregated state.<sup>[6]</sup> The mechanically induced switchable emission leads to phase transformation and can be regulated easily by a variety of factors.<sup>[7]</sup> The MFC behaviour can be tuned by subtle changes in the molecular packing which are dependent on twisting or planarity in the structures, steric hindrance, inclusion of alkyl chains or heavy atoms, intermolecular interactions due to heteroatom or halogen effect, positional isomerization *etc.*<sup>[8]</sup> Polymorphism is a phenomenon in which organic molecules that can adopt different conformations exist in

more than one crystalline form for the same molecular skeleton.<sup>[9]</sup> The generation of polymorphs can result in distinct molecular packing modes which is also an effective strategy for realizing MFC behaviour in solid state.<sup>[10]</sup>

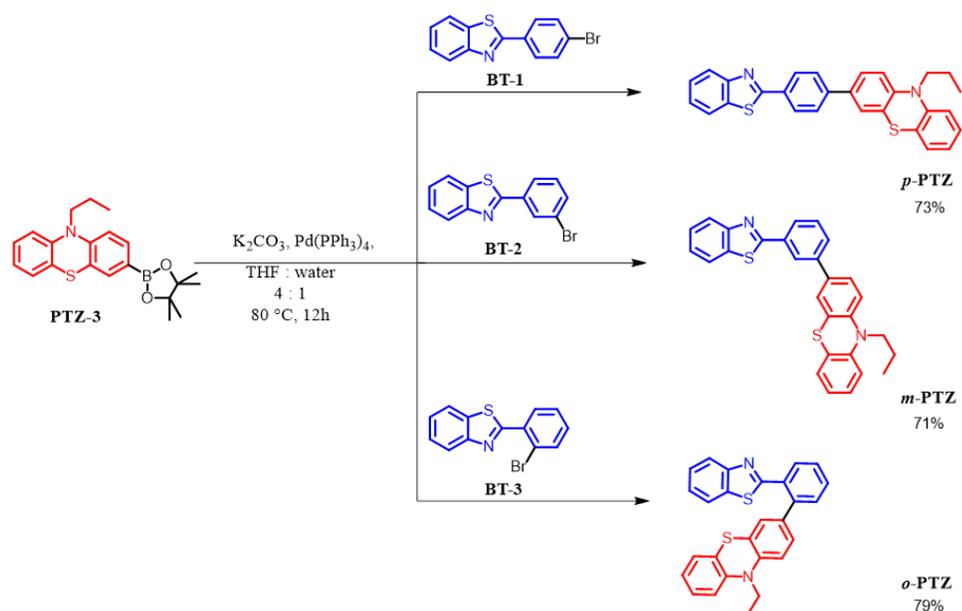
The D-A, D-A-D or D- $\pi$ -A organic frameworks have been utilized to create emissive solid-state materials displaying MFC behaviour.<sup>[11]</sup> The incorporation of non-planar twisted AIEgens like tetraphenylethylene (TPE), hexaphenylsilole (HPS), cyanostilbene *etc.* in organic donor-acceptor architectures assist in achieving high emission in aggregated state by reducing stacking and can easily get converted in different metastable states by forming more planar structures.<sup>[12]</sup> Phenothiazine (PTZ) is a familiar core with good utility in devices like OLEDs, solar cells, chemosensors and thermally activated delayed fluorescence (TADF) materials. The PTZ moiety has also surfaced as a desirable component for MFC materials following its strong electron donating nature due to “S” and “N” atoms and an unusual butterfly shape of the central heterocyclic ring.<sup>[13]</sup> Benzothiazole (BT) is a popular electron acceptor which has many pharmacological as well as material applications with easy functionalization and facile synthesis.<sup>[14]</sup> The integration of BT moiety with PTZ moiety may give rise to interesting emissive properties in solid state. In our previous work, we have coupled the BT core with TPE and investigated its AIE and MFC properties.<sup>[15]</sup> In the present contribution, we have coupled the PTZ moiety to the phenyl ring of the BT moiety at its *para*, *meta* and *ortho* position to yield D-A positional isomers ***p*-PTZ**, ***m*-PTZ** and ***o*-PTZ** respectively. The combination of BT and PTZ could produce highly emissive solid-state materials with fascinating AIE and MFC properties. The free heteroatoms in the two moieties have the ability to display supramolecular interactions and weak hydrogen bonding that can easily affect the solid-state properties. The functionalization of the donor PTZ at *para*, *meta* and *ortho* positions of acceptor phenyl **BT** was exploited to modulate the donor-acceptor character and molecular packing in the

isomers. The N-atom of PTZ moiety was alkylated using propyl chain for increasing its solubility. The twisting induced by positional isomerization results in enhancement in intensity in aggregated state with reversible MFC and effectively sense trifluoroacetic acid (TFA). Additionally, the conformational flexibility of N-alkylated PTZ moiety gives rise to self-reversible colour switching and polymorphism. The isomers display contrast charge transfer characteristics due to formation of twisted intramolecular charge transfer (TICT) state. The present study shows a detailed comparison of the AIE, mechanochromic, solvatochromic and photophysical of the D-A positional isomers *p*-PTZ, *m*-PTZ and *o*-PTZ.

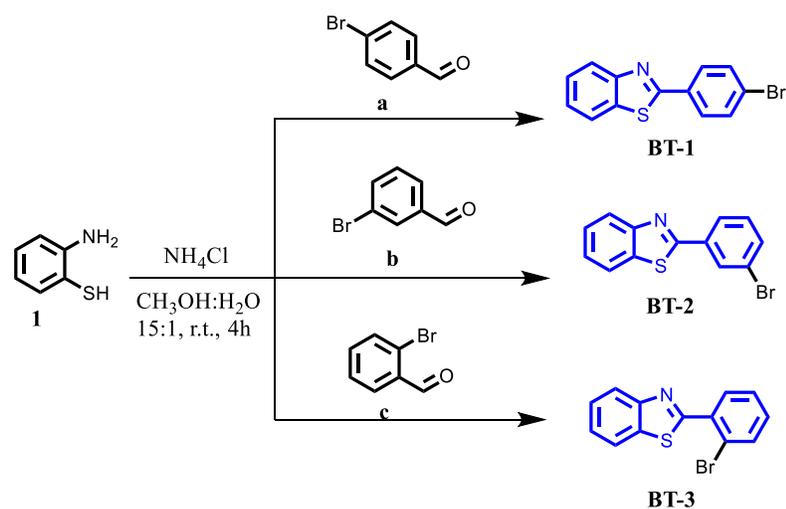
## 6.2. Results and Discussions

### Synthesis

The isomers *p*-PTZ, *m*-PTZ and *o*-PTZ involving a positional change of the phenothiazine (PTZ) moiety at the *para*, *meta* and *ortho* positions of the phenyl benzothiazole BT ring were synthesized as discussed in Scheme 6.1. The condensation reaction of 2-aminobenzenethiol **1** with 4-bromobenzaldehyde **a**, 3-bromobenzaldehyde **b** and 2-bromobenzaldehyde **c** using ammonium chloride in methanol/water produced the respective benzothiazole intermediates **BT-1**, **BT-2** and **BT-3** (Scheme 6.2).<sup>[16a]</sup> The **PTZ** moiety was converted into N-propyl phenothiazine boronate **PTZ-3** ester by a three-step approach (Scheme 6.2).<sup>[16b]</sup>



**Scheme 6.1.** Synthesis of isomers *p*-PTZ, *m*-PTZ and *o*-PTZ.

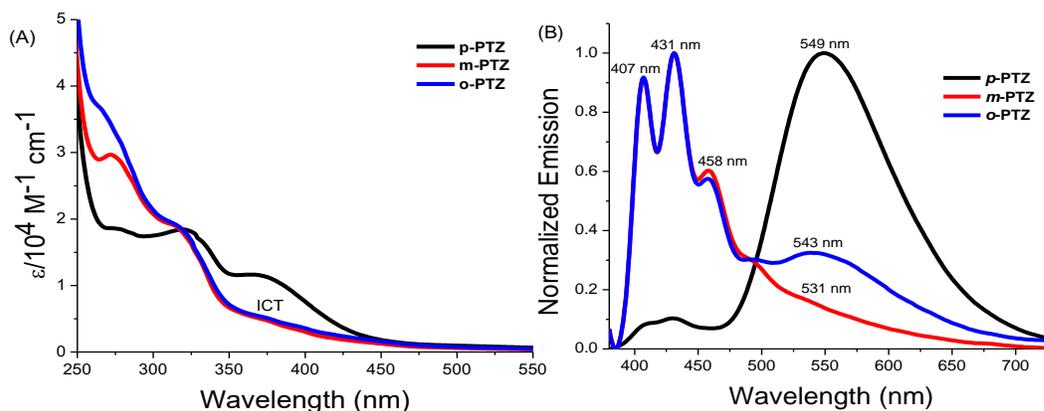


**Scheme 6.2.** Synthetic routes to intermediates.

The alkylation of **PTZ** using N-propyl iodide resulted in 10-propyl-10*H*-phenothiazine **PTZ-1** which on selective bromination with bromine in acetic acid yielded 3-bromo-10-propyl-10*H*-phenothiazine **PTZ-2**. The  $Pd(dppf)Cl_2$  catalysed borylation reaction of **PTZ-2** and bis-pinnacolatodiboron in 1,4-dioxane afforded N-propyl phenothiazine boronate ester **PTZ-3**. The **PTZ-3** was coupled in presence of  $Pd(PPh_3)_4$

with **BT-1**, **BT-2** and **BT-3** via Suzuki-cross coupling reaction to successfully form the desired isomers *p*-PTZ, *m*-PTZ and *o*-PTZ in 73%, 71% and 79% yields, respectively. All the isomers have good solubility in common organic solvents such as tetrahydrofuran (THF), dichloromethane (DCM), chloroform, toluene *etc.* and were completely characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, HRMS and single crystal X-ray analysis.

### 6.3. Photophysical Properties



**Figure 6.1.** Electronic absorption spectra (A) and normalized emission spectra (B) of isomers *p*-PTZ, *m*-PTZ and *o*-PTZ measured in chloroform ( $2 \times 10^{-5}$  M).

The photophysical properties of the isomers *p*-PTZ, *m*-PTZ and *o*-PTZ were examined in chloroform solution by electronic absorption and emission spectroscopy (Figure 6.1.). The absorption spectra (Figure 6.1. (A)) of the isomers show bands at shorter wavelength region (250–330 nm) which could be assigned to the  $\pi\text{-}\pi^*$  transitions. The *p*-PTZ isomer shows a very strong absorption band at 375 nm possibly due to the intramolecular charge transfer (ICT) occurring from the donor PTZ to the acceptor BT moiety. A significant change was observed in the optical properties on positional change. The charge transfer band at 372 nm in *m*-PTZ and *o*-PTZ are weakened as compared to *p*-PTZ. This could possibly be explained by the formation of a twisted intramolecular charge transfer state due to the higher amount of twisting in *meta* and *ortho* isomers as compared to *para*.

The emission spectra of the isomers also confirm the different optical properties of *p*-PTZ (Figure 6.1. (B)). All the isomers show emission between 400–500 nm which could be ascribed to the localized excited (**LE**) states in the molecules. Other than the LE emission, the *p*-PTZ exhibits a strong emission at 549 nm which could be ascribed to ICT transition. On the other hand, the *m*-PTZ and *o*-PTZ have significant LE emissions and low intensity ICT emissions at longer wavelength (above 500 nm). The photophysical data are summarized in Table 6.1. and the effect of positional change on the ICT transition have been explored in detail using solvatochromic studies.

**Table 6.1.** Photophysical properties of isomers *p*-PTZ, *m*-PTZ and *o*-PTZ.

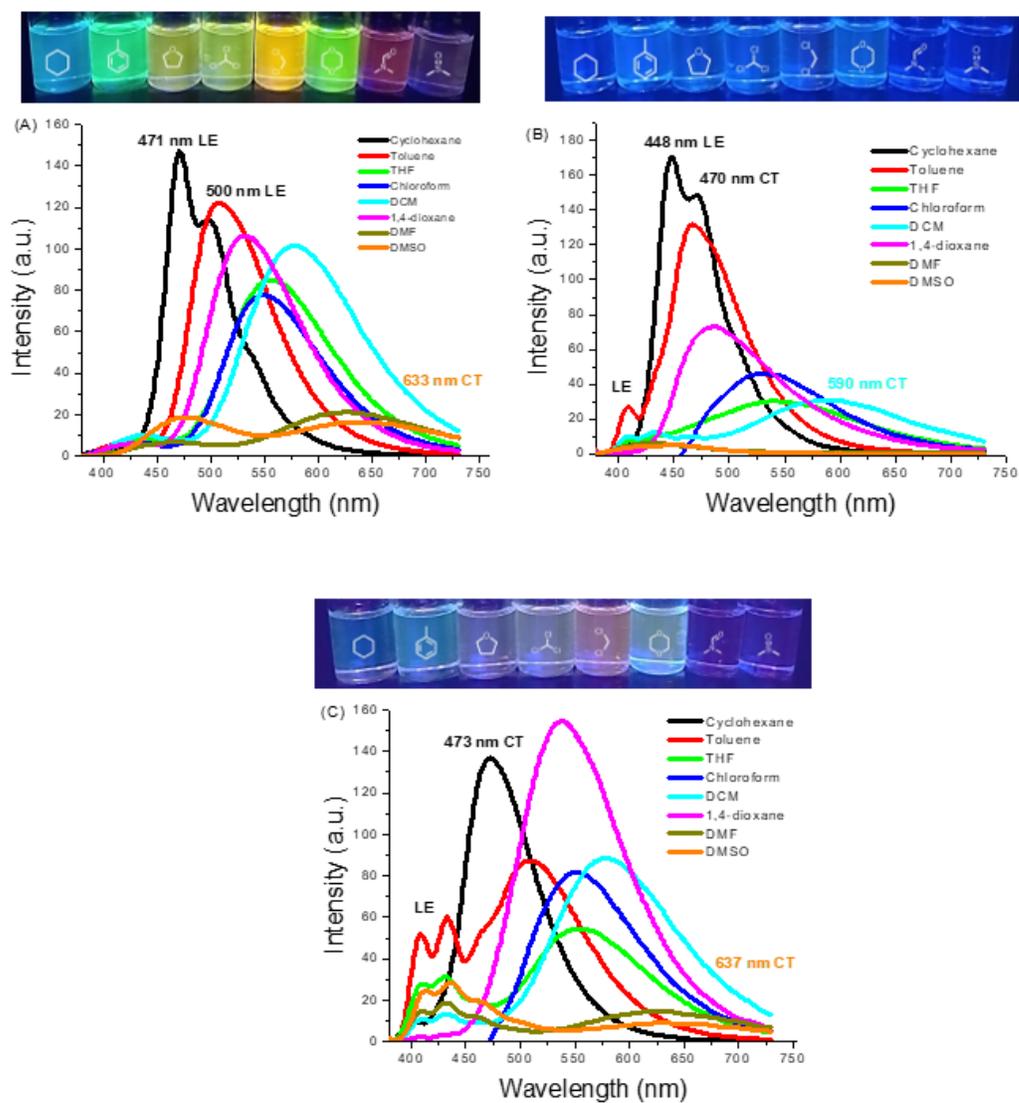
Compounds	$\lambda_{ab}[\text{nm}] (\epsilon[\text{Lmol}^{-1}\text{cm}^{-1}])^a$	$\lambda_{em} (\text{nm})^a$	$\phi^b$
<i>p</i> -PTZ	272(18620), 324(18200), 375(11280)	407,431,549	0.63
<i>m</i> -PTZ	272(29675), 316(18760), 372(4920)	407,431,458,531	0.11
<i>o</i> -PTZ	265(36730), 314(19265), 372(5280)	407,431,458,543	0.16

<sup>a</sup> Measured in chloroform ( $2 \times 10^{-5}$  M), <sup>b</sup> Fluorescence quantum yields recorded using quinine sulphate as a standard in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution ( $\lambda_{exc} = 370\text{nm}$ ).

#### 6.4. Solvatochromism

The ICT transition arising in D-A molecules is easily affected by changes in solvent polarity and could be further influenced by the positional change in *p*-PTZ, *m*-PTZ and *o*-PTZ.<sup>[17a]</sup> The isomers were dissolved in solvents of different polarity from non-polar to polar (cyclohexane, toluene, THF, chloroform, DCM, 1,4-dioxane, dimethylformamide (DMF), dimethylsulphoxide (DMSO)) and the effect of solvent polarity and

positional change on ICT transition was explored in detail by emission (Figure 6.2.) and absorption spectroscopy (Figure 6.3.).

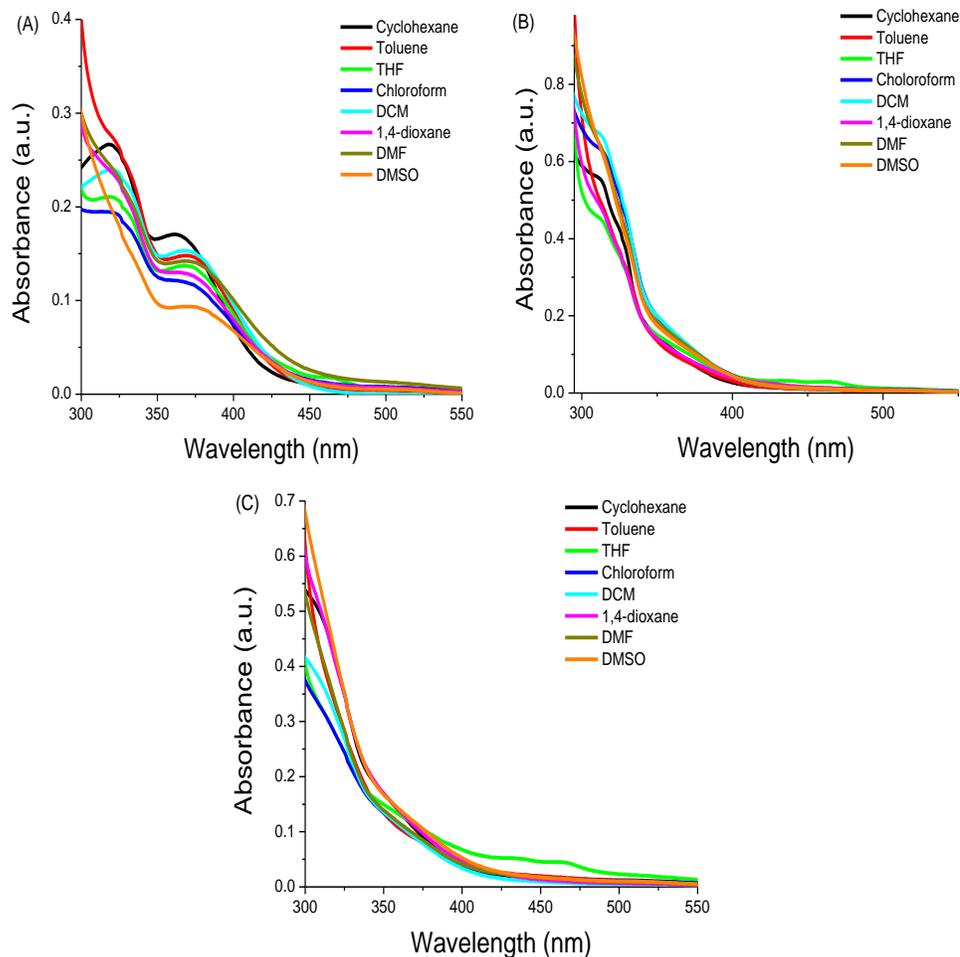


**Figure 6.2.** Emission spectra of (A) *p*-PTZ, (B) *m*-PTZ and (C) *o*-PTZ in solvents of varying polarity. ( $\lambda_{exc} = 370\text{nm}$ ) (Photographs taken under 365 nm UV illumination, from left to right cyclohexane, toluene, THF, chloroform, DCM, 1,4-dioxane, DMF and DMSO)

The *p*-PTZ isomer emits at 471 nm due to the localized-excited (LE) state with a shoulder at 500 nm corresponding to the ICT transition cyclohexane. The emission intensity of the ICT increases in toluene while the LE

emission appears as a low intensity peak. The ICT peak is further stabilized and red shifted on increasing the polarity and emits at 637 nm in DMSO. The ICT transition creates a polarized excited state stabilized by reorganization of solvent molecules around it thereby lowering its energy resulting in a red shifted weakened emission in polar solvents <sup>[17a]</sup> In cyclohexane, the *m*-PTZ isomer similarly exhibits LE emission at 448 nm and emission at 470 nm as a shoulder due to charge transfer (CT) state. On increasing the polarity from toluene to DCM, the CT emission is significant, whereas the LE emission appears as a low intensity peak. The CT emission is stabilized in moderately polar solvent like DCM with red shifted emission at 590 nm. The close vicinity of the LE and CT states rationalizes the dual emission in solvents of various polarity.<sup>[18a]</sup> Although, the intensity of CT emission substantially decreases in highly polar solvents such as DMF and DMSO with the LE emission remaining intact. The drastic reduction in emission intensity in highly polar solvents could be associated to TICT state.<sup>[18b]</sup> The free rotation around the single bond in the *meta* isomer makes it twisted which is accompanied with an instantaneous charge transfer from donor to acceptor forming a relaxed perpendicular TICT state. In non-polar solvents, a high intensity LE emission was observed at lower wavelength due to D-A coplanar conformation stabilized by mesomeric interactions, whereas in highly polar solvents the D-A relaxed perpendicular TICT state creates a non-radiative channel resulting in little or no emission.<sup>[18c,d]</sup> The *o*-PTZ isomer emits strongly at 473 nm in cyclohexane from CT state along with LE emissions below 450 nm. The increase in polarity results in stabilization of the CT emission accompanied by bathochromic shift. In DMSO, the isomer exhibits dual emission at lower wavelength due to LE states and higher wavelength due to CT state. The *ortho* isomer shows significant LE emission in highly polar solvents and the emission from CT state is slightly quenched owing to the TICT state. The *ortho* isomer has higher twisting as compared to *meta* isomer, however the electronic communication at the *ortho* position is more pronounced as compared to

*meta* position. The synergistic effect of the TICT state and the electronic communication at *ortho* position results in intermediate solvatochromic behaviour as compared to the *para* and *meta* isomer.



**Figure 6.3.** Electronic absorption spectra of (A) *p*-PTZ, (B) *m*-PTZ and (C) *o*-PTZ in solvents of various polarity.

The absorption spectra (Figure 6.3.) of the isomers are not much affected by changing the solvent polarity which establishes existence of more polarized excited state in contrast to ground electronic state.<sup>[17b]</sup> The quantum yield for the isomers in different solvents has been given in Table 6.2.

