

A new Class of tricoordinate Boron Based Donor-Acceptor (D-A) Systems Exhibiting External Stimuli Responsive Properties, Delayed Emission and Room Temperature Phosphorescence

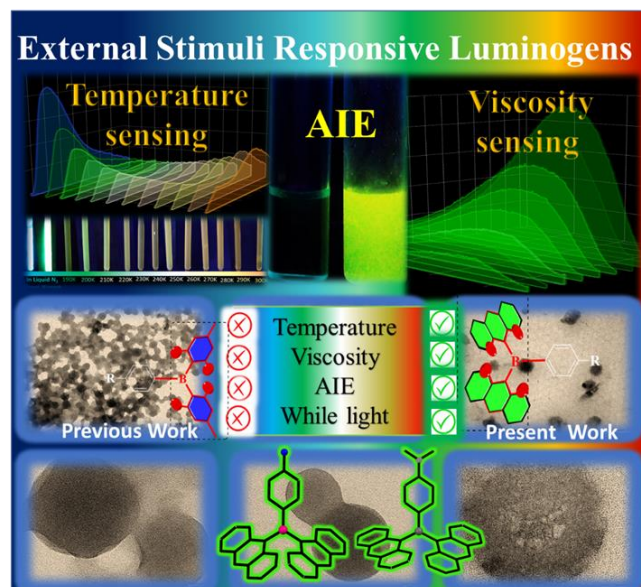
The main thrust of this thesis is the design and development of a