**Table 6.2.** Quantum yield of *p*-PTZ, *m*-PTZ and *o*-PTZ in various solvents.

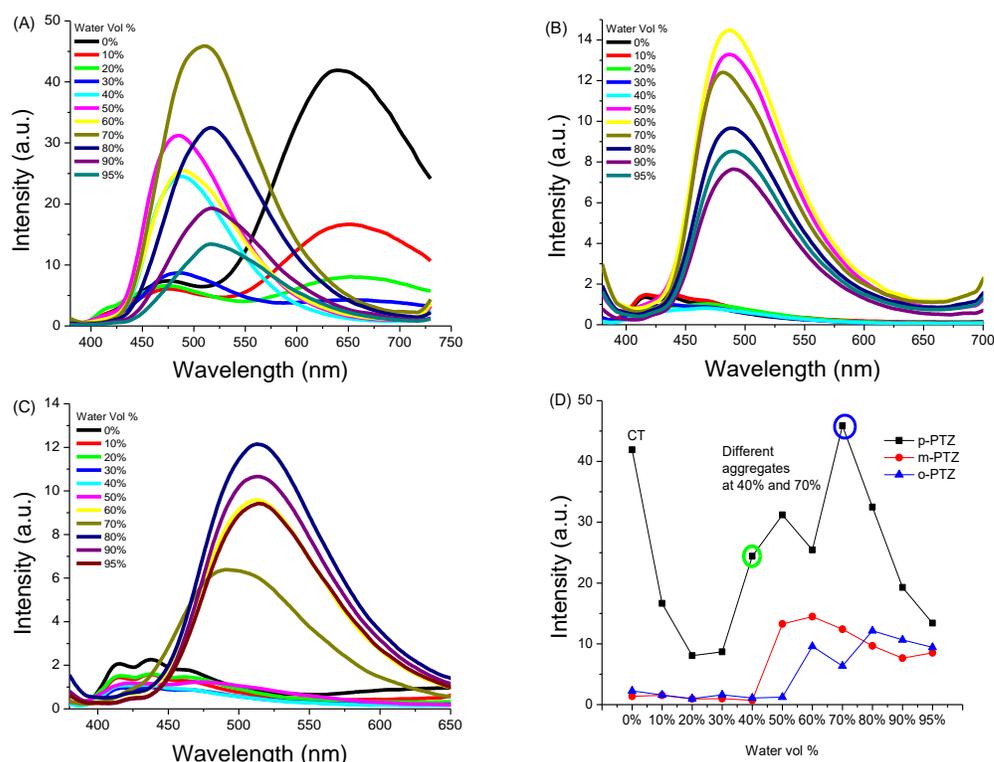
Solvents	$\phi_f^a$		
	<i>p</i> -PTZ	<i>m</i> -PTZ	<i>o</i> -PTZ
Cyclohexane	0.36	0.11	0.09
Toluene	0.50	0.13	0.12
THF	0.43	0.04	0.06
Chloroform	0.68	0.05	0.12
DCM	0.51	0.03	0.12
1,4-dioxane	0.53	0.08	0.14
DMF	0.14	0.004	0.03
DMSO	0.26	0.004	0.02

<sup>a</sup> Fluorescence quantum yields recorded using quinine sulphate as a standard in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution ( $\lambda_{exc} = 370\text{nm}$ ).

### 6.5. Aggregation-induced emission

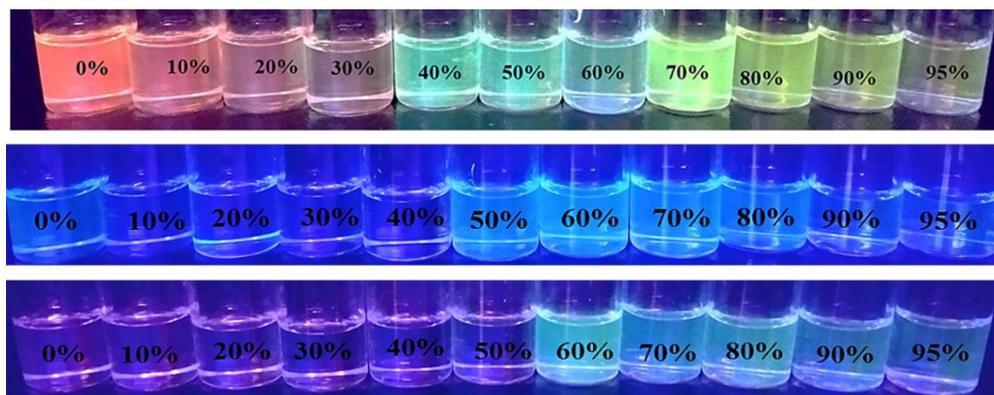
The butterfly type structure of PTZ and the twisting in the isomers provided non-planar molecules with aggregation-induced emission characteristics which were investigated using emission spectroscopy (Figure 6.4.). The isomers *p*-PTZ, *m*-PTZ and *o*-PTZ are readily soluble in DMSO but insoluble in water; hence consistent increase of water in DMSO initiated the nano-aggregate formation. The *p*-PTZ has an emission maximum at 639 nm in pure DMSO contrast to the standard AIEgens as a result of the exclusive ICT transition present in the isomer. The emission intensity of ICT peak decreases on increasing the water fraction upto 30% and shifts bathochromically to 658 nm, which shows the stabilization of intramolecular charge transfer peak in polar medium. At 40% water fraction, the aggregation occurs which enhances the intensity accompanied by blue shifted emission at 485 nm. The aggregation causes intensity enhancement upto 50% water fraction, although a slight drop in intensity

was observed at 60% water fraction which could be caused by the larger sized aggregates which are less exposed to radiation. The 70% DMSO-water fraction experiences a substantial enhancement in emission intensity with appearance of new peak at 511 nm. This could be attributed to the formation of two different types of aggregates at 40% and 70% water fraction.<sup>[19a]</sup> The higher water percentage (*i.e.* 80% and above) again experience minor drop in intensity due to formation of larger sized aggregates.<sup>[19b,c]</sup> Thus, the emission at low water fractions in *p*-PTZ isomer is mainly due to the ICT which later at higher water fractions is majorly governed by aggregation.<sup>[19d]</sup>



**Figure 6.4.** Emission spectra of (A) *p*-PTZ, (B) *m*-PTZ and (C) *o*-PTZ in DMSO-water mixtures with different water fractions. (Luminogen conc.  $2 \times 10^{-5}$  M) (D) Plot of intensity vs water fraction; intensity calculated at  $\lambda_{\max}$  ( $\lambda_{\max}$  with highest intensity considered for calculation).

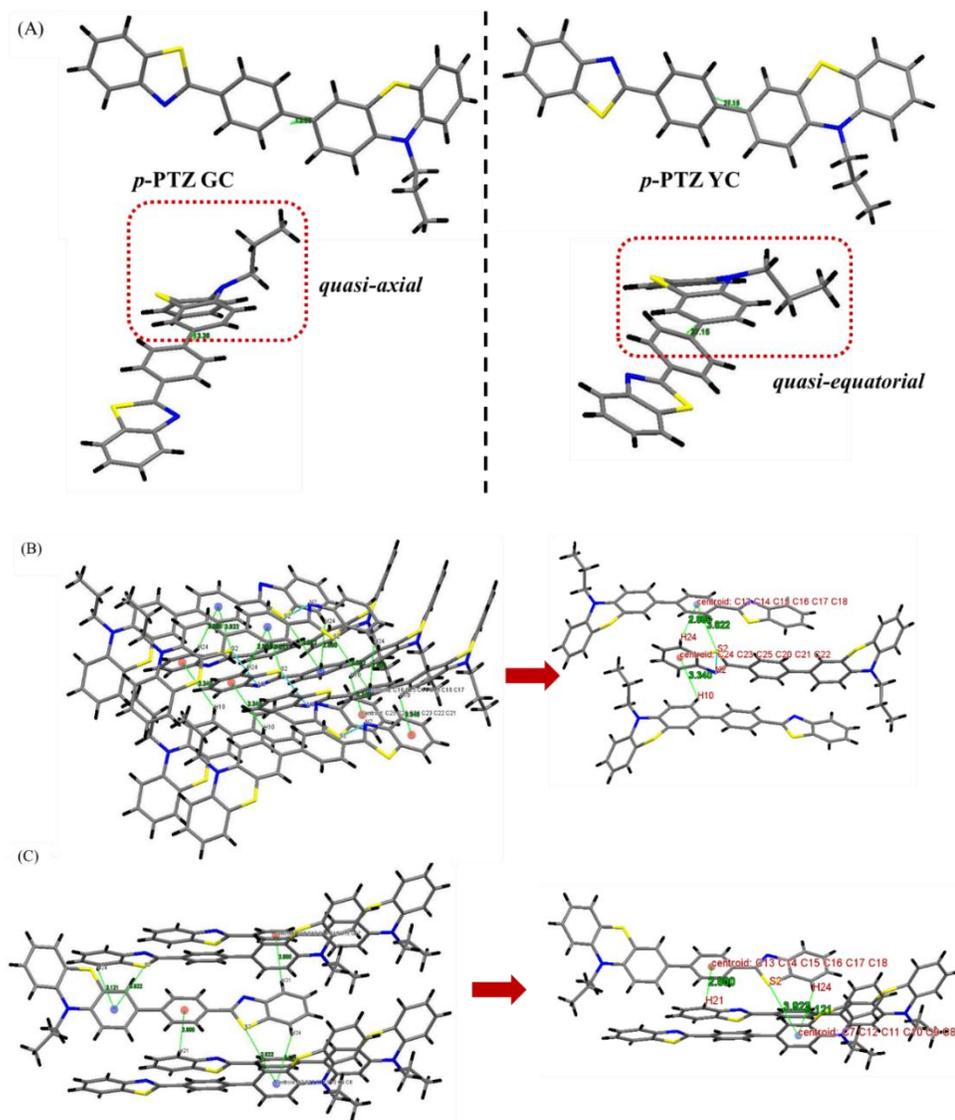
In *p*-PTZ isomer, the AIE behaviour was observed at different wavelengths for two water fraction 40% and 70%, which may be due to formation of two different aggregates. The *m*-PTZ and *o*-PTZ isomers display contrast AIE behaviour as a consequence of the TICT state. Both the isomers have weakened emissions in pure DMSO solutions. The emission intensifies at 50% DMSO-water and 60% DMSO-water for *m*-PTZ and *o*-PTZ respectively owing to aggregate formation. The emission reduces at higher water percentage similar to *p*-PTZ. The *meta* and *ortho* isomer behave as typical AIEgens unlike the *para* isomer. The unique AIE properties in the isomers are an outcome of the TICT state formed due to positional change. The pictures of AIE behaviour are given in Figure 6.5.



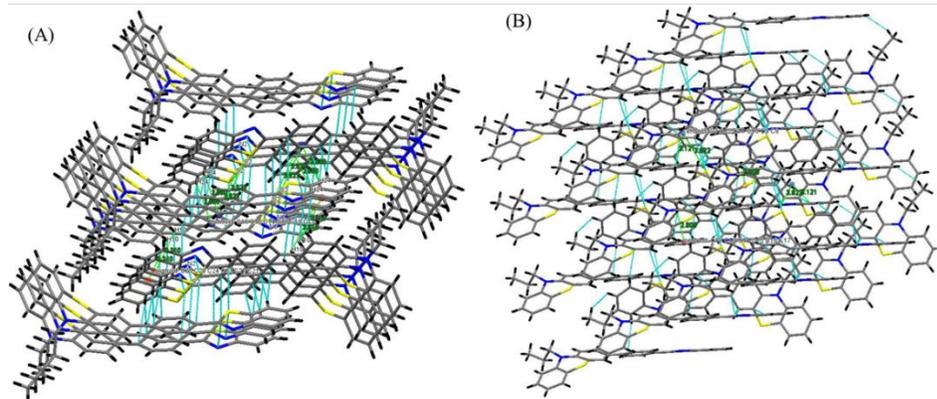
**Figure 6.5.** Photographs of *p*-PTZ, *m*-PTZ and *o*-PTZ in DMSO–water mixtures with different water fractions (10  $\mu$ M) under 365 nm UV illumination.

### 6.6. Single crystal X-ray analysis

The single crystal X-ray analysis is useful for structure elucidation and inference of properties in aggregated state. The slow evaporation of *p*-PTZ isomer in DCM serendipitously resulted in two different types of crystals. The polymorphs were denoted as *p*-PTZ GC ( $P2_1$  monoclinic system) and *p*-PTZ YC ( $Pna2_1$  orthorhombic system) according to their physical appearances; *p*-PTZ GC being green coloured rod shaped and *p*-PTZ YC being yellow plate shaped crystal (Figure 6.6 (A)).



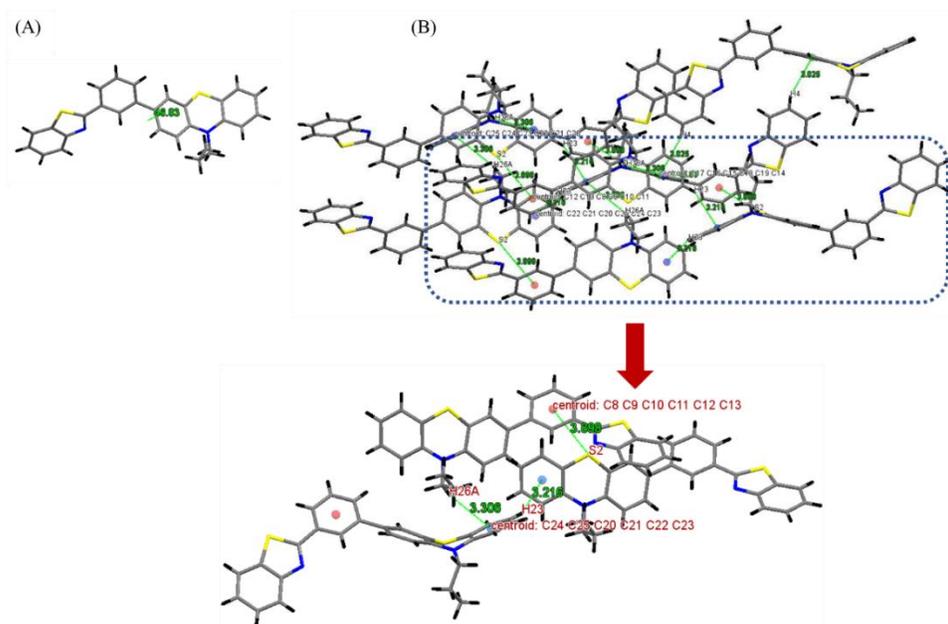
**Figure 6.6.** (A) Crystal structures of polymorphs *p*-PTZ GC and *p*-PTZ YC in its different confirmations, Crystal packing diagram and the intermolecular interactions of (B) *p*-PTZ GC and (C) *p*-PTZ YC.



**Figure 6.7** Crystal packing diagram of (A) *p*-PTZ GC and (B) *p*-PTZ YC.

In *p*-PTZ GC, the PTZ moiety attaches at para position with a dihedral angle of  $13.36^\circ$  in a way that the N and S of PTZ are on the same side as compared to N and S of BT moiety (Figure 6.6 (A)). In *p*-PTZ YC, the dihedral angle between BT and PTZ moiety is  $27.15^\circ$  which is higher compared to *p*-PTZ GC and the N and S of PTZ moiety are anti to the N and S of BT moiety (Figure (6.6. (B))). The major difference in the polymorphs can be visualized in the terms of orientation of the propyl chain attached to the N atom of PTZ. The central six membered ring of PTZ moiety prefers a boat confirmation due to the butterfly shape of PTZ moiety. In *p*-PTZ GC, the propyl chain is quasi axial whereas in *p*-PTZ YC it is quasi equatorial (Figure 6.6. (A)) in context to the boat confirmation of PTZ moiety.<sup>[20]</sup> In *p*-PTZ GC, two molecules lie perpendicular in a head to tail arrangement and each molecule stacks parallelly in respective direction forming a tightly packed 2D stacked structure (Figure 6.7. (A)). In the aggregated state two molecules of *p*-PTZ GC exhibit two C–H..... $\pi$  interactions C(20)–H(10)..... $\pi$ (red centroid C20 C21 C22 C23 C24 C25, 3.340 Å), C(13)–H(24)..... $\pi$ (blue centroid C13 C14 C15 C16 C17 C18, 2.880 Å) and one lone pair..... $\pi$  interaction *i.e.* S(2)..... $\pi$ (blue centroid C13 C14 C15 C16 C17 C18, 3.822Å) (Figure 6.6. (B)). In *p*-PTZ YC, each molecule is surrounded by one head to head stack molecule and another molecule remaining in an antiparallel arrangement which forms 2D stacked

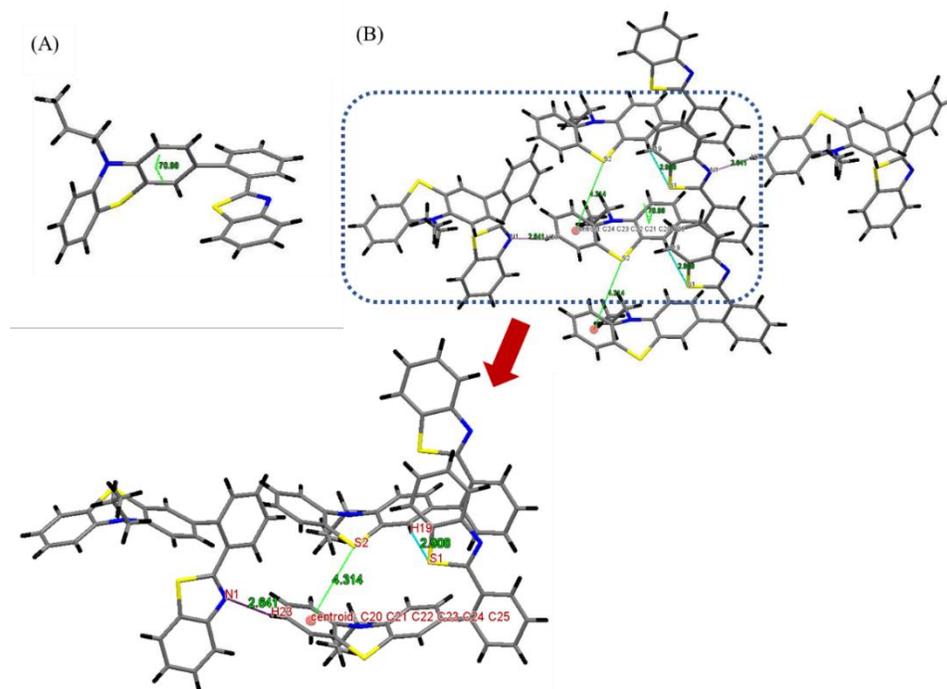
ladder type structure (Figure 6.7. (B)). The interactions observed in ***p*-PTZ YC** are two C–H..... $\pi$  interactions C(7)–H(24)..... $\pi$ (blue centroid C7 C8 C9 C10 C11 C12, 3.121 Å), C(18)–H(21)..... $\pi$ (red centroid C13 C14 C15 C16 C17 C18, 2.880 Å) and one lone pair..... $\pi$  interaction *i.e.* S(2)..... $\pi$  (blue centroid C7 C8 C9 C10 C11 C12, 3.922Å) (Figure 6.6. (C)).



**Figure 6.8.** (A) Crystal structure of ***m*-PTZ** and (B) crystal packing diagram of ***m*-PTZ** depicting the intermolecular interactions.

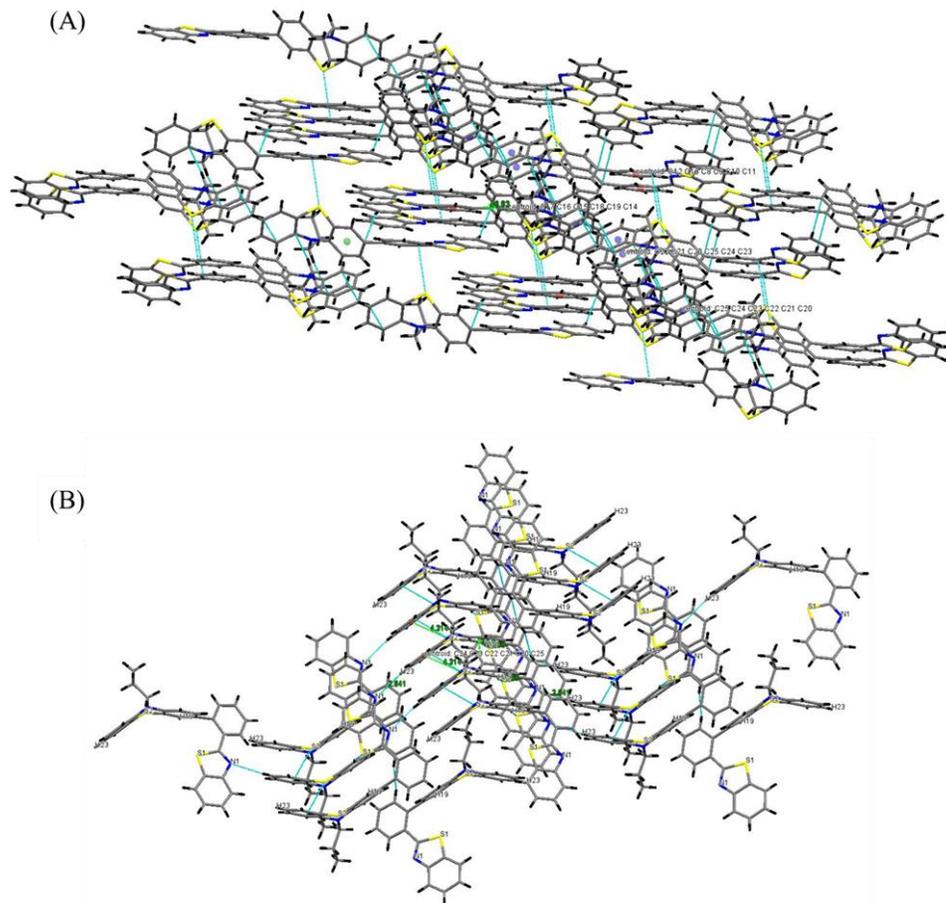
The ***m*-PTZ** isomer crystallizes as  $P2_1/c$  monoclinic system by slow evaporation of compound in hexane. The crystals for ***o*-PTZ** isomer were generated by evaporation of ethyl-acetate/hexane mixture as  $P2_1/c$  monoclinic system. The dihedral angle between the donor (**PTZ**) and acceptor (**BT**) in ***m*-PTZ** is  $46.83^\circ$  (Figure 6.8. (A)) and in ***o*-PTZ** is  $70.90^\circ$  (Figure 6.9. (A)). There is a clear increment in the dihedral angle between the donor benzothiazole moiety and the acceptor phenothiazine in the following order ***o*-PTZ**>***m*-PTZ**>***p*-PTZ**, thereby altering the degree of twisting in the isomers, which could affect its solid-state emission properties. In the solid state of ***m*-PTZ** isomer, each molecule interacts with four other molecules by three C–H..... $\pi$  interactions *i.e.* C(14)–

H(4)..... $\pi$ (centroid C14 C15 C16 C17 C18 C19, 3.025 Å), C(20)–H(26A)..... $\pi$ (blue centroid C20 C21 C22 C23 C24 C25, 3.306 Å), C(25)–H(23)..... $\pi$ (blue centroid C20 C21 C22 C23 C24 C25, 3.216 Å) and one lone pair..... $\pi$  interaction *i.e.* S(2)..... $\pi$ (red centroid C8 C9 C10 C11 C12 C13, 3.898Å) (Figure 6.8. (B)). The multiple interactions give rise to a tight 2D sheet type packing in meta isomer (Figure 6.10 (A)).



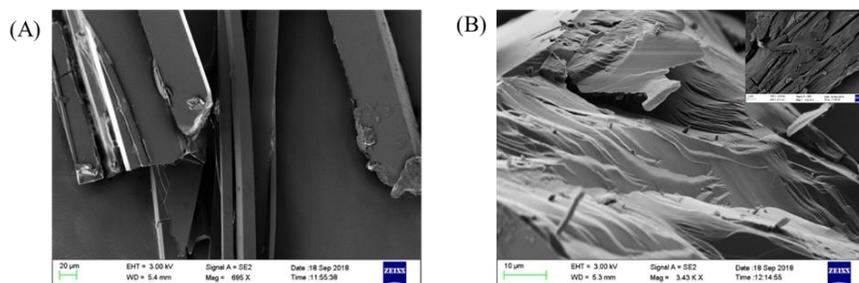
**Figure 6.9.** (A) Crystal structure of *o*-PTZ and (B) crystal packing diagram of *o*-PTZ depicting the intermolecular interactions.

On the other hand, the *o*-PTZ isomer has no C–H..... $\pi$  interactions, however exhibits one lone pair..... $\pi$  interaction S(2)..... $\pi$ (red centroid C20 C21 C22 C23 C24 C25, 4.314 Å) and two different kind of weak hydrogen bonding interactions from N and S of BT moiety *i.e.* C–H(23).....N(1) (2.641 Å) and C–H(19).....S(1) (2.908 Å) (Figure 6.9. (B)). The absence of multiple interactions in *o*-PTZ isomer results in a loosely packed zig-zag 2D arrangement (Figure 6.10. (B)).



**Figure 6.10.** Crystal packing diagram of (A) *m*-PTZ and (B) *o*-PTZ.

The variable packing and twisting in the isomers could initiate intriguing properties in solid state. The **p**-PTZ GC exhibits sheet like morphology, whereas the morphology of **p**-PTZ YC has small aggregates. The crystal information for the isomers is compiled in Table 6.3. The polymorphs of **p**-PTZ isomer were also studied using scanning electron microscopy (SEM) as shown in Figure 6.11.



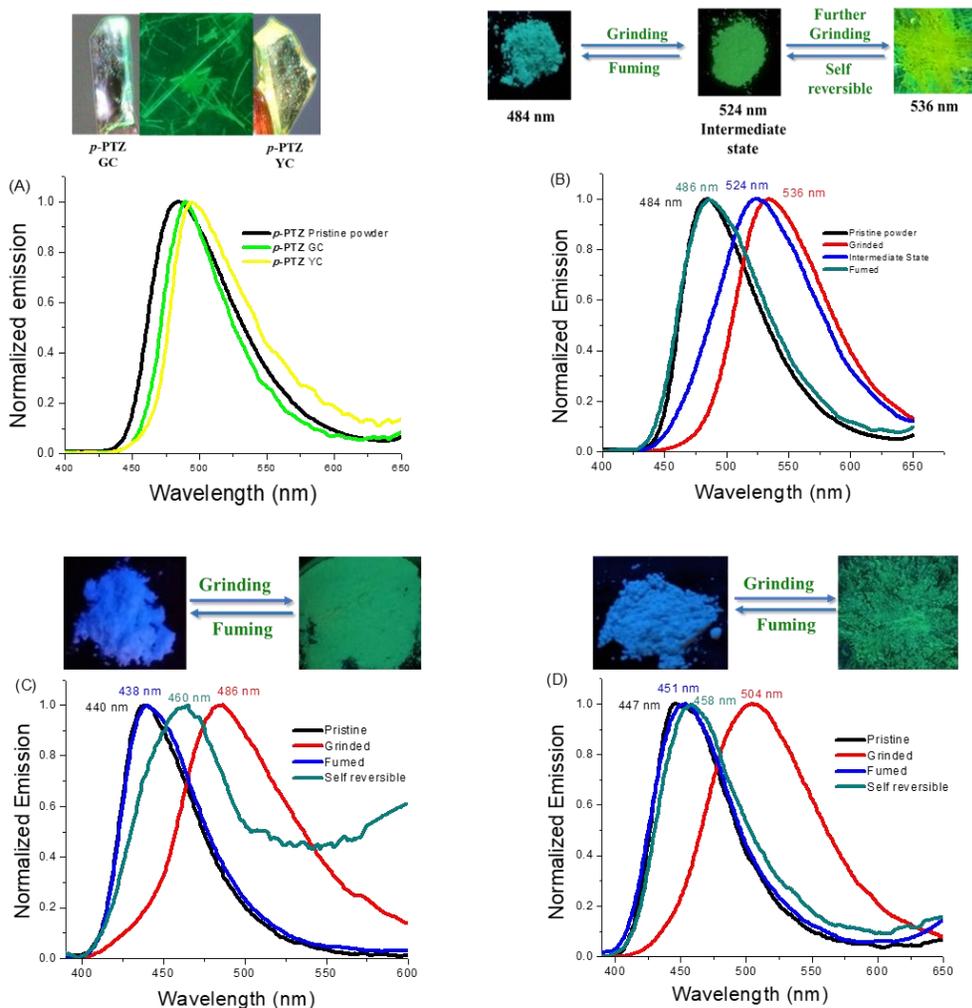
**Figure 6.11.** SEM images of the polymorphs (A) *p*-PTZ GC and (B) *p*-PTZ YC.

**Table 6.3.** Crystal data and structure refinement for *p*-PTZ GC, *p*-PTZ YC, *m*-PTZ and *o*-PTZ.

Identification code	rm259	rm257	shelx	Shelx
Empirical formula	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> S <sub>2</sub>
Formula weight	450.59	450.59	450.59	450.59
Temperature	293(2) K	293(2) K	293(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P 2 <sub>1</sub>	Orthorhombic, P n a 2 <sub>1</sub>	Monoclinic, P 2 <sub>1</sub> /c	Monoclinic, P 2 <sub>1</sub> /c
a/(Å)	8.5948(5)	39.769(3)	9.5843(3)	5.7861(2)
b/(Å)	5.5944(3)	7.1785(5)	8.1855(4)	23.6600(7)
c/(Å)	23.1405(11)	7.7524(8)	28.7754(13)	16.4878(5)
Alpha/(°)	90	90	90	90
Beta/(°)	95.751(5)	90	92.432(4)	92.684(2)
Gamma/(°)	90	90	90	90
Volume	1107.06(10) Å <sup>3</sup>	2213.2(3) Å <sup>3</sup>	2255.46(17) Å <sup>3</sup>	2254.69(12) Å <sup>3</sup>
Z, Calculated density	2, 1.352 mg/m <sup>-3</sup>	4, 1.352 mg/m <sup>-3</sup>	4, 1.327 mg/m <sup>-3</sup>	4, 1.327 mg/m <sup>-3</sup>
Absorption coefficient	0.260 mm <sup>-1</sup>	0.260 mm <sup>-1</sup>	0.255 mm <sup>-1</sup>	0.255 mm <sup>-1</sup>
F(000)	472	944	944	944

Crystal size	0.230 x 0.180 x 0.130 mm	0.260 x 0.230 x 0.180 mm	0.250 x 0.100 x 0.060 mm	0.300 x 0.103 x 0.030 mm
$\Theta$ range for data collection/(°)	3.384 to 29.083	2.820 to 30.551	3.273 to 29.132	1.506 to 28.433
Reflections collected / unique	9102 / 4635 [R(int) = 0.0708]	23519 / 5412 [R(int) = 0.0968]	25562 / 5521 [R(int) = 0.0674]	24538 / 5645 [R(int) = 0.0691]
Completeness to theta	$\Theta = 25.242$ 99.6 %	$\Theta = 25.242$ 99.9 %	$\Theta = 25.242$ 99.8 %	$\Theta = 25.242$ 99.7 %
Refinement method	Full-matrix least- squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least- squares on $F^2$	Full-matrix least- squares on $F^2$
Data / restraints / parameters	4635 / 3 / 290	5412 / 1 / 289	5521 / 0 / 289	5645 / 2 / 299
Goodness-of-fit on $F^2$	1.105	1.066	1.029	0.918
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.1287, wR2 = 0.3277	R1 = 0.0762, wR2 = 0.2056	R1 = 0.0612, wR2 = 0.1138	R1 = 0.0537, wR2 = 0.1199
R indices (all data)	R1 = 0.2379, wR2 = 0.4181	R1 = 0.1058, wR2 = 0.2487	R1 = 0.1204, wR2 = 0.1353	R1 = 0.1379, wR2 = 0.1538
Extinction coefficient	0.050(18)	n/a	n/a	n/a
Largest diff. peak and hole (e. $\text{\AA}^{-3}$ )	0.972 and - 0.606	0.658 and - 0.623	0.413 and - 0.278	0.383 and - 0.280

## 6.7. Mechanochromism

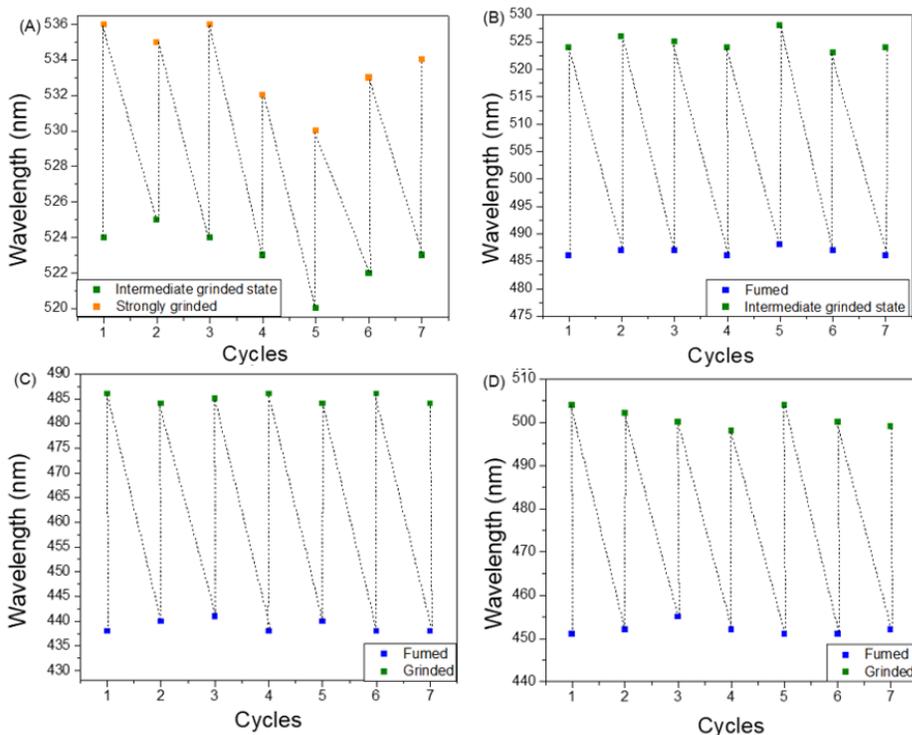


**Figure 6.12.** Solid-state emission spectra of (A) *p*-PTZ and its polymorphs (*p*-PTZ GC and *p*-PTZ YC), (B) *p*-PTZ, (C) *m*-PTZ and (D) *o*-PTZ as their pristine, grinded, fumed and self-reversible solids and photographs taken under 365 nm UV illumination.

The non-planarity and twisting in the isomers lead to significant emission in the solid state which is responsive to mechanical force. Additionally, the inclusion of PTZ moiety resulted in polymorphs for the *para* isomer owing to the formation of different conformers due to flexibility of the butterfly confirmation. Taking in consideration the above structural features, the mechanochromic behaviour of the isomers and polymorphism of *p*-PTZ

was investigated in detail using solid-state emission spectroscopy (Figure 6.12.). The ***p*-PTZ** pristine powder exhibits green emission at 484 nm, whereas its polymorphs ***p*-PTZ GC** and ***p*-PTZ YC** emit at 490 nm and 494 nm respectively. The grinding of ***p*-PTZ** pristine powder in mortar pestle resulted in bathochromically shifted bright green emission at 524 nm. The green emission red shifted to a yellow emission at 536 nm on further strong grinding, which dynamically reversed to an intermediate emission at 524 nm in about one minute. The self-reversible change from yellow emission (536 nm) to green emission (524 nm) was studied upto 7 cycles (Figure 6.13. (A)). The intermediate green emission at 524 nm was stable although restored to the pristine state with bluish green emission at 486 nm on fuming with dichloromethane for 4–5 minutes. The ***p*-PTZ** isomer exhibited a three-fold mechanochromic behaviour from bluish green to yellow via green emission with a spectral shift of 52 nm. The three-fold stepwise colour switching in ***p*-PTZ** could be ascribed to the flexible conversion of different conformers of **PTZ** moiety. The ***m*-PTZ** and ***o*-PTZ** isomers display a blue emission in its pristine state at 440 nm and 447 nm respectively. A bright green emission is generated on grinding at 486 nm and 504 nm for ***m*-PTZ** and ***o*-PTZ** respectively. The grinded solids of ***m*-PTZ** and ***o*-PTZ** restored their original blue emission at 438 nm and 451 nm respectively on fumigation with hexane for 5–7 minutes. The grinding induced spectral shift for ***m*-PTZ** and ***o*-PTZ** is 47 nm and 58 nm respectively. The grinded solid of ***m*-PTZ** when left at room temperature for over a week displayed self-reversible switching of its emission upto 460 nm whereas the grinded solid of ***o*-PTZ** switched its emission merely in 2-3 days self reversibly upto 458 nm which is close to its pristine state. The self-reversible switching of emission observed in all the isomers could be due to the flexible interconversion between different conformers of the **PTZ** moiety.<sup>[21]</sup> The isomer ***o*-PTZ** is highly twisted and is less susceptible to achieve planar confirmation on grinding and reaches to a metastable state on grinding which can easily revert to the original state. Thus, the self-recovering

mechanochromic behaviour is highest in ortho isomer which shows that self-reversible switching somewhat also depends on the flexibility of the donor and acceptor moieties.



**Figure 6.13.** Repeated switching of the solid-state fluorescence of (A) *p*-PTZ in its intermediate and strongly grinded state and (B) *p*-PTZ, (C) *m*-PTZ and (D) *o*-PTZ by repeated grinding and fuming cycles.

The highest spectral shift initiated by grinding was observed in *o*-PTZ which is associated to a loosely packed structure. The *o*-PTZ isomer has absence of multiple C–H..... $\pi$  interactions and shows weak H-bonds which could be easily perturbed on grinding assuming a more planar structure resulting in higher bathochromic shift. The tightly packed crystal structure of *m*-PTZ driven by extensive C–H..... $\pi$  interactions makes it less susceptible to mechanical stimuli. The reversible mechanochromism by fumigation could be repeated upto many cycles for all the isomers (Figure 6.13.). The wavelength for pristine, grinded, fumed and self-reversible solids are given in Table 6.4. The PLQY of *p*-PTZ pristine powder and its

polymorphs ***p*-PTZ GC** and ***p*-PTZ YC** are 0.22, 0.26 and 0.21 respectively. The PLQY for ***p*-PTZ** at 524 nm is 0.19 and at 536 nm is 0.20. The fumed solid of ***p*-PTZ** has PLQY 0.24. The PLQY for pristine, grinded and fumed solids of ***m*-PTZ** is 0.02, 0.04 and 0.03 respectively. The PLQY for pristine, grinded and fumed solids of ***o*-PTZ** is 0.02, 0.01 and 0.01 respectively.

**Table 6.4.** Peak emission wavelengths ( $\lambda$ , in nm) of ***p*-PTZ**, ***m*-PTZ** and ***o*-PTZ** as pristine, grinded and fumed solids.

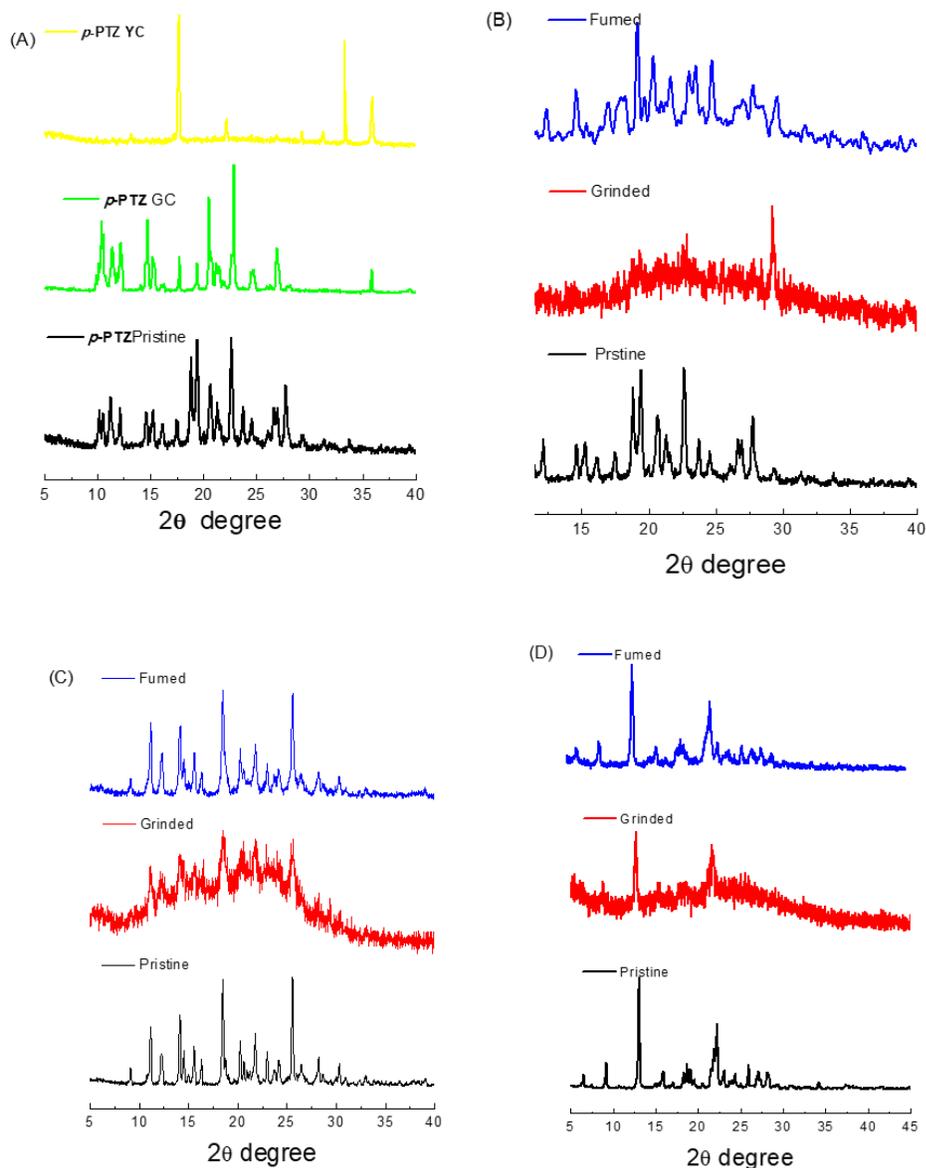
Compounds	Emission			
	$\lambda_{\text{pristine}}$ (nm)	$\lambda_{\text{ground}}$ (nm)	$\lambda_{\text{fumed}}$ (nm)	$\Delta\lambda^{\text{a}}$ (nm)
<b><i>p</i>-PTZ</b>	484	524 (intermediate state)	486	52
		536 (strong grinding)		
<b><i>m</i>-PTZ</b>	440	486	438	47
<b><i>o</i>-PTZ</b>	447	504	451	58

<sup>a</sup> Grinding-induced spectral shift,  $\Delta\lambda = \lambda_{\text{ground}} - \lambda_{\text{fumed/pristine}}$

## 6.8. Powder X-ray diffraction studies

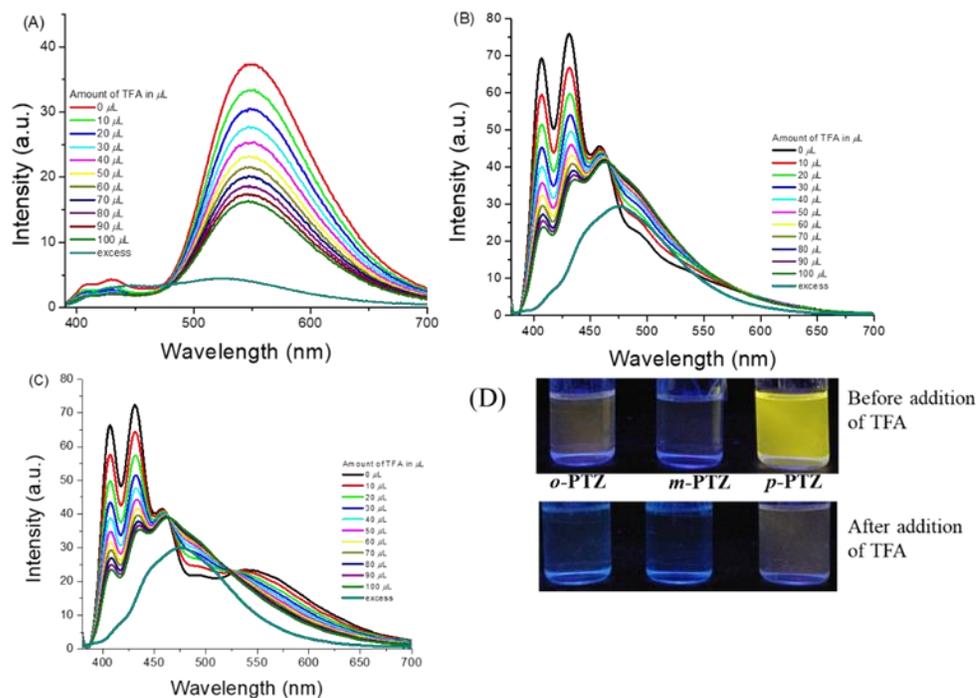
The powder X-ray diffraction studies were carried out for the pristine, grinded and fumed solids of the isomers to find out the underlying mechanism for mechanochromic behaviour (Figure 6.14.). The ***p*-PTZ GC** and ***p*-PTZ YC** possess different diffraction patterns confirming its polymorphic nature. The sharp and intense diffraction patterns for pristine solids of all the isomers establish their crystalline nature. The intense peaks are lost on grinding and a wide diffused peak is observed for the grinded solids. The crystallinity is regained on fumigation which can be seen from the sharp patterns obtained for the fumed solids. The PXRD results prove that the crystalline pristine solids form an amorphous metastable state on grinding and the fumigation regenerates the crystallinity. The stimuli reactive colour change can therefore be related to a phase transition from

crystalline to amorphous caused by the disturbance in molecular packing on applying mechanical force.



**Figure 6.14.** PXRD patterns of (A) *p*-PTZ pristine and its polymorphs *p*-PTZ GC and *p*-PTZ YC and (B) *p*-PTZ, (C) *m*-PTZ and (D) *o*-PTZ in its pristine, grinded and fumed forms.

## 6.9. Acidochromism

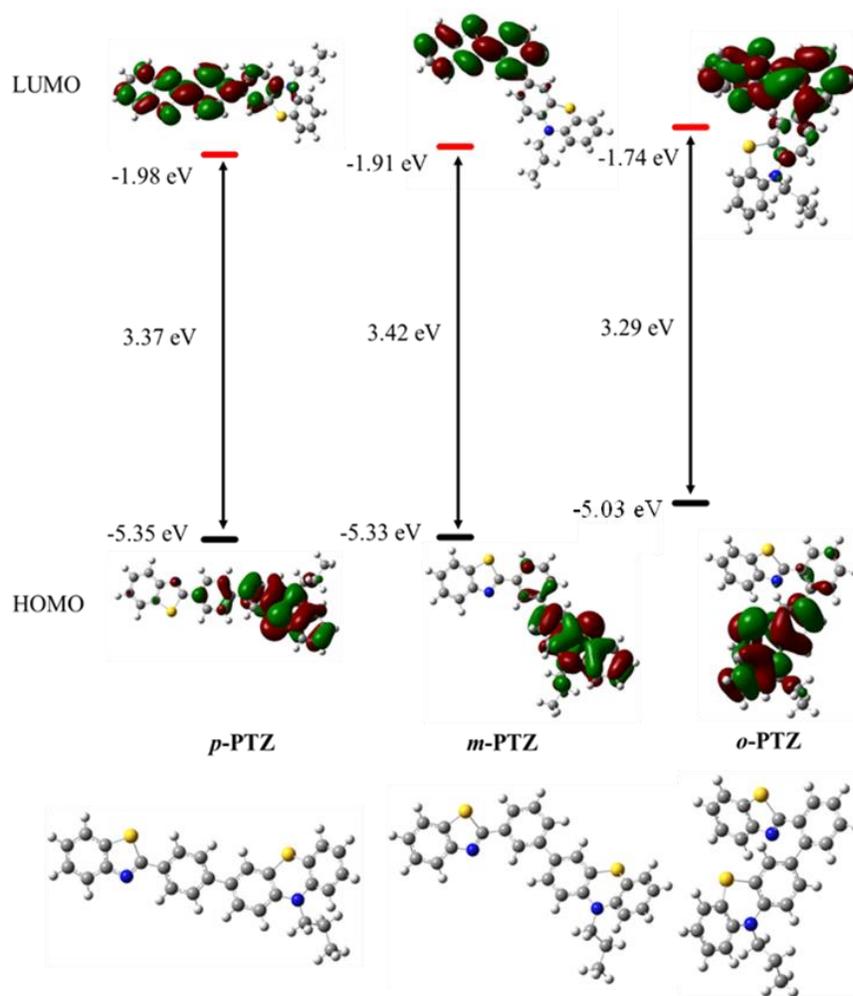


**Figure 6.15.** Emission spectra of (A) *p*-PTZ, (B) *m*-PTZ and (C) *o*-PTZ in  $\text{CHCl}_3$  on titration with known amounts of TFA ( $10\mu\text{L}$ - $100\mu\text{L}$ ), (Conc.  $2\times 10^{-5}$  M). (D) Emission photographs of *p*-PTZ, *m*-PTZ and *o*-PTZ in response to TFA.

The free N atom present in the **BT** moiety of the isomers are capable of protonation owing to which the response of isomers on treating with trifluoroacetic acid (TFA) was studied using fluorescence spectroscopy (Figure 6.15).<sup>[22]</sup> The experiment was carried out by titrating solution of the isomers in  $\text{CHCl}_3$  ( $2\times 10^{-5}$  M) against known amounts of TFA. The intensity emission maxima of *p*-PTZ at 549 nm due to ICT quenches on addition of TFA ( $10\mu\text{L}$ - $100\mu\text{L}$ ). On excess addition of TFA a low intensity blue shifted broad emission was observed at 524 nm. The addition of TFA ( $10\mu\text{L}$ - $100\mu\text{L}$ ) to the solution of *m*-PTZ isomer results in quenching of its localized emissions (407 nm, 431 nm and 458 nm) and a broad red shifted low intensity emission peak was seen at 475 nm on excess addition of TFA. The *o*-PTZ isomer in  $\text{CHCl}_3$  displays LE emission (407 nm, 432 nm and

458 nm) and CT emission at 539 nm. The addition of TFA ( $10\mu\text{L}$ - $100\mu\text{L}$ ) quenches the LE emissions and causes the CT emission to broaden and disappear. In excess TFA a broad emission is observed at 475 nm. The quenching efficiency of the emission maxima for *p*-PTZ, *m*-PTZ and *o*-PTZ is 87%, 61% and 58% respectively. The effective quenching of the emission of the isomers confirms that they are responsive to TFA and can act as potential TFA sensors.

### 6.10. Density functional theory calculations



**Figure 6.16.** Energy level diagram showing the HOMO and LUMO energy levels of *p*-PTZ, *m*-PTZ and *o*-PTZ as determined at the B3LYP/6-31G+(d,p) level and their optimized structures.

The density functional theory calculations were done to analyse the geometries and the electronic distribution present in ground state for the isomers by utilizing the basis set B3LYP/631-G+ (d,p).<sup>[23]</sup> The optimized structures of the isomers are in accordance with the single crystal structure. The *o*-PTZ isomer has an extremely twisted structure as compared to the *m*-PTZ and *p*-PTZ isomer. Figure 6.16. depicts the optimized structures and calculated frontier orbitals whose values are listed in Table 6.5. The highest occupied molecular orbital (HOMO) is mainly concentrated on the donor PTZ moiety extending towards the phenyl ring while the lowest unoccupied molecular orbital (LUMO) is concentrated on the acceptor BT moiety. The calculated HOMO-LUMO gap for *p*-PTZ, *m*-PTZ and *o*-PTZ are 3.37 eV, 3.42 eV and 3.29 eV respectively.

**Table 6.5.** DFT calculations of *p*-PTZ, *m*-PTZ and *o*-PTZ.

Compounds	DFT calculations		
	HOMO <sup>a</sup> eV	LUMO <sup>a</sup> eV	HOMO-LUMO gap eV
<i>p</i> -PTZ	-5.35	-1.98	3.37
<i>m</i> -PTZ	-5.33	-1.91	3.42
<i>o</i> -PTZ	-5.03	-1.74	3.29

<sup>a</sup> Theoretical values at B3LYP/6-31G +(d,p) level.

## 6.11. Experimental details

### General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker Avance III instrument by using CDCl<sub>3</sub>. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent

residual peak (CDCl<sub>3</sub>, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet), and the coupling constants, *J*, are given in hertz. <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). UV–visible absorption spectra were recorded on a Perkin Elmer Lambda 35 UV–visible spectrophotometer. Emission spectra were taken in a The Fluoromax-4C, S/n.1579D-1417-FM Fluorescence software Ver 3.8.0.60. The relative quantum yields in solution were calculated using Quinine sulphate in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution as standard. The quantum yields in solid state were measured using K-sphere Integrating sphere. The excitation and emission slits were 2/2 nm for the emission measurements and 3/3 for solid quantum yield measurements. All the measurements were done at 25 °C. HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. Single-crystal X-ray structural studies of *p*-PTZ GC and *p*-PTZ YC were performed on a CCD equipped SUPERNOVA diffractometer from Agilent Technologies with Oxford Instruments low-temperature attachment under argon/nitrogen using standard Schlenk and vacuum-line techniques. Single-crystal X-Ray structural studies for *m*-PTZ was collected using (BRUKER KAPPA APEX II CCD Duo) with graphite monochromatic Mo K $\alpha$  radiation (0.71073 Å), on an Xcalibur, Eos, Gemini diffractometer. Single crystal X-ray structural studies for compound *o*-PTZ were collected on a Bruker D8 VENTURE diffractometer equipped with CMOS Photon 100 detector and MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation was used. The acidochromism was performed using 0.1 M stock solution of TFA in CHCl<sub>3</sub>. The PXRD studies were done using powdered samples on Rigaku SmartLab, Automated Multipurpose x-ray Diffractometer, equipped with a high-accuracy theta-theta goniometer featuring a horizontal sample mount. Scanning Electron Microscope (FE-SEM) was performed on Supra55 Zeiss, GEMINI Technology.

### Synthesis and characterization of *p*-PTZ, *m*-PTZ and *o*-PTZ.

General procedure for the synthesis of *p*-PTZ, *m*-PTZ and *o*-PTZ. **BT-1** (1.03 mmol), **PTZ-3** (1.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.16 mmol) were dissolved in a mixture of tetrahydrofuran (20.0 mL)/ H<sub>2</sub>O (4.0 mL) and the solution was degassed. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.10 mmol) was added to the resulting mixture and was stirred at 80 °C for 24 h under an argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue was subjected to column chromatography on silica (hexane–DCM 70:30 in vol) to yield the desired product *p*-PTZ as a green powder. The same procedure was employed using intermediates **PTZ-3** and **BT-2** to obtain product *m*-PTZ as white powder. The product *o*-PTZ was also obtained as white powder by applying the above procedure using intermediates **PTZ-3** and **BT-3**.

*p*-PTZ Yield: 73%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.13 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.37–7.46 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.87–6.94 (m, 3H), 3.86 (t, *J* = 8.0 Hz, 2H), 1.83–1.91 (m, 2H), 1.04 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ 167.7, 154.2, 145.1, 144.8, 142.4, 135.3, 135.0, 134.0, 132.1, 128.9, 128.0, 127.5, 127.3, 126.8, 126.3, 125.9, 125.7, 125.4, 125.1, 124.3, 123.1, 122.5, 121.6, 115.5, 115.4, 49.2, 20.1, 11.3, 0.0 ppm; HRMS (ESI): calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>S<sub>2</sub> [M + H]<sup>+</sup>: 451.1297. Found: 451.1296.

*m*-PTZ Yield: 71%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.27 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.64–7.66 (m, 1H), 7.46–7.55 (m, 4H), 7.39–7.43 (m, 1H), 7.15–7.18 (m, 2H), 6.88–6.95 (m, 3H), 3.87 (t, *J* = 8.0 Hz, 2H), 1.83–1.92 (m, 2H), 1.04 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ 168.0, 154.1, 154.1, 144.9, 140.9, 135.1, 134.3, 134.1, 129.4, 129.0, 127.4, 127.3, 126.3, 126.1, 126.0, 125.8, 125.4, 125.4, 125.2, 124.4, 123.2, 122.5, 121.6, 115.5, 115.4, 49.2, 20.1, 11.3, 0.0 ppm; HRMS (ESI): calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup>: 450.1219. Found: 450.1201.

***o*-PTZ** Yield: 79%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.05–8.07 (m, 2H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.43–7.52 (m, 3H), 7.30–7.38 (m, 2H), 7.10–7.16 (m, 3H), 6.99 (d,  $J = 8.0$  Hz, 1H), 6.91 (t,  $J = 8.0$  Hz, 1H), 6.85 (d,  $J = 8.0$  Hz, 1H), 6.73 (d,  $J = 8.0$  Hz, 1H), 3.79 (t,  $J = 8.0$  Hz, 2H), 1.76–1.88 (m, 2H), 1.01 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  167.7, 152.8, 144.9, 144.9, 140.6, 136.7, 134.1, 132.5, 130.8, 130.4, 130.0, 129.2, 128.3, 127.6, 127.4, 127.2, 125.8, 124.8, 124.7, 124.3, 123.2, 122.4, 121.4, 115.3, 114.9, 49.3, 20.0, 11.3, 0.0 ppm; HRMS (ESI): calcd. for  $\text{C}_{28}\text{H}_{22}\text{N}_2\text{S}_2$   $[\text{M} + \text{H}]^+$ : 451.1297. Found: 451.1228.

## 6.12. Conclusion

In conclusion, a series of D-A positional isomers ***p*-PTZ**, ***m*-PTZ** and ***o*-PTZ** were designed and synthesized using Suzuki cross-coupling reaction in order to regulate the donor-acceptor character as well as the intermolecular interactions in solid state. The functionalization of phenothiazine (**PTZ**) at *para*, *meta* and *ortho* positions of phenyl **BT** resulted in contrasting photophysical and electronic properties. The ***p*-PTZ** isomer displayed strong ICT characteristics owing to enhanced conjugation due to lower degree of twisting. In contrast, the ***m*-PTZ** and ***o*-PTZ** displayed quenching of emission in polar solvents due to formation of TICT state. The non-planar twisted structures of the isomers assist in intensity enhancement in aggregated state and endow them with reversible MFC characteristics. The MFC behaviour is associated with generation of metastable states and is reflected from the crystalline to amorphous phase transformation studied by PXRD. The isomers exhibit self-reversible colour switching owing to the conformational flexibility of PTZ moiety. The unique butterfly shape of PTZ moiety allows it to exist in different conformations namely quasi axial and quasi equatorial in ***p*-PTZ** isomer resulting in polymorphism, which was also explored using SEM, PXRD and SCXRD. The single crystal X-ray analysis of the ***m*-PTZ** reveals multiple C–H..... $\pi$  interactions driven tightly packed structure, which makes it less

susceptible to grinding as compared to *o*-PTZ which has weak H-bonds and absence of C–H... $\pi$  interactions thereby exhibiting highest grinding induced spectral shift. The DFT optimized structures are in accordance with the single crystal structures. The isomers due to the presence of free N atom display sensing of trifluoroacetic acid. The work is of great importance for designing MFC materials with self-recovering mechanism. The adaptable conformations of PTZ moiety can regulate the intermolecular interactions resulting in molecules with distinct photophysical properties. The chosen strategy opens new avenues for producing smart stimuli responsive materials with modulate solid state properties.

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## Chapter 7

### Structure-property relationship in multi-stimuli responsive D-A-A' benzothiazole functionalized isomers

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#### 7.1. Introduction

The solid state materials which are susceptible to changes by external stimuli (mechanical forces, solvent and acid vapors, heat and light) are beneficial.<sup>[1]</sup> following their utilization in a range of promising applications such as optical information storage, fluorescent switches, memory devices, deformation detectors, optical recording, fluorescent bio-probes, security systems, mechanical sensors and optoelectronic devices.<sup>[2]</sup> The category of solid state materials, that manifest change in emission as a response to mechanical force such as grinding or rubbing are known as mechanofluorochromic (MFC) materials.<sup>[3]</sup> A significant emission in the solid state is crucial for mechanofluorochromism and is primarily determined by the nature of molecular packing and intermolecular interactions in the solid state.<sup>[4]</sup> The response to mechanical forces is associated with phase transitions or the disturbance in the basic molecular stacking interactions, consequently producing metastable states.<sup>[5]</sup> The factors such as effective conjugation, donor-acceptor interaction, and incorporation of alkyl or aryl substituent, electronegative or heavy atoms and their position play a pivotal role in regulating the MFC properties.<sup>[6]</sup> The common organic dyes in their aggregated state quench their emission due to the aggregation caused quenching (ACQ) which restricts their usage as MFC materials.<sup>[7]</sup> Recently, the concept of aggregation-induced emission (AIE) contributed by Tang *et al.* has successfully resulted in materials with enhanced emission in aggregated state. The non-planar architecture of AIE luminogens diminishes  $\pi$ - $\pi$  stacking in aggregated state and by the virtue of restriction of intramolecular rotations (RIR) induces extensive emission in

aggregated state.<sup>[8]</sup> The ACQ fluorophores have been successfully converted into solid state emitting materials by attaching to well-known AIEgens.<sup>[9]</sup> Tetraphenylethylene (TPE) is one of the widely used AIEgen because of its easy synthesis, bulky size and propeller shape. The TPE has been used as a weak electron donor in donor-acceptor systems resulting in highly emissive solid materials with a range of applications in material chemistry and electronics.<sup>[10]</sup>

It is familiar that organic molecules constituting of donor and acceptor fragments allowing fine tuning of the MFC properties. Organic molecules with D-A, D-A-D, D- $\pi$ -A *etc.* serve as excellent candidates for MFC with applications in optoelectronics.<sup>[11]</sup> Benzothiazole (BT) and benzothiadiazole (BTD) are well established electron acceptors and have been successfully explored for the synthesis of AIE active MFC materials.<sup>[12]</sup> Both BT and BTD based materials have been successfully employed in organic light emitting diodes (OLEDs) and organic solar cells (OSCs) and can be combined for potential applications in a multichromophoric assembly.<sup>[13]</sup>

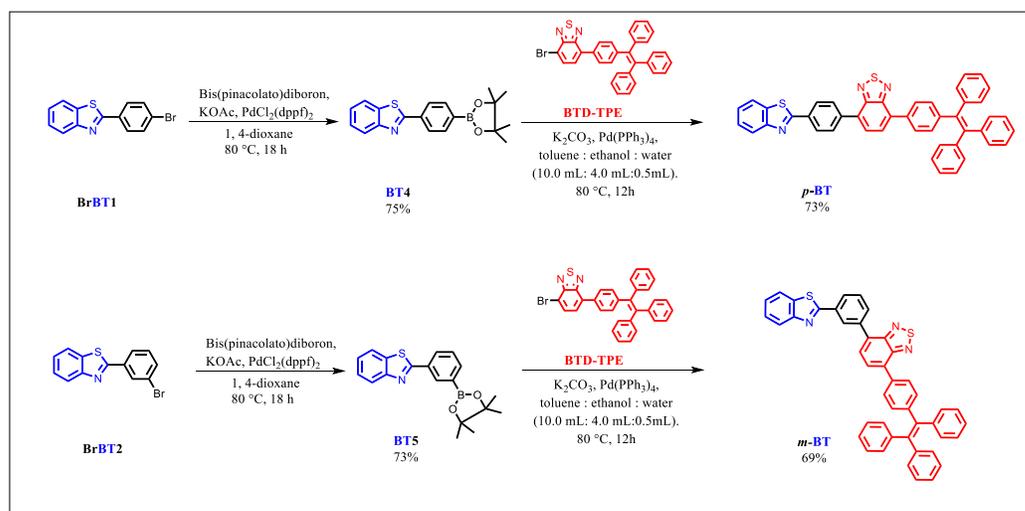
We were interested in design and synthesis of MFC materials. We have reported BT-TPE and BTD-TPE for MFC and successfully tuned their AIE and MFC behavior and have shown that MFC behavior can be tuned by controlling the strength of donor or acceptor.<sup>[11(c),14]</sup> Herein, we have designed and synthesized series of multichromophoric isomers ***p*-BT**, ***m*-BT** and ***o*-BT** based on BT, BTD and TPE with an aim of achieving high solid-state emission and MFC behavior. In this design strategy, we aim to control the acceptor strength and molecular packing by changing the position of BTD-TPE unit *ortho*, *meta* and *para* to BT unit. The variation of the position with respect to BT unit is expected in modulating the acceptor strength and molecular packing. The BT unit was selected because of moderate electron accepting behavior and presence of two hetero atoms “S and N”, as S-atom is well known for its strong supramolecular

interactions. The comparative study of the change in the photophysical, AIE and MFC properties of isomers with position has been carried out using crystal analysis and theoretical calculations. The photophysical, thermal, electrochemical, solvatochromic, mechanochromic, AIE and acidochromic properties of *p*-BT, *m*-BT and *o*-BT have been investigated. The isomers exhibit enhanced emission on aggregation with distinct MFC and acid sensing.

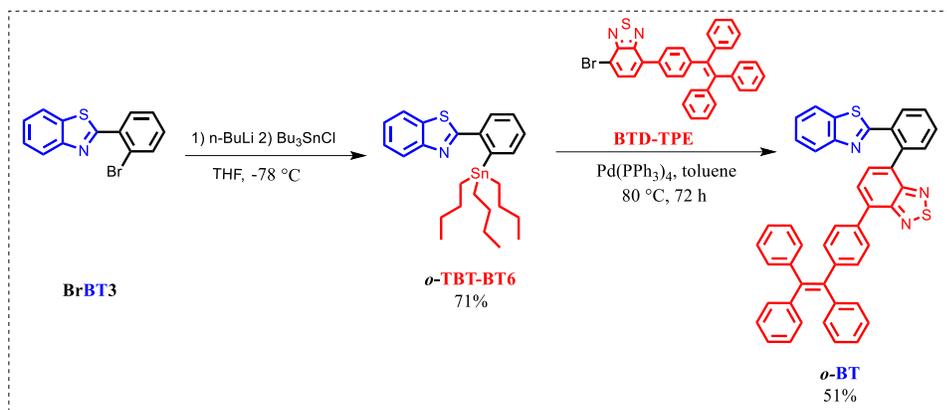
## 7.2. Results and discussions

### Synthesis

The *p*-BT, *m*-BT and *o*-BT are D-A-A' type molecules and were designed to evaluate the change in the photophysical and electronic properties as a result of altering the position of attachment of the BTD-TPE unit to the Ph-BT moiety. The synthetic route to the isomers *p*-BT and *m*-BT is given in Scheme 7.1 and for *o*-BT is as outlined in Scheme 7.2. The benzothiadiazole-tetraphenylethylene (BTD-TPE) moiety was attached at the 4-position, 3-position and 2-position of the phenyl ring of benzothiazole to furnish the para (*p*-BT), meta (*m*-BT) and ortho (*o*-BT) isomers respectively.

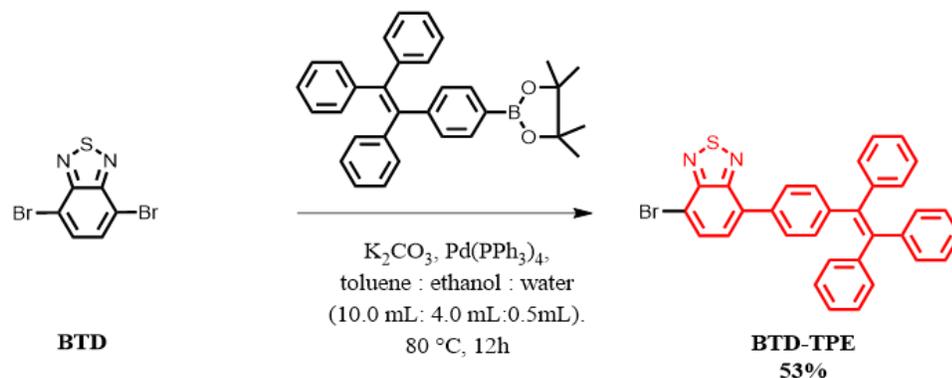


**Scheme 7.1.** Synthetic routes for *p*-BT and *m*-BT.



**Scheme 7.2.** Synthetic route for *o*-BT

To achieve this, firstly the tetraphenylethylene was selectively coupled to one side of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole using the Suzuki cross-coupling reaction to yield intermediate **BTD-TPE** (Scheme 7.3).<sup>[14]</sup>



**Scheme 7.3.** Synthetic route to **BTD-TPE**.

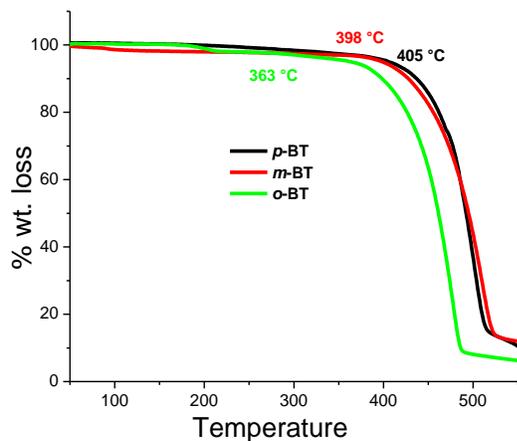
Further, the benzothiazole intermediates **BT 4** and **BT 5** required for coupling with **BTD-TPE** were synthesized. 2-(4-bromophenyl)benzo[*d*]thiazole (**BrBT1**), 2-(3-bromophenyl)benzo[*d*]thiazole (**BrBT2**) and 2-(2-bromophenyl)benzo[*d*]thiazole (**BrBT3**) were obtained by the condensation reaction of 2-aminothiophenol and respective bromobenzaldehydes using literature procedures.<sup>[15]</sup> The Miyaura borylation reaction of **BrBT1** and **BrBT2** with bis(pinacolato)diboron

using [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride as catalyst generated the boronate esters of benzothiazole at 4 position (**BT4**) and 3 position (**BT5**) respectively.<sup>[16]</sup> However, the Miyaura Borylation reaction of **BrBT3** did not proceed successfully to yield the boronate ester; alternatively the Stille intermediate *o*-**TBT-BT6** was synthesized. The in-situ anion formation of **BrBT3** using n-BuLi followed by addition of tributyltin chloride supplied the intermediate *o*-**TBT-BT6** in 71% yield. The Suzuki cross coupling reaction of **BTD-TPE** with **BT4** and **BT5** using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst afforded *para* and *meta* isomers *p*-**BT** and *m*-**BT** with a yield of 73% and 69% respectively. The Stille cross-coupling reaction of **BTD-TPE** with *o*-**TBT-BT6** and Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst resulted in the *ortho* isomer *o*-**BT** with a yield of 51%. All the target compounds (*p*-**BT**, *m*-**BT** and *o*-**BT**) and the newly synthesized intermediate *o*-**TBT-BT6** were characterized with <sup>1</sup>H, <sup>13</sup>C NMR spectra and HR-ESI mass spectroscopy. The *para* (*p*-**BT**) and *ortho* (*o*-**BT**) isomers produced good crystals for single crystal X-ray analysis. The synthesized isomers are highly soluble in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF), chloroform *etc.*, although insoluble in ethanol, methanol, water and acetonitrile.

### 7.3. Thermogravimetric analysis

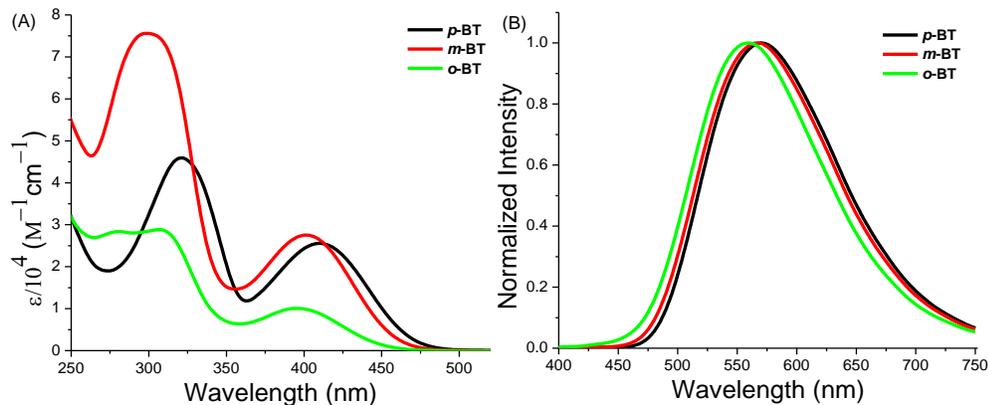
High thermal stability is essential for molecules to be utilized in solid state applications. The thermal properties of *p*-**BT**, *m*-**BT** and *o*-**BT** were evaluated by thermogravimetric analysis (TGA). The TGA curves are shown in Figure 7.1. and the decomposition temperature (*T<sub>d</sub>*) are listed in Table 7.1. The isomer *p*-**BT** exhibits the highest decomposition temperature of 405 °C corresponding to 5% weight loss. The isomer *m*-**BT** and *o*-**BT** show thermal decomposition temperatures of 398 °C and 363 °C respectively for 5% weight loss. The *p*-**BT** molecule has a lower twisting as compared to *m*-**BT** and *o*-**BT** and exhibits an extended conjugated structure. The *p*-**BT** isomer due to a planar conjugated structure engages in higher

intermolecular interactions in its crystal packing lattice leading to a densely packed structure which could be a reason for the higher thermal stability as compared to *m*-BT and *o*-BT.



**Figure 7.1.** TGA curves of *p*-BT, *m*-BT and *o*-BT at a heating rate of  $10^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere.

#### 7.4. Photophysical properties



**Figure 7.2.** (A) UV-vis absorption spectra and (B) normalized emission spectra of *p*-BT, *m*-BT and *o*-BT in THF ( $2 \times 10^{-5}$  M).

The optical properties of *p*-BT, *m*-BT and *o*-BT were analyzed in THF by UV-vis absorption (Figure 7.2 (A)) and fluorescence spectroscopy (Figure

7.2 (B)) and the results are compiled in Table 7.1. The isomers possess two major absorption bands arising from  $\pi$ - $\pi^*$  transitions in lower wavelength region (250–330nm) and intramolecular-charge transfer (ICT) transitions between the donor-acceptor strands in higher wavelength region (390–415nm) with a high extinction coefficient. The emission maxima of the isomers are in the range of 555–575nm with blue shifted emission for ***o*-BT** as a result of the decrease in the conjugation induced by the highly twisted structure.

**Table 7.1** Photophysical and thermal properties of ***p*-BT**, ***m*-BT** and ***o*-BT**.

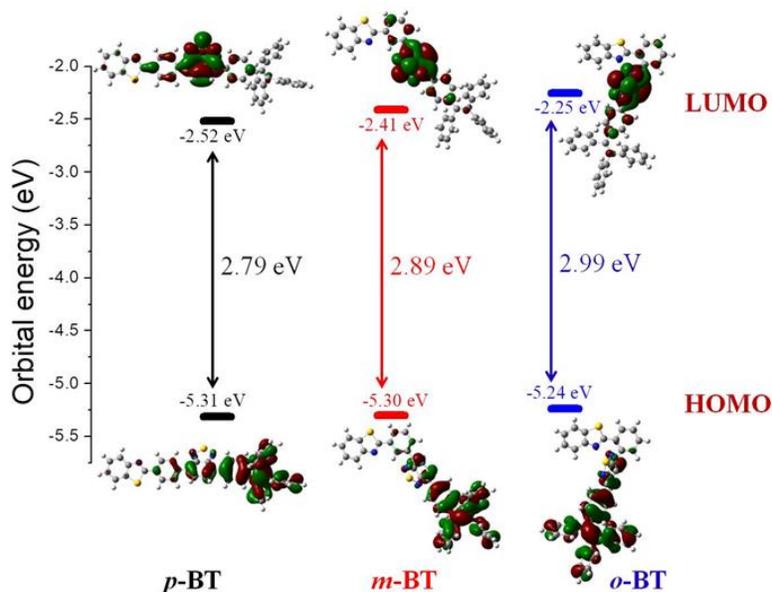
Compounds	$\lambda_{ab}$ [nm] ( $\epsilon$ [Lmol <sup>-1</sup> cm <sup>-1</sup> ]) <sup>a</sup>	$\lambda_{em}$ (nm) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>
<b><i>p</i>-BT</b>	321(45939), 411(25544)	570	405 °C
<b><i>m</i>-BT</b>	300(75575), 402(27525)	567	398 °C
<b><i>o</i>-BT</b>	279(28335) 307(28838), 396(10068)	559	363 °C

<sup>a,b</sup> Recorded in tetrahydrofuran, <sup>c</sup> Decomposition temperature.

### 7.5. Density functional theory calculations

The density functional theory (DFT) calculations were conducted at the B3LYP-6-31G(d,p) level for further accurate examination of the ground state electronic structures and geometries of the isomers ***p*-BT**, ***m*-BT** and ***o*-BT**.<sup>[17]</sup> The calculated frontier molecular orbitals are depicted in Figure 7.3 and the values are compiled in Table 7.2. The DFT optimized structures of the ***p*-BT** and ***o*-BT** isomers are in well accordance with the crystal structures. The isomers have propeller shaped geometry for TPE moiety and twisted structures with highest twisting in ***o*-BT**. The highest occupied molecular orbital (HOMO) is localized on the weakly donating TPE moiety whereas the lowest unoccupied molecular orbital (LUMO) resides on the benzothiadiazole moiety which confirms its higher electron accepting nature over benzothiazole. The HOMO-LUMO gap for ***p*-BT**, ***m*-BT** and ***o*-BT** are 2.79 eV, 2.89 eV and 2.99 eV respectively. The HOMO and LUMO

are well separated allowing a distinct intramolecular charge transfer (ICT) from the donor to acceptor.



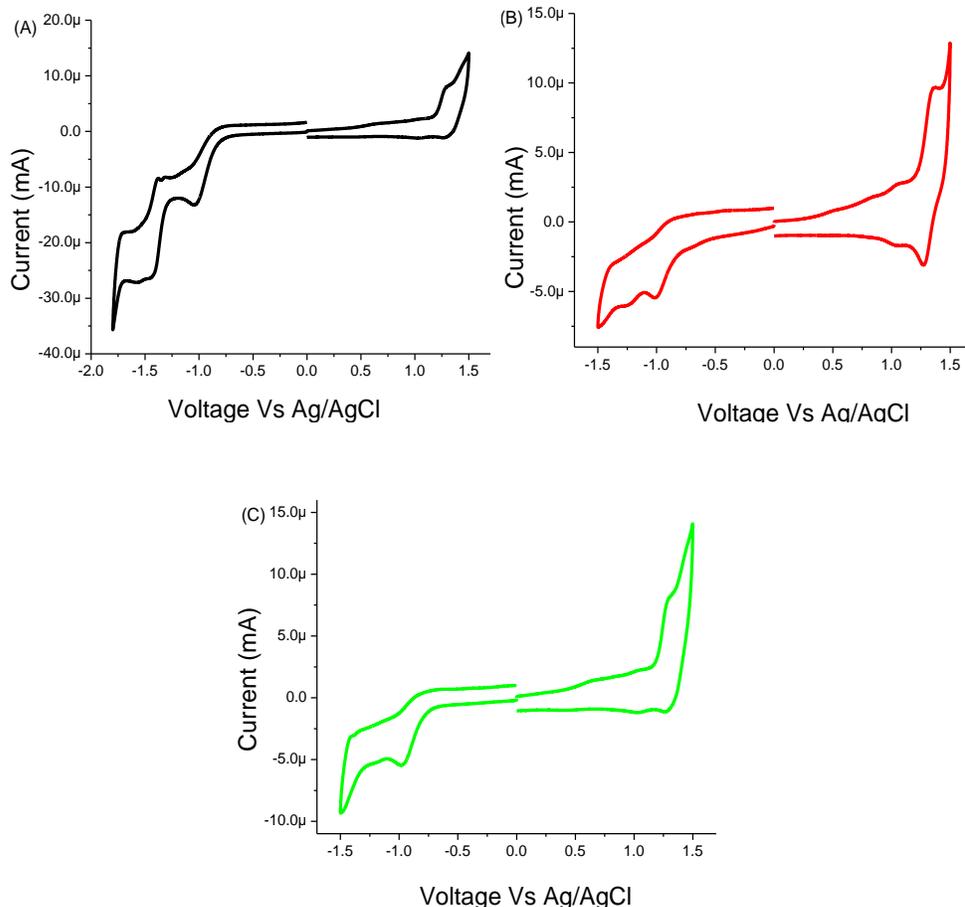
**Figure 7.3.** Energy level diagram showing the HOMO and LUMO energy levels of *p*-BT, *m*-BT and *o*-BT as determined at the B3LYP/6-31G(d,p) level.

	Electrochemical properties			DFT calculations		
	HOMO <sup>a</sup> eV	LUMO <sup>a</sup> eV	HOMO -LUMO gap eV	HOMO <sup>b</sup> eV	LUMO <sup>b</sup> eV	HOMO -LUMO gap eV
<i>p</i> -BT	-5.54	-3.62	1.92	-5.31	-2.52	2.79
<i>m</i> -BT	-5.56	-3.62	1.94	-5.30	-2.41	2.89
<i>o</i> -BT	-5.58	-3.68	1.90	-5.24	-2.25	2.99

**Table 7.2.** Electrochemical properties and DFT calculations of *p*-BT, *m*-BT and *o*-BT.

<sup>a</sup> Calculated from CV: Reference electrode- Ag/AgCl <sup>b</sup> Theoretical values at B3LYP/6-31g(d,p) level.

## 7.6. Electrochemical properties

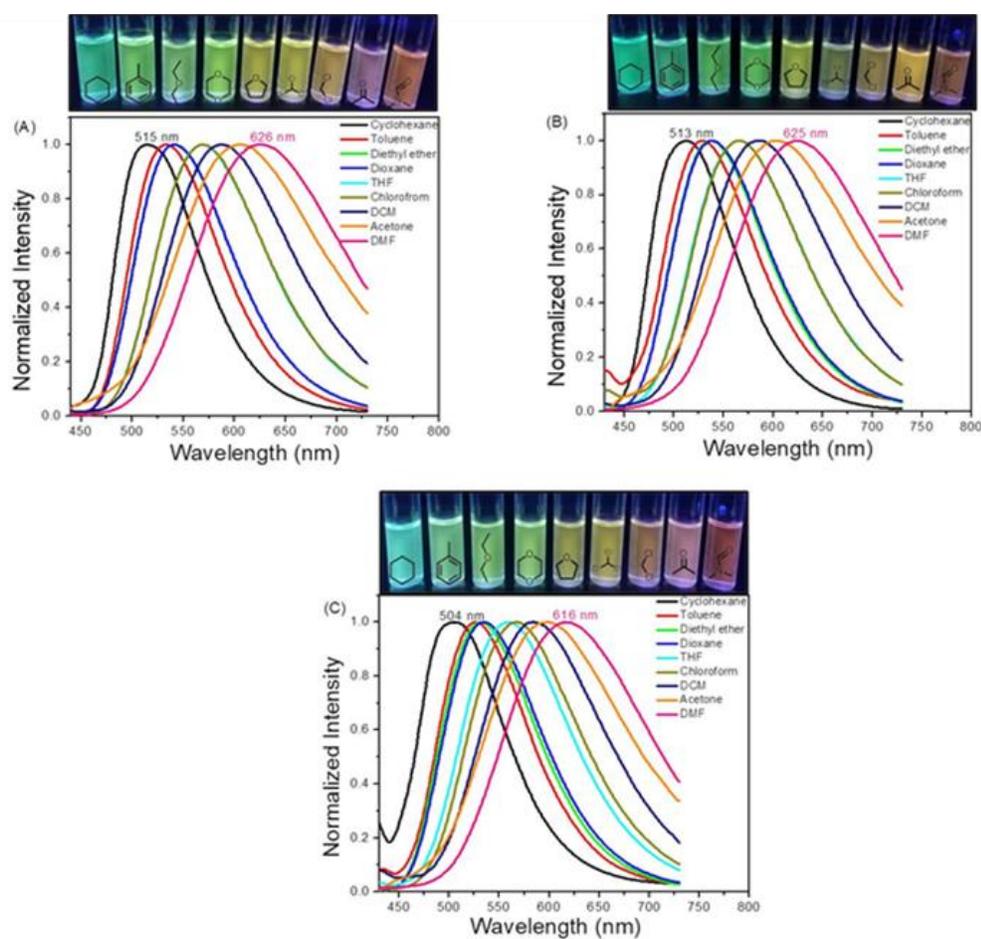


**Figure 7.4.** Cyclic voltammetry (CV) plots of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT.

The energy levels and electrochemical properties were examined by employing cyclic voltammometry using tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte for a solution of the isomers in DCM. Figure 7.4. shows the irreversible nature of the cyclic voltammograms and Table 7.2. lists the corresponding data for the electrochemical study of *p*-BT, *m*-BT and *o*-BT. The HOMO and LUMO values were calculated from the onset value of oxidation or reduction wave ( $E_{\text{onset}}$ ) utilizing the equation  $\text{HOMO/LUMO} = - (E_{\text{onset}} + 4.4) \text{ eV}$ .<sup>[18]</sup> The

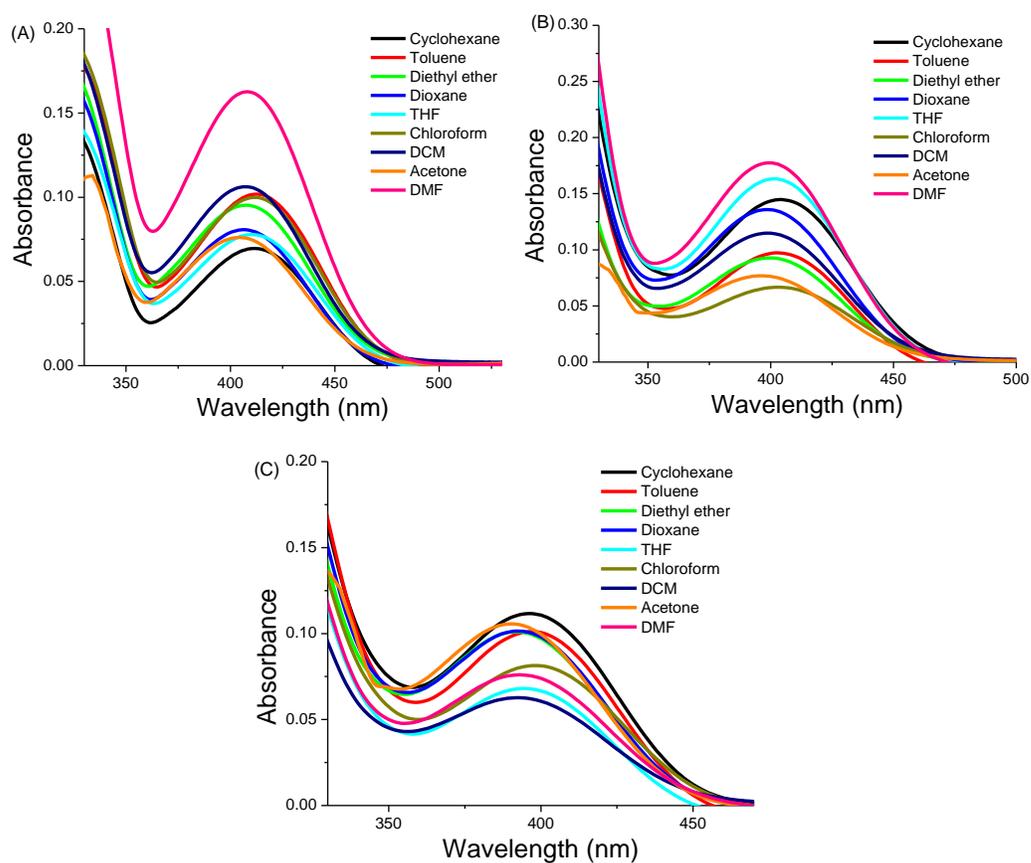
values for HOMO levels of *p*-BT, *m*-BT and *o*-BT are -5.54 eV, -5.56 eV and -5.58 eV respectively and the values of LUMO levels are -3.62 eV, -3.62 eV and -3.68 eV respectively. The electrochemical HOMO-LUMO gaps for *p*-BT, *m*-BT and *o*-BT are 1.92 eV, 1.94 eV and 1.90 eV respectively. The CV graphs exhibit one oxidation wave and two reduction waves corresponding to a donor TPE and acceptors BTD and BT respectively.

## 7.7. Solvatochromism



**Figure 7.5.** Emission spectra of the isomers (A) *p*-BT, (B) *m*-BT and (C) *o*-BT (excitation wavelength or  $\lambda_{\text{ex}}=370$  nm) in solvents of different polarities. (Photographs taken under 365 nm illumination, from left to right- cyclohexane, toluene, diethyl ether, 1,4-dioxane, THF, chloroform, DCM, acetone, DMF.)

The intramolecular charge transfer (ICT) transition is greatly influenced by change in solvent polarity and is a distinct feature in donor-acceptor molecule.<sup>[19]</sup> The target isomers are comprised of a D-A-A' structural unit owing to which the result of change in the solvent polarity was investigated using fluorescence spectroscopy (Figure 7.5.) and electronic absorption spectroscopy (Figure 7.6.) in a range of solvents from non-polar to polar (cyclohexane, toluene, diethyl ether, 1,4-dioxane, THF, chloroform, dichloromethane(DCM), acetone and N,N-dimethylformamide(DMF)).



**Figure 7.6.** Electronic absorption spectra of the isomers (A) *p*-BT, (B) *m*-BT and (C) *o*-BT (excitation wavelength or  $\lambda_{ex}$ =370 nm) in solvents of different polarities.

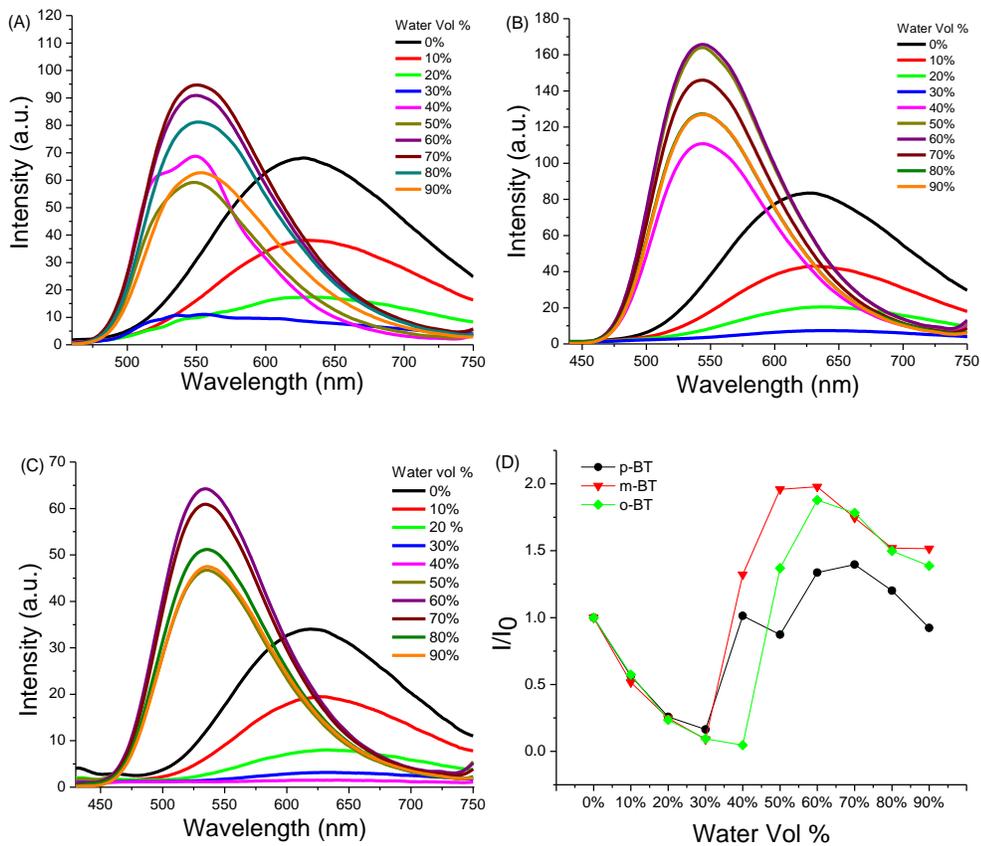
In comparison to the fluorescence spectra, the absorption spectra exhibited minor changes on changing the polarity of solvent which suggests the presence of more polarized excited states than the ground electronic states.

The *p*-BT and *m*-BT isomers manifest a bright green fluorescence in cyclohexane at 515 nm and 513 nm respectively whereas the *o*-BT isomer emits at 504 nm in cyclohexane with a bluish green fluorescence. The isomers *p*-BT, *m*-BT and *o*-BT emit a yellow fluorescence in moderate polar solvents like 1,4-dioxane, THF, CHCl<sub>3</sub>. In polar solvent like DMF, a bright orange fluorescence was observed at 626 nm, 625 nm and 616 nm respectively enabling the isomers to achieve a wide range of colours in the visible region. The isomers *p*-BT, *m*-BT and *o*-BT exhibit similar changes in emission on gradually increasing the solvent polarity and a bathochromic shift of 111 nm, 112 nm and 112 nm respectively was observed (Figure 7.5.). In all the isomers, the HOMO mainly resides on the weak donor TPE and LUMO mainly resides on the BT unit and does not involve the benzothiazole unit as observed by the DFT calculations. The ICT transition occurs from TPE unit to the BT unit and does not involve the BT unit owing to which the positional isomerism does not have a significant effect on the ICT transition. The transfer of electron from donor to acceptor causes charge separation in the excited state resulting in polarized excited state possessing an enhanced transition dipole moment which can be stabilized by the reorganization of polar solvent molecules resulting in reduced energy of the excited state leading to noteworthy bathochromic changes in the emission spectra.

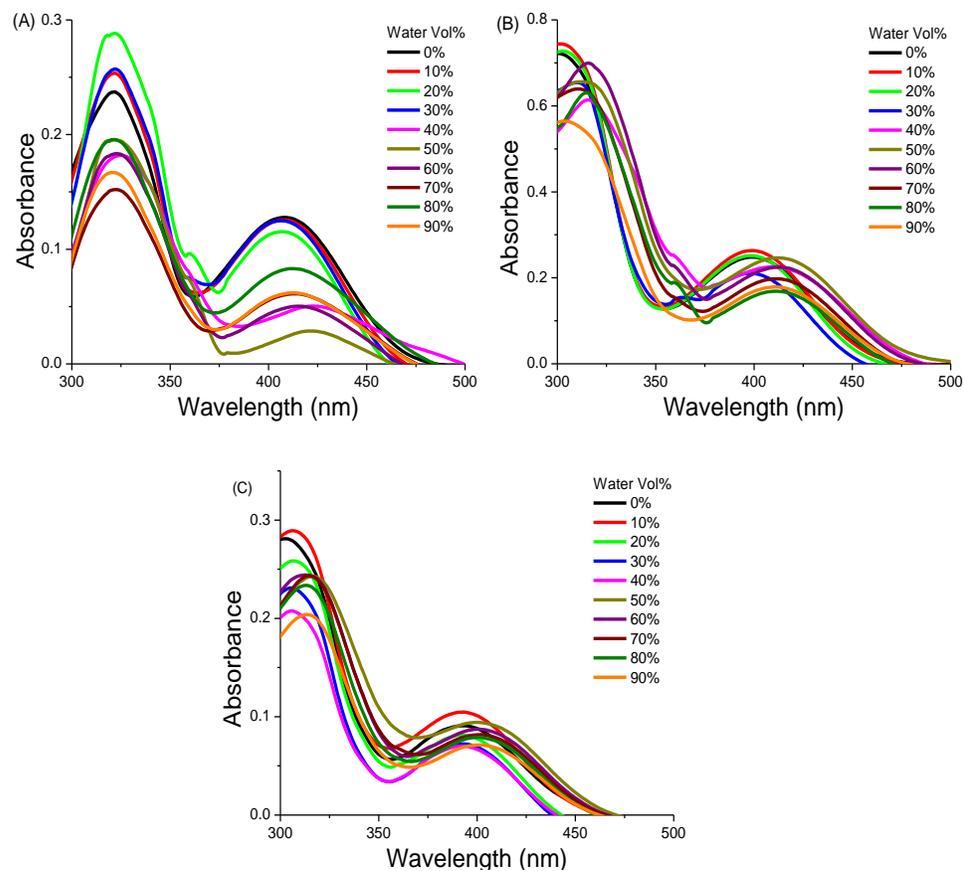
### 7.8. Aggregation-induced emission

The isomers were designed with tetraphenylethylene core to accomplish solid-state emission induced by aggregation. The formation of nanoaggregates was initiated by progressive addition of non-solvent (water) to the solvent system (DMF) and the AIE character of the isomers was measured using fluorescence (Figure 7.7.) and absorption spectroscopy (Figure 7.8.). The isomers *p*-BT, *m*-BT and *o*-BT emit at 626 nm, 627 nm and 618 nm respectively with a pink fluorescence at 0% water fraction or pure DMF solution due to significant ICT transition, unlike other TPE

containing molecules that are non-emissive in solution. The relative quantum yields (QY) for *p*-BT, *m*-BT and *o*-BT at 0% water fraction are 0.37, 0.20 and 0.21 respectively. The *o*-BT isomer shows reduction of intensity up to 40% while *m*-BT and *o*-BT isomer exhibit reduction of intensity up to 30% water fraction. This behavior can be attributed to the stabilized CT states resulting from increase in solvent polarity. The *p*-BT, *m*-BT and *o*-BT isomers display sharp intensity enhancement and a blue shift in wavelength (bright green emission) above 40-50% water fraction due to formation of nanoaggregates. The relative QY for *p*-BT, *m*-BT and *o*-BT at 90% water fraction are 0.60, 0.34 and 0.26 respectively. It can be concluded that the emission at lower water percentage is governed by ICT; however greatly influenced by aggregate formation at higher water percentage. Above 70% water fraction, a slight drop in emission intensity is observed due to the formation of the large-sized aggregates, which decreases the effective dye concentration in the solution and are less exposed to radiation as compared to smaller aggregates.<sup>[20]</sup>



**Figure 7.7.** Emission spectra of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT in DMF-water mixtures (0%–90% water), (D) Plot of fluorescence intensity vs. % of water fraction ( $f_w$ ). Luminogen concentration: 10  $\mu$ M; intensity calculated at  $\lambda_{max}$ .



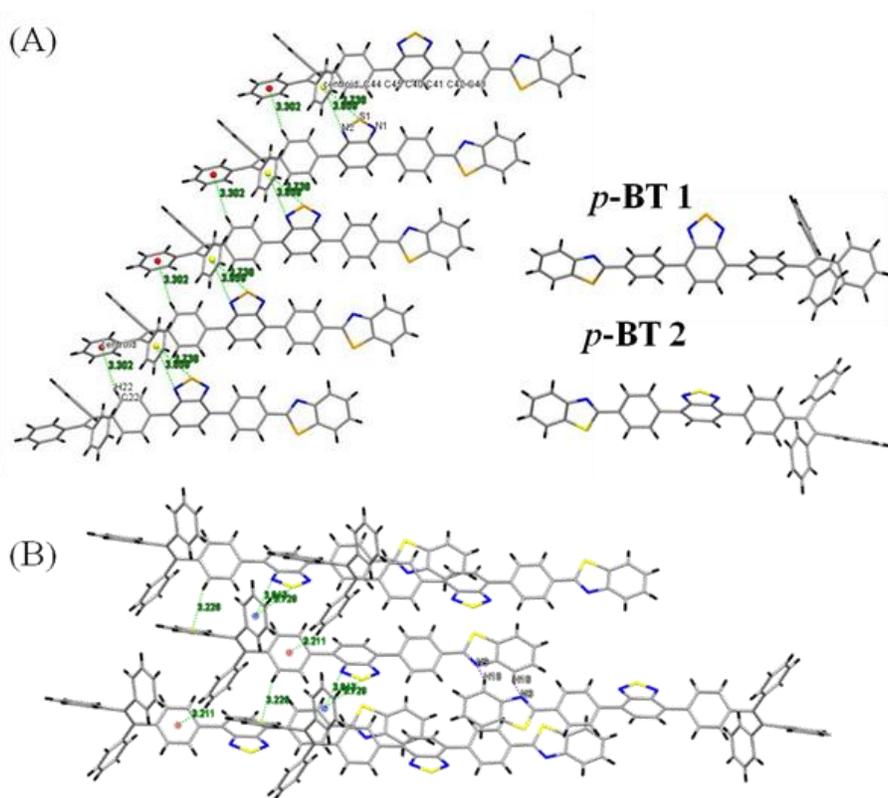
**Figure 7.8.** Electronic absorption spectra of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT in DMF-water mixtures (0% to 90% water), Luminogen concentration: 10  $\mu$ M; intensity calculated at  $\lambda_{max}$ .



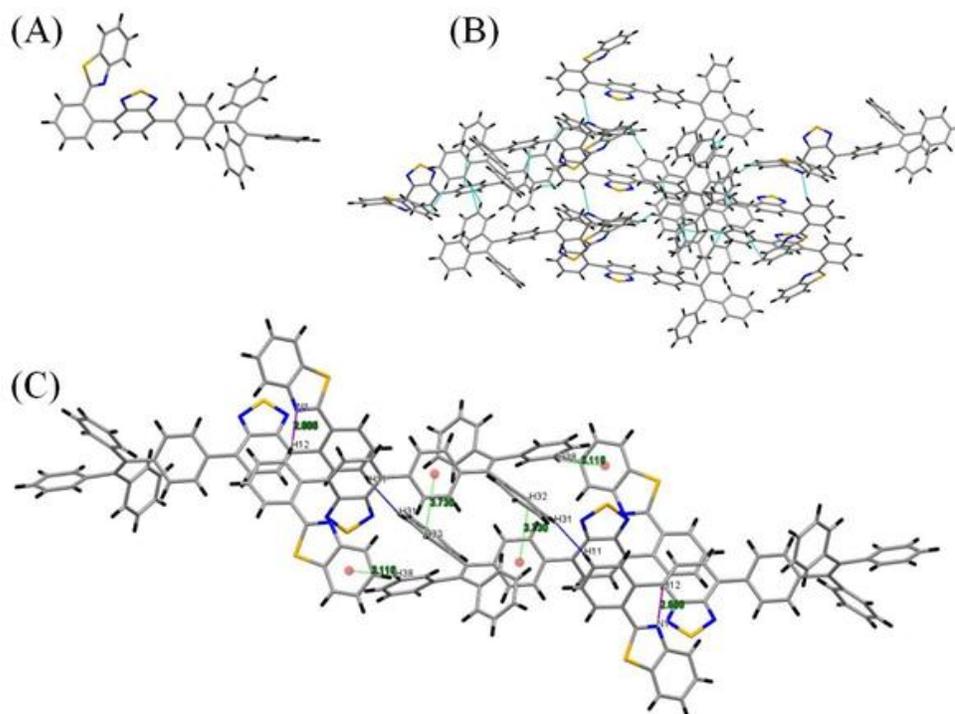
**Figure 7.9.** Photograph of (A) *p*-BT (B) *m*-BT and (C) *o*-BT in THF-water mixtures with different water fractions (10  $\mu$ M) (0% water to 90% water from left to right) under 365 nm UV illumination.

The Mie scattering effect of light can be witnessed in the electronic absorption spectra (Figure 7.8.) of *p*-BT, *m*-BT and *o*-BT as a consequence of nano-aggregate formation at 40% water fraction for the isomers.<sup>[21]</sup> The recorded AIE phenomenon can be visualized from the photographs given in Figure 7.9.

### 7.9. Single crystal X-ray analysis



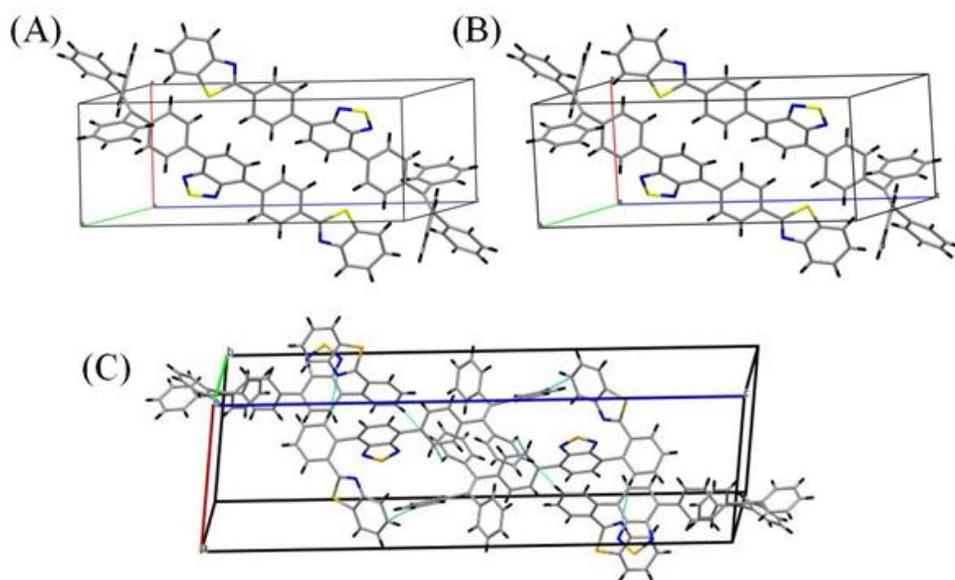
**Figure 7.10.** Crystal structure of *p*-BT 1 and *p*-BT 2; (A) Intermolecular interactions in (C-H $\cdots$  $\pi$  depicted by red centroid, N $\cdots$  $\pi$  and S $\cdots$  $\pi$  depicted by yellow centroid) in the crystal packing diagram of *p*-BT 1 (1-D ladder), (B) Intermolecular interactions (C-H $\cdots$  $\pi$  depicted by red and yellow centroid, N $\cdots$  $\pi$  and S $\cdots$  $\pi$  depicted by blue centroid, C-H $\cdots$ N weak hydrogen bonding interactions depicted by purple lines) in the crystal packing diagram of *p*-BT 2 (2-D framework).



**Figure 7.11.** (A) Crystal structure of *o*-BT. (B) Crystal packing diagram of *o*-BT (anti-parallel arrangement and 3-D framework) (C) Intermolecular interactions (C-H... $\pi$  depicted by red centroid and green line, C-H...N weak hydrogen bonding interactions depicted by purple lines) in the crystal packing diagram of *o*-BT.

The successful interpretation of the observed properties can be achieved by deducing the structural information achieved from single crystal X-ray analysis. The slow evaporation of dichloromethane (DCM)/hexane and chloroform/hexane solvent mixtures was used to grow good quality crystals for *p*-BT (fluorescent green) and *o*-BT (yellow) respectively. However, the crystallization of *p*-BT isomer in different batches using the same solvent system by slow evaporation serendipitously resulted in two different crystal forms namely *p*-BT 1 and *p*-BT 2. The *o*-BT isomer belongs to monoclinic crystal system and P21/n space group. The two crystalline forms of *p*-BT isomer belong to the triclinic crystal system with P-1 space group but differ from each other in orientation of the TPE moiety and degree of twisting

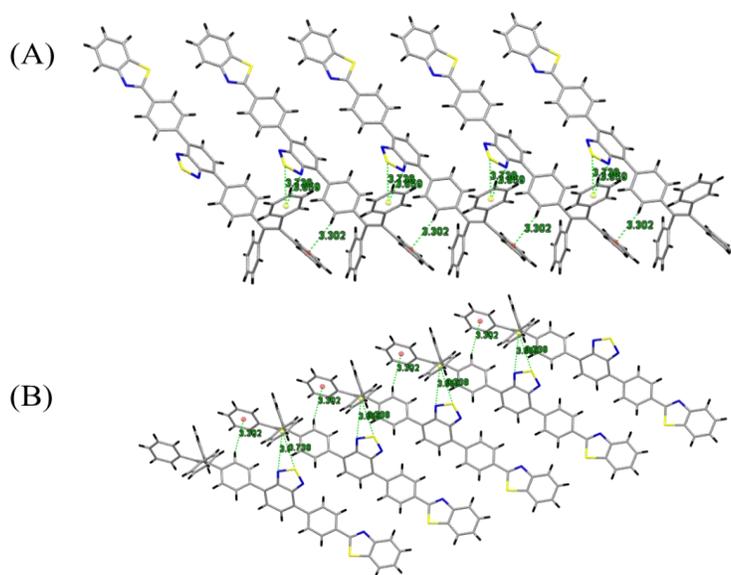
resulting in different crystal packing diagrams. The difference in the crystal packing of *p*-BT 1 and *p*-BT 2 results in interesting emission properties. The crystal structures of *p*-BT 1, *p*-BT 2 (Figure 7.10.) and *o*-BT (Figure 7.11. (A)) revealed twisted geometries for the tetraphenylethylene moiety as predicted and extensive twisting was observed in *o*-BT as compared to *p*-BT 1 and *p*-BT 2. The unit cell of *o*-BT crystal (Figure 7.12. (C)) consists of four molecules arranged anti-parallel with multiple intermolecular interactions in contrast to the unit cell of *p*-BT 1 and *p*-BT 2 (Figure 7.12. (A, B)) having absence of interactions between two anti-parallel arranged molecules.



**Figure 7.12.** Unit cell diagrams for the crystal of (A) *p*-BT 1, (B) *p*-BT 2 and (C) *o*-BT.

The crystal packing diagram of *p*-BT 1 (Figure 7.10. (A)) reveals C(22)–H(22)⋯ $\pi$  (red centroid-C34–C35–C36–C37–C38–C39, 3.302 Å) and lone-pair⋯ $\pi$  i.e. N(2)⋯ $\pi$ (3.859 Å) and S(1)⋯ $\pi$  (3.738 Å) ( $\pi$  depicted by yellow centroid- C40–C41–C42–C43–C44–C45) leading to 1-D ladder type formation. The *p*-BT 2 (Figure 7.10. (B)) contrarily displays extensive intermolecular interactions leading to a densely packed 2-D framework. The

interactions observed in ***p*-BT 2** are C(20)–H(31)⋯ $\pi$  (red centroid-C20–C21–C22–C23–C24–C25, 3.211 Å), C(35)–H(24)⋯ $\pi$  (yellow centroid-C34–C35–C36–C37–C38–C39, 3.226 Å), lone-pair⋯ $\pi$  i.e. N(1)⋯ $\pi$ (3.842 Å) and S(1)⋯ $\pi$  (3.729 Å) ( $\pi$  depicted by blue centroid- C40–C41–C42–C43–C44–C45) and weak H-bonding with N of the benzothiazole moiety C–H(18)⋯N(3) 2.748 Å. The crystal packing diagram of ***o*-BT** (Figure 7.11. (C)) confirms C–H(38) ⋯ $\pi$  3.118 Å, C–H(32) ⋯ $\pi$  3.730 Å ( $\pi$ -red centroid) and weak H-bonding with N of the benzothiazole moiety C–H(12) ⋯N(1) 2.686 Å. The presence of abundant intermolecular interactions in ***o*-BT** constructs a head to tail driven 3-D framework. The highly twisted structure of ***o*-BT** a 3D framework of the crystal lattice makes the isomer resistant to physical structural changes caused by mechanical stimuli.<sup>[22]</sup> The top view and side views of the crystal packing diagrams for ***p*-BT 1**, ***p*-BT 2** and ***o*-BT** are given in Figure 7.13., Figure 7.14. and Figure 7.15. respectively. The crystallographic data is summarized in Table 7.3.



**Figure 7.13.** Crystal packing diagram of ***p*-BT 1** (A) side view and (B) top view.



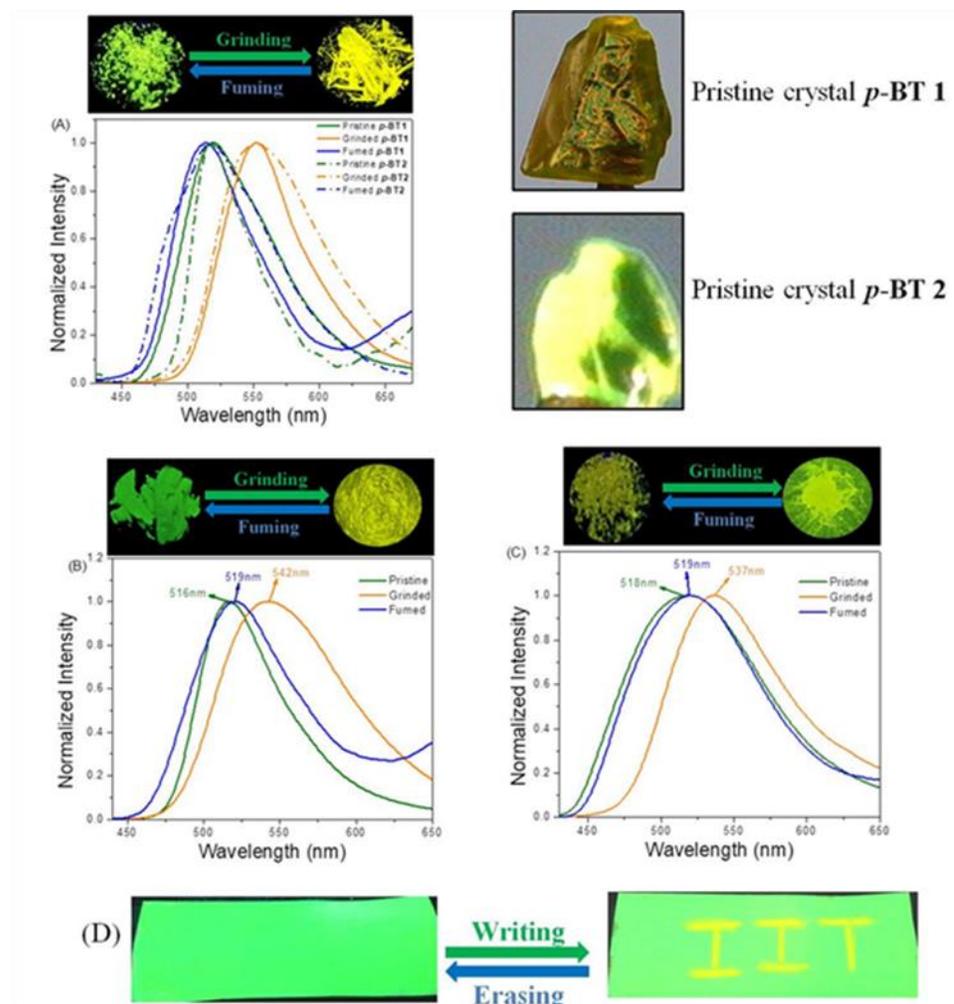
**Table 7.3.** Crystal data and structure refinement for *p*-BT 1, *p*-BT 2 and *o*-BT

Identification code	rm211	rm262	rm241
Empirical formula	C45 H29 N3 S2	C45 H29 N3 S2	C45 H29 N3 S2
Formula weight	675.83	675.83	675.83
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	1.54184 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P -1	Triclinic, P -1	Monoclinic, P 21/n
a/(Å)	7.6932(3)	7.6440(8)	11.0588(10)
b/(Å)	9.9070(2)	9.8294(8)	8.5477(7)
c/(Å)	22.3507(6)	22.3403(19)	36.929(3)
Alpha/(°)	88.016(2)	87.824(7)	90
Beta/(°)	83.522(3)	83.835(8)	98.260(7)
Gamma/(°)	83.631(2)	83.258(7)	90
Volume	1681.75(9) Å <sup>3</sup>	1656.8(3) Å <sup>3</sup>	3454.6(5) Å <sup>3</sup>
Z, Calculated density	2, 1.335 mg/m <sup>-3</sup>	2, 1.355 mg/m <sup>-3</sup>	4, 1.299 mg/m <sup>-3</sup>
Absorption coefficient	1.727 mm <sup>-1</sup>	0.200 mm <sup>-1</sup>	0.192 mm <sup>-1</sup>
F(000)	704	704	1408
Crystal size	0.230 x 0.180 x 0.140 mm	0.230 x 0.180 x 0.130 mm	0.230 x 0.180 x 0.130 mm
Θ range for data collection/(°)	3.982 to 71.221	2.938 to 29.320	3.026 to 29.143
Reflections collected / unique	10875 / 6398 [R(int) = 0.0207]	20784 / 7817 [R(int) = 0.1927]	29511 / 8224 [R(int) = 0.1475]
Completeness to theta	Θ = 67.684 99.8 %	Θ = 25.242 99.8 %	Θ = 25.242 99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents

Max. and min. transmission	1.00000 and 0.42833	-	1.00000 and 0.52239
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data /restraints / parameters	6398 / 0 / 451	7817 / 0 / 451	8224 / 0 / 451
Goodness-of-fit on F <sup>2</sup>	1.043	0.944	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1336	R1 = 0.0985, wR2 = 0.2157	R1 = 0.0897, wR2 = 0.2097
R indices (all data)	R1 = 0.0483, wR2 = 0.1378	R1 = 0.2544, wR2 = 0.3547	R1 = 0.1470, wR2 = 0.2435
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.229 and -0.393	0.607 and -0.737	0.332 and -0.407

## 7.10. Mechanochromism

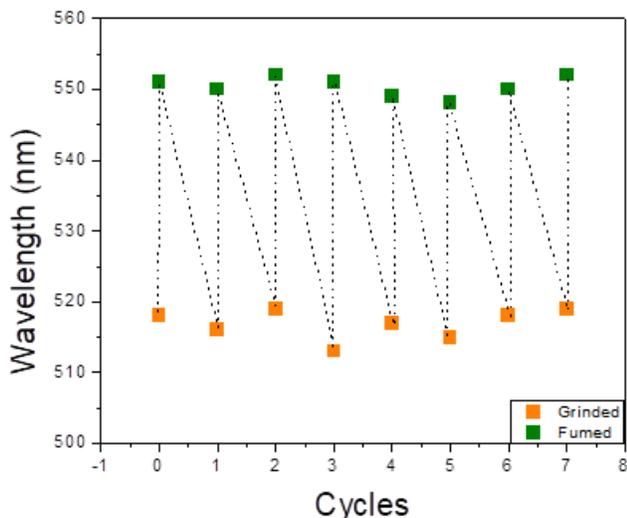
The *p*-BT, *m*-BT and *o*-BT were predicted to exhibit mechano-responsive solid-state emission taking in account the non-planar framework and AIE nature of TPE. The *para*, *meta* and *ortho* attachment of BT-D-TPE to benzothiazole moiety could vary the mechanochromic nature owing to the amount of twisting and/or acceptor strength in these isomers. The isomers were subjected to mechanical stimuli by grinding with mortar and pestle and the behaviour was explored using solid-state emission spectroscopy (Figure 7.16.) and the data are tabulated in Table 7.4. The crystals of *p*-BT isomer (*p*-BT 1 and *p*-BT 2) and *o*-BT isomer were considered as pristine samples while the *m*-BT isomer did not form any crystal owing to which the as-synthesized sample was considered as pristine.



**Figure 7.16.** Solid-state emission spectra of pristine, grinded and fumed solids of (A) *p*-BT 1 and *p*-BT 2, (B) *m*-BT and (C) *o*-BT (D) writing and erasing on a filter paper coated with *p*-BT, illustrating ink free rewritable system. (Photographs taken under 365 nm UV light) (Inset: Pristine crystals *p*-BT 1 and *p*-BT 2).

The *p*-BT 1 and *p*-BT 2 crystals have same structure but differ in their orientation in space resulting in different crystal packing. The pristine crystals *p*-BT 1 and *p*-BT 2 exhibit a bright green emission at same wavelength of 519 nm. Grinding of the *p*-BT 1 and *p*-BT 2 bathochromically shifts the wavelength to 552 nm with a yellow emission. The fumigation of the grinded forms of *p*-BT 1 and *p*-BT 2 using DCM-hexane for 15-20 minutes reverted the emission to 513 nm and 516 nm

respectively. The reversibility by fumigation for *p*-BT 1 and *p*-BT 2 was repeated up to 7 times and obtain wavelength of the fumed samples in the range of 513-518 nm (Figure 7.17.).



**Figure 7.17.** Repeated switching of the solid-state fluorescence of *p*-BT by repeated grinding and fuming cycles.

**Table 7.4.** Peak emission wavelengths ( $\lambda$ , in nm) of *p*-BT, *m*-BT and *o*-BT as pristine, grinded and fumed solids.

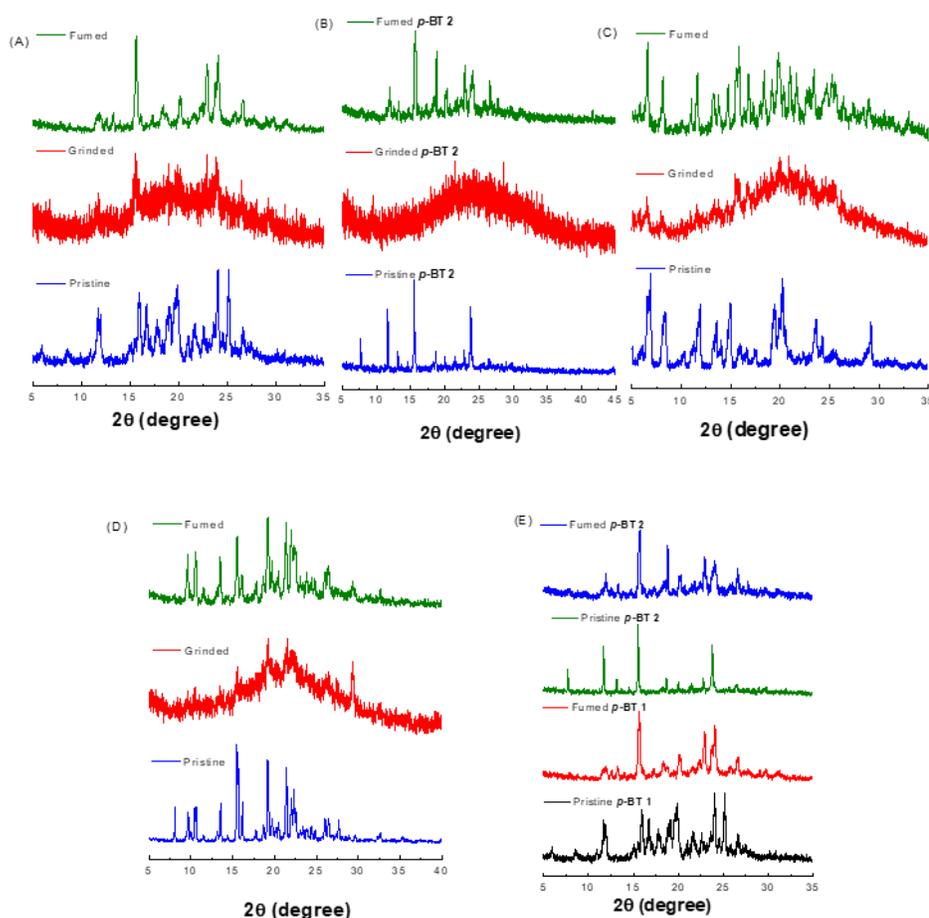
Compounds	Emission			
	$\lambda_{\text{pristine}}$ (nm)	$\lambda_{\text{ground}}$ (nm)	$\lambda_{\text{fumed}}$ (nm)	$\Delta\lambda^a$ (nm)
<i>p</i> -BT 1	519	552	513	39
<i>p</i> -BT 2	519	552	516	36
<i>m</i> -BT	516	542	519	26
<i>o</i> -BT	519	537	518	19

<sup>a</sup> Grinding-induced spectral shift,  $\Delta\lambda = \lambda_{\text{ground}} - \lambda_{\text{fumed/pristine}}$

The pristine solid of *m*-BT and *o*-BT exhibit a bright green emission at 518 nm and dark green emission at 519 nm respectively. The grinded forms of *m*-BT and *o*-BT display yellow and greenish yellow fluorescence at 542 nm

and 537 nm respectively. The fumed (DCM and hexane) solids of *m*-BT and *o*-BT emit at 519 nm and 518 nm, respectively. The spectral shift generated due to grinding in *p*-BT 1, *p*-BT 2, *m*-BT and *o*-BT is 39 nm, 36 nm, 26 nm and 19 nm respectively and follows the order *p*-BT > *m*-BT > *o*-BT.

### 7.11. Powder X-ray diffraction studies



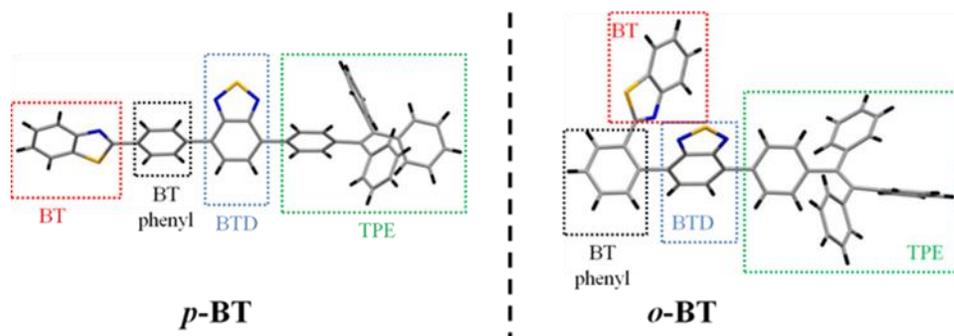
**Figure 7.18.** PXRD patterns of pristine, grinded and fumed solids of (A) *p*-BT 1 (B) *p*-BT 2 (C) *m*-BT and (D) *o*-BT, (E) Fumed patterns of *p*-BT 1 and *p*-BT 2.

The powder X-ray diffraction technique was used for interpretation of the reversible mechanochromic behavior. The PXRD patterns (Figure 7.18.) for the pristine solids of the isomers reveal sharp diffraction patterns due to the

crystalline nature. The grinded solids exhibit broad diffused PXRD pattern due to its amorphous nature. However, the sharp diffraction patterns reappeared on solvent fumigation indicating reversion to crystalline nature. The reversible mechanochromism can be assigned to morphology change from crystalline to amorphous caused due to modification of molecular arrangement on grinding. The different crystalline pristine forms ***p*-BT 1** and ***p*-BT 2** exhibit similar mechanochromic behavior but difference in their absolute quantum yields. The absolute quantum yields for the crystalline pristine forms ***p*-BT 1** and ***p*-BT 2** are 0.33 and 0.51 respectively. The absolute quantum yields of the grinded and fumed form for ***p*-BT 1** are 0.53 and 0.65 respectively and for ***p*-BT 2** are 0.51 and 0.63 respectively. The grinded and fumed forms of ***p*-BT 1** and ***p*-BT 2** exhibit similar quantum yields but a noticeable difference can be seen in the quantum yields of the pristine forms. The ***p*-BT 1** pristine crystal has very low quantum yield as compared to the pristine crystal ***p*-BT 2** and the grinded and fumed forms of ***p*-BT 1** and ***p*-BT 2**. The difference in the quantum yields of the two pristine crystals could be a consequence of their crystal packing.<sup>[23]</sup> The ***p*-BT 2** crystal confirms presence of abundant intermolecular interactions and weak H-bonding forming a tightly packed 2-D framework. On the other hand, the crystal packing of ***p*-BT 1** possesses a loosely packed 1-D structure which may result in the loss of excited state energy in terms of vibrational relaxation, lowering the quantum yield substantially. The two crystals exhibit difference in packing due to different orientation of TPE in space resulting in distinct PXRD patterns and absolute quantum yields. The fumed forms ***p*-BT 1** and ***p*-BT 2** are also crystalline in nature and possess similar PXRD patterns and quantum yields, however exhibit higher quantum yields as compared to pristine crystals of ***p*-BT 1** and ***p*-BT 2**. The fumigation of the sample is done over a short period of time which does not allow the molecule to orient in different ways resulting in similar quantum yields. The fumed forms of ***p*-BT 1** and ***p*-BT 2** exhibit highest quantum yields and blue shifted emission as compared to the two pristine crystalline

states which may possibly be an outcome of highest twisting of TPE in these crystalline forms resulting in a densely packed crystal structure. The absolute quantum yield of *m*-BT in its pristine, grinded and fumed forms is 0.74, 0.65 and 0.76 respectively. The absolute quantum yield of *o*-BT in its pristine, grinded and fumed forms is 0.34, 0.40 and 0.33 respectively.

## 7.12. Structure-property relationship

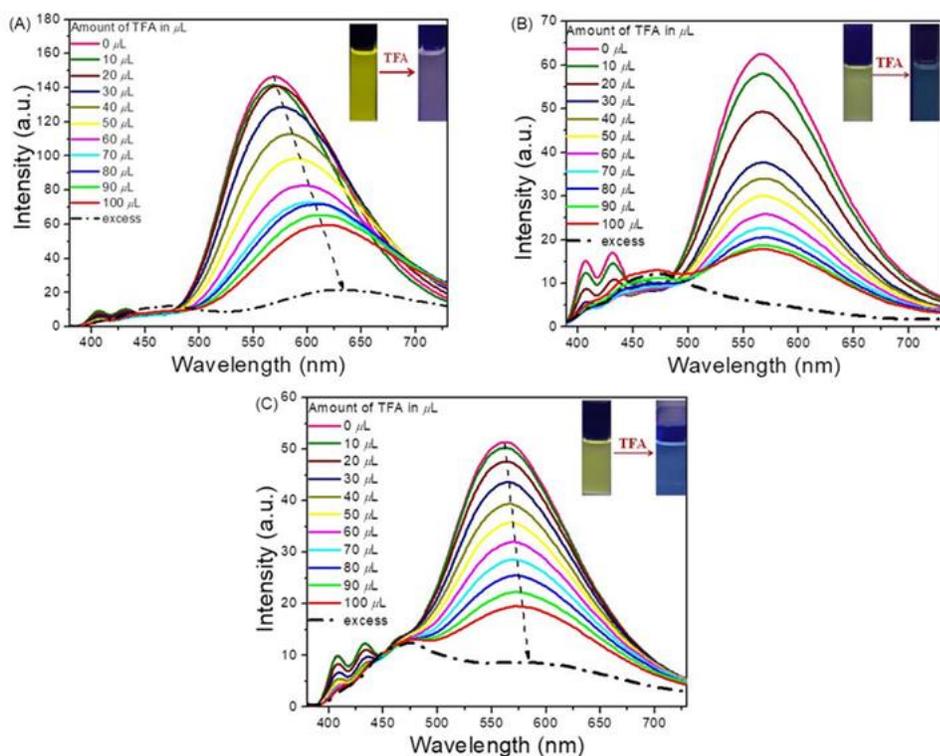


**Figure 7.19.** Schematic diagram for measurement of dihedral angles.

The difference in the mechano-responsive nature of the isomers can be inferred from the crystal analysis. The aromatic fragments in the *p*-BT and *o*-BT isomers were depicted as **BT** (benzothiazole), **BT phenyl** (phenyl attached to benzothiazole), **BTD** (benzothiadiazole) and **TPE** (tetraphenylethylene) as shown in Figure 7.19. for the measurement of dihedral angles. The dihedral angle between the **BT** plane and **BT phenyl** plane for *p*-BT 1, *p*-BT 2 and *o*-BT is 8.26°, 8.14° and 37.80° respectively and between **BT phenyl** and **BTD** for *p*-BT 1, *p*-BT 2 and *o*-BT is 35.09°, 34.42° and 62.25° respectively. The higher values of dihedral angle for *o*-BT over *p*-BT 1, *p*-BT 2 suggests an extremely twisted structure for *o*-BT reducing its susceptibility towards higher bathochromic shift on grinding. The highly twisted structure of *o*-BT makes it difficult in achieving planarity or furnishing meta-stable states after grinding thereby leading to poor mechanochromism. The twisting of donor moiety is essential for mechanochromism but higher twisting between the donor-acceptor moieties makes the structure rigid to move towards a planar structure. The dihedral

angle between **BT** plane and **TPE** plane in **p-BT 1**, **p-BT 2** is 44.13°, 46.22° and in **o-BT** is 40.53°. The higher twisting of the donor moiety in **p-BT** can also be one of the reasons for increased mechanochromism. The combined effect of the twisting and flexibility of the D-A moieties varies the degree of mechanochromism in the isomers.

### 7.13. Acidochromism

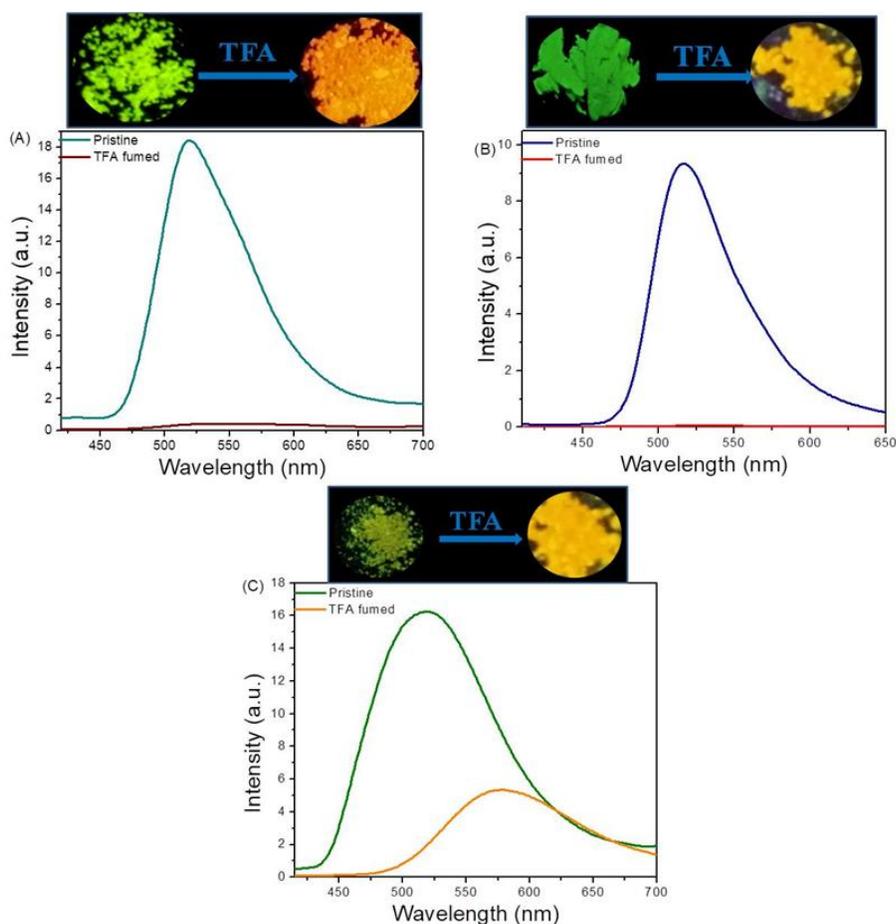


**Figure 7.20.** Emission spectra of (A) **p-BT**, (B) **m-BT** and (C) **o-BT** in response to known amounts of TFA in  $\text{CHCl}_3$ . (Conc.  $2 \times 10^{-5}$  M in  $\text{CHCl}_3$ ).

The spectral behavior of the isomers towards acid was analyzed taking in account the lone pair of N atoms which are susceptible to protonation.<sup>[24]</sup>

The solutions of the isomers **p-BT**, **m-BT** and **o-BT** in  $\text{CHCl}_3$  ( $2 \times 10^{-5}$  M) were titrated against known amounts of trifluoroacetic acid (TFA in  $\text{CHCl}_3$  stock solution) and studied using emission spectroscopy (Figure 7.20.). The emission maxima for the isomers **p-BT**, **m-BT** and **o-BT** at 569 nm, 566

nm and 562 nm respectively display quenching in emission intensity on gradual addition of TFA from 10 $\mu$ L to 100 $\mu$ L. The emission intensity at maximum wavelength quenched upto 91%, 90 % and 51% for ***p*-BT**, ***m*-BT** and ***o*-BT** respectively on excess addition of TFA. The ***p*-BT** isomer shows highest red shift of the emission maxima from 569 nm to 613 nm with reduced intensity on addition of 100 $\mu$ L TFA. Similarly, ***o*-BT** exhibits a bathochromic shift for the emission maxima from 562 nm to 576 nm on addition of 100 $\mu$ L. However, in case of ***m*-BT**, the excess addition of acid only resulted in extensive decrease of emission maxima. The peak between 460-465 nm was unaffected and appeared prominently on excess addition of TFA for all the isomers. The reduction in intensity for emission maxima confirms the response of isomers towards acid. The increased acceptor strength due to protonation of N atom by acid could result in a higher donor-acceptor interaction consequently causing a bathochromic shift. The isomers were exposed towards TFA vapors to further explore the changes in its solid-state emission. The emission intensity of ***p*-BT**, ***m*-BT** and ***o*-BT** was extensively decreased on fumigation with TFA (Figure 7.21.) for few minutes. The quenching of intensity can also be visualized by the color change of the fluorescent green solids to pale yellow. The absolute quantum yield of ***p*-BT**, ***m*-BT** and ***o*-BT** in its pristine form is 0.33, 0.74 and 0.34 respectively which on fumigation with TFA decreases to 0.01, 0.05 and 0.09 respectively. The isomers are highly reactive towards TFA in solution as well as solid state allowing its use as a fluorescent sensor for TFA.



**Figure 7.21.** Emission spectra of the pristine and TFA fumed solids of (A) *p*-BT, (B) *m*-BT and (C) *o*-BT.

## 7.14. Experimental details

### General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker Avance III instrument by using  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ( $\text{CDCl}_3$ , 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet), and the coupling constants,  $J$ , are given in hertz.  $^{13}\text{C}$  NMR chemical shifts are reported relative to the solvent

residual peak (CDCl<sub>3</sub>, 77.0 ppm). Thermogravimetric analyses were performed on the Mettler Toledo thermal analysis system. UV–visible absorption spectra were recorded on a Cary-100 Bio UV–visible spectrophotometer. Emission spectra were taken in a The Fluoromax-4C, S/n.1579D-1417-FM Fluorescence software Ver 3.8.0.60. The quantum yields in solid state were measured using K-sphere Integrating sphere. The excitation and emission slits were 2/2 nm for the emission measurements and 3/3 for solid quantum yield measurements. All of the measurements were done at 25 °C. HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. The voltammograms were recorded on a CHI620D electrochemical analyzer in dichloromethane solvent and 0.1 M TBAF<sub>6</sub> as the supporting electrolyte. The electrodes used were glassy carbon as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode. Single-crystal X-ray structural studies of **1** and **4** were performed on a CCD equipped SUPERNOVA diffractometer from Agilent Technologies with Oxford Instruments low-temperature attachment under argon/nitrogen using standard Schlenk and vacuum-line techniques. The acidochromism was performed using 0.1 M stock solution of TFA in CHCl<sub>3</sub>. The rewritable-ink free paper was prepared using Whatman filter paper. The compound *p*-BT was dissolved in DCM, and then the filter paper was coated with *p*-BT. After drying, an ink-free plastic tip was used to write “IIT” on the *p*-BT loaded paper.

### Synthesis and characterization of *p*-BT and *m*-BT

General procedure for synthesis of *p*-BT and *m*-BT. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mmol) was added to a well degassed solution of BT4 (0.4 mmol), BTD-TPE (0.4 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol) in a mixture of toluene (24.0 mL)/ethanol (8.0 mL)/H<sub>2</sub>O (4.0 mL). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue was subjected to column chromatography on silica (Hexane–DCM 30:70 in vol.) to yield the desired product *p*-BT as a green

crystals. The same procedure was employed using **BT5** and **BT-D-TPE** to obtain the desired product **m-BT** as a yellowish green powder.

**p-BT**: Yield: 73%;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.27 (d,  $J = 8.0$  Hz, 2H), 8.11-8.14 (m, 3H), 7.94 (d,  $J = 8.0$  Hz, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.80 (d,  $J = 8.0$  Hz, 3H), 7.52 (t,  $J = 8.0$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.05-7.15 (m, 15H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  167.5, 154.3, 154.0, 144.0, 143.7, 143.6, 141.6, 140.4, 139.9, 135.2, 135.1, 133.5, 133.3, 131.9, 131.6, 131.5, 131.4, 131.3, 129.8, 128.4, 128.3, 127.8, 127.6, 126.6, 126.5, 126.4, 125.3, 123.3, 121.6, 0.0 ppm; HRMS (ESI): Calcd. for  $\text{C}_{45}\text{H}_{29}\text{N}_3\text{S}_2$   $[\text{M} + \text{Na}]^+$ : 698.1695. Found: 698.1690.

**m-BT**: Yield: 69%;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.69 (s, 1H), 8.17 (d,  $J = 8.0$  Hz, 1H), 8.12 (t,  $J = 8.0$  Hz, 2H), 7.94 (d,  $J = 8.0$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 1H), 7.81 (d,  $J = 8.0$  Hz, 3H) 7.68 (t,  $J = 8.0$  Hz, 1H), 7.52 (t,  $J = 8.0$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.06-7.14 (m, 15H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  167.8, 154.2, 154.0, 153.9, 144.0, 143.7, 143.6, 141.5, 140.5, 138.3, 135.1, 134.1, 133.4, 132.0, 131.8, 131.6, 131.5, 131.4, 131.3, 129.3, 128.4, 128.2, 127.8, 127.7, 127.6, 127.4, 126.6, 126.5, 126.4, 125.3, 123.3, 121.6, 0.0 ppm; HRMS (ESI): Calcd. for  $\text{C}_{45}\text{H}_{29}\text{N}_3\text{S}_2$   $[\text{M} + \text{Na}]^+$ : 698.1695. Found: 698.1687.

**Synthesis and characterization of o-BT**: The mixture of **BT-D-TPE** (0.4 mmol) and **o-TBT-BT6** (0.4 mmol) in toluene (15 mL) was degassed and  $\text{Pd}(\text{PPh}_3)_4$  (0.01 mmol) was added to it. The resulting mixture was heated at 80 °C for 72 h. The reaction was monitored using thin-layer chromatography. The mixture was cooled and the solvent was evaporated to dryness. The residue was subjected to column chromatography on silica (Hexane-DCM 20:80 in vol.) to yield the desired product **o-BT** as orange-yellow crystals. Yield: 51%;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.20-8.22 (m, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.80-7.83 (m, 2H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.60-7.64 (m, 5H), 7.37 (dt,  $J = 8.0$  Hz, 1H), 7.26-7.27 (m, 1H),

7.23-7.25 (m, 1H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.09-7.15 (m, 12H), 7.04-7.06 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  167.1, 165.1, 153.2, 152.8, 144.0, 143.7, 143.6, 141.5, 140.4, 137.0, 136.0, 135.0, 133.5, 132.6, 131.6, 131.5, 131.4, 131.3, 130.6, 130.5, 130.2, 128.8, 128.4, 129.3, 128.4, 127.8, 127.7, 127.6, 126.6, 126.5, 125.9, 124.9, 123.2, 121.2, 0.0 ppm; HRMS (ESI): Calcd. for  $\text{C}_{45}\text{H}_{29}\text{N}_3\text{S}_2$   $[\text{M} + \text{H}]^+$ : 676.1876. Found: 676.1874.

**Synthesis and characterization of *o*-TBT-BT6:** n-BuLi 1.6 M (1.89 mmol) was added dropwise to a stirred solution of **BrBT3** dissolved in THF under argon atmosphere at -78 °C (10.0 ml). The solution was stirred for 1 h at -78 °C. To this solution, tributyltin chloride (1.89 mmol) was added dropwise and the reaction was left overnight. The reaction mixture was neutralized using aqueous  $\text{NH}_4\text{Cl}$  and the aqueous layer was extracted using dichloromethane. The combined extracts were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica (Hexane-DCM 50:50 in volume) to give desired product ***o*-TBT-BT6** as colourless oil. Yield: 71%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.88-7.92 (m, 2H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.38-7.53 (m, 4H), 1.45-1.55 (m, 6H), 1.23-1.32 (m, 6H), 1.09 (t,  $J = 8.0$  Hz, 6H), 0.82 (t,  $J = 8.0$  Hz, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  170.2, 153.1, 144.0, 139.1, 137.8, 135.1, 129.9, 129.0, 128.4, 126.1, 125.0, 122.6, 121.6, 29.2, 27.4, 13.6, 12.6, 0.0 ppm; HRMS (ESI): Calcd. for  $\text{C}_{21}\text{H}_{26}\text{NSn}$   $[\text{M} - \text{nBu}]^+$ : 444.0804. Found: 444.0803.

### 7.15. Conclusion

In conclusion, we have designed and synthesized multichromophoric D-A-A' isomers incorporating benzothiazole (BT) and benzothiadiazole (BTD) as acceptors and tetraphenylethylene (TPE) as donor. The acceptor strength was varied by changing the position of BTD-TPE with respect to the *ortho*, *meta* and *para* positions of BT. A comparative study about the structure-property relationship has been established for the isomers. The ***p*-BT**, ***m*-**

**BT** and ***o*-BT** isomers were synthesized by coupling BTD-TPE with BT using the Suzuki and Stille cross-coupling reactions. The isomers exhibit high thermal stability essential for fabrication in solid state devices. The isomers display distinct solvatochromic behavior in various polarity solvents with emission ranging from blue to orange with high bathochromic shifts. The non-planar framework of the isomers results in enhancement of intensity in the aggregated state. The ***p*-BT**, ***m*-BT** and ***o*-BT** exhibit reversible mechanochromism between green to yellow in the order ***p*-BT**>***m*-BT**>***o*-BT** and has been exploited for the development of ink-free rewritable papers. The PXRD studies reveal that a morphological conversion from crystalline to amorphous state is responsible for mechanochromism and leads to formation of metastable states. The single crystal X-ray analysis shows that the ***o*-BT** isomer has an extensively twisted structure and tightly packed 3-D framework as compared to ***p*-BT**, which explains the reason of lower response to mechanical stimuli. The higher twisting and tight packing of ***o*-BT** reduces the flexibility of the donor moiety to achieve planarization on grinding. The DFT studies reveal good separation of HOMO and LUMO supporting a distinct ICT transition. The isomers display changes in emission wavelength and intensity in solution and solid state in response to trifluoroacetic acid and can act as potential sensors for its detection. The combination of the three chromophores helps in achieving enhanced emission in solid state suitable for mechanochromic materials. The positional changes allow fine tuning of acceptor strength and molecular packing inducing changes in the mechano-responsive behaviour. The opted strategy provides a new pathway in design of AIE active mechanochromic materials suitable for application as mechano-sensors, security paper, light emitting devices and other optoelectronic applications.

## 7.16. References

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## Chapter 8

### Conclusions and future scope

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#### 8.1. Conclusion

The development of organic molecules with tunable solid-state emission is of great importance owing to their wide range of applications such as organic light emitting diodes (OLEDs), sensors, bioimaging, stimuli-responsive materials and other optoelectronic devices.<sup>[1]</sup> Organic molecules exhibiting changes in their optical properties as a response to various external stimuli (such as pressure, light, pH, temperature) are known as stimuli-responsive materials.<sup>[2]</sup> Mechanochromic materials have emerged as one of the most promising stimuli-responsive materials owing to their potential applications in pressure sensors, rewritable inks, photo modulation, memory devices, luminescent switches, fluorescent probes, data storage materials.<sup>[3]</sup> The application of external stimuli for most of the stimuli-responsive materials has been successfully exploited in their solid state. Hence, stimuli-responsive materials essentially require solid-state emission which can be achieved by the phenomenon of aggregation-induced emission (AIE) discovered by Tang *et. al.*<sup>[4]</sup> The introduction of (AIE) active luminogens in conventional organic fluorophores that are usually non-emissive in solid state has proved to be a useful technique for furnishing solid-state emissive stimuli responsive materials.<sup>[5]</sup> The well-known AIE active molecules such as tetraphenylethylene, triphenylamine, phenothiazine have been utilized for the development of mechanochromic materials.<sup>[6]</sup> The solid-state emission majorly depends on the molecular packing modes and intermolecular interaction in the solid state.<sup>[6]</sup> Hence, tunable emission can be achieved by subtle changes in the molecular packing which are dependent on twisting or planarity in the structures, steric hindrance, inclusion of alkyl chains or heavy atoms, intermolecular interactions due to heteroatom or halogen effects, positional

isomerization.<sup>[6]</sup> Organic molecules utilizing different donor-acceptor frameworks such as D-A, D-A-D, D- $\pi$ -A *etc.* serve as excellent candidates for stimuli-responsive materials with applications in optoelectronics.<sup>[7]</sup> The incorporation of various heterocyclic acceptors and AIE donors can further allow modulation of the electronic, photophysical and stimuli-responsive properties. We have designed and synthesized donor-acceptor functionalized organic molecules and investigated the photophysical, electronic and stimuli-responsive properties such as mechanochromism, solvatochromism and acidochromism of these systems.

In Chapter 3, we have synthesized set of novel T-shaped donor-acceptor-donor type luminophores employing phenanthrene-quinoxaline (**PQ**) as acceptor **A** and acenaphthene-quinoxaline (**AQ**) as acceptor **A'** as central units substituted with phenothiazine (**PTZ**) as donor **D** and tetraphenylethylene (**TPE**) as donor **D'**. The D-A-D based symmetrical quinoxaline luminophores display intramolecular charge transfer (ICT) transitions which is confirmed by solvatochromism. In comparison to the TPE substituted luminophores, the PTZ based symmetrical luminophores possess higher donor-acceptor character to the owing to the higher donor character of PTZ. All the symmetrical quinoxaline luminophores exhibit emission enhancement induced by aggregation (AIE) due to the incorporation of AIEgens PTZ and TPE which makes them suitable solid-state emitters. The symmetrical quinoxaline luminophores display reversible mechanochromic behavior with a good color contrast and a morphological change from crystalline to amorphous is responsible for mechanochromism. The AIEgen PTZ exhibits better stimuli-responsive behavior as compared to AIEgen TPE owing to the better conformational flexibility of butterfly shaped PTZ unit. The contrasting donor-acceptor interaction between the two set of symmetrical quinoxaline luminophores can be exploited to tune the photophysical and electronic properties of these materials. The attachment of AIEgens PTZ and TPE to quinoxaline results in efficient solid-state emission with stimuli-responsive properties.<sup>[8]</sup>

In Chapter 4, we have designed and synthesized phenanthrene-quinoxaline (PQ) (acceptor A) and acenaphthene-quinoxaline (AQ) (acceptor A') based D-A-D'/D-A'-D' quinoxaline derivatives substituted with three different donors namely phenothiazine (PTZ), tetraphenylethylene (TPE) and N-substituted PTZ in an unsymmetrical fashion. The quinoxaline derivatives exhibit contrasting photophysical properties due to the unsymmetrical substitution of different donors which majorly affects the D-A character, structural geometries and intermolecular interactions in the solid state. The set of unsymmetrical derivatives using donors PTZ and TPE exhibit intense ICT emissions originating from both the TPE and PTZ donors which are highly solvent-dependent. The ICT emission corresponding to PTZ donor are highly polarized and stabilized in polar solvents as compared to the TPE due to the stronger donating ability of PTZ in comparison to TPE. In contrast, the unsymmetrical quinoxaline derivatives having N-PTZ substitution along with PTZ display reduced or quenched CT emissions in polar solvents owing to the formation of a twisted intramolecular charge transfer (TICT) state originating from the almost perpendicular positioned N-PTZ unit. The presence of AIEgens PTZ and TPE in one set of unsymmetrical derivatives allows intense emission in the aggregated state; however the unsymmetrical derivatives containing N-PTZ unit display quenching of emission in their aggregated state. The PTZ-TPE based unsymmetrical derivatives derivative display reversible emission switching on grinding with very high grinding induced spectral shift making them suitable stimuli-responsive materials and the mechanochromic performance is related to crystalline to amorphous phase change. The PTZ and N-PTZ based quinoxaline derivatives possess non-fluorescent solids although exhibit grinding induced color-switching. The donors PTZ and TPE turn out to be favorable in developing AIE active stimuli-responsive materials as compared to N-PTZ donor. The work gives a detailed analysis of utilizing donors with different strengths in unsymmetrical fashion with heterocyclic

$\pi$ -conjugated acceptor unit and its effect on the photophysical and electronic properties, solid-state emission and stimuli-responsive properties.<sup>[8]</sup>

In Chapter 5, we have designed and synthesized phenanthroimidazole (PI) functionalized positional isomers comprising of a weak donor tetraphenylethylene TPE and a strong donor triphenylamine TPA. The PI based positional isomers exhibit high thermal stability making them suitable for practical applications. The single crystal analysis reveals a propeller orientation of the TPA unit and TPE unit which endows the derivatives with strong AIE characteristics making the derivatives excellent solid-state emitters. The PI positional isomers display reversible emission changes in response to mechanical stimuli with a good colour contrast corresponding to a morphological change from amorphous state to crystalline state. The positional change alters the sensitivity of PI isomers towards mechanical stimuli. The combination of phenanthroimidazole, TPA and TPE synergistically result in high stimuli responsive solid-state emission.<sup>[9]</sup>

In Chapter 6, a series of D-A positional isomers were designed and synthesized by the functionalization of phenothiazine (**PTZ**) at *para*, *meta* and *ortho* positions of phenyl **BT**. The isomers were designed to regulate the donor-acceptor character as well as the intermolecular interactions in solid state and resulted in contrasting photophysical and electronic properties. The *para* isomer displayed strong ICT characteristics owing to enhanced conjugation due to lower degree of twisting compared to the *meta* and *ortho* isomers which displayed emission quenching in polar solvents due to formation of TICT state. All the isomers exhibit intensity enhancement in aggregated state and reversible mechanochromic characteristics owing to their non-planar twisted structures. The mechanochromic behaviour is associated with generation of metastable states and the crystalline to amorphous phase transformation. The isomers exhibit self-reversible colour switching owing to the conformational flexibility of PTZ moiety. The *para* isomer exhibits polymorphism owing

to the unique butterfly shape of PTZ moiety. The *meta* isomer has tightly packed crystal structure, which makes it less susceptible to grinding as compared to *ortho* isomer which has loosely packed structure, thereby exhibiting highest grinding induced spectral shift. The isomers are employed for sensing of trifluoroacetic acid. The adaptable conformations of PTZ moiety can regulate the intermolecular interactions resulting in molecules with distinct photophysical properties and stimuli-responsive materials with self-recovering mechanism.<sup>[10]</sup>

In Chapter 8, we have designed and synthesized multichromophoric D-A-A' isomers using benzothiazole (BT) and benzothiadiazole (BTD) as acceptors and tetraphenylethylene (TPE) as donor. The change of position of BTD-TPE with respect to the *ortho*, *meta* and *para* positions of BT also varies the acceptor strength. The isomers possess high thermal stability essential for fabrication in solid state devices. The isomers display distinct solvatochromic behavior in various polarity solvents with emission ranging from blue to orange with high bathochromic shifts. The non-planar framework of the isomers results in enhancement of intensity in the aggregated state. The isomers exhibit reversible mechanochromism between green to yellow in the order *para*>*meta*> *ortho* which has been exploited for the development of ink-free rewritable papers. A morphological conversion from crystalline to amorphous state is responsible for mechanochromism and leads to formation of metastable states. The highly twisted structure and tightly packed 3-D framework in *ortho* isomer results in lower response to mechanical stimuli as compared to *para*. The higher twisting and tight packing of *ortho* isomer reduces the flexibility of the donor moiety to achieve planarization on grinding. The isomers act as potential sensors for trifluoroacetic acid in solution and solid state. The combination of the three chromophores helps in developing effective solid-state emitters and stimuli-responsive materials. The positional changes allow fine tuning of acceptor strength and molecular packing inducing changes in the mechano-responsive behaviour.<sup>[11]</sup>

## 8.2. Future scope

The thesis highlights design strategies for development of donor-acceptor based stimuli-responsive materials. The use of various heterocyclic acceptors and AIE donors of different strengths in different donor-acceptor frameworks resulted in efficient solid-state emitters and stimuli-responsive materials. Further, the use of donor-acceptor systems, positional changes, different substitutions and incorporation of conformationally flexible moieties further helps in effective modulation of the photophysical, electronic and stimuli-responsive properties which was achieved by subtle changes in the molecular packing and intermolecular interactions. The solid-state emission and mechanochromic properties were explored and tuned depending upon the conjugation length and strength of donor-acceptor interaction. We have proposed that the change from twisted to planar structures is responsible for reversible mechanochromism and is associated with morphological transition from crystalline to amorphous forms. The donor-acceptor systems can also be successfully employed as sensors for acid detection and as rewritable inks. The work is of great importance and provides insights for designing different donor-acceptor functionalized solid-state emitters with reversible stimuli-responsive properties which can be finely tuned with physical structural changes. The opted strategy provides a new pathway in design of AIE active stimuli-responsive materials suitable for application as mechano-sensors, security paper, light emitting devices and other optoelectronic applications.

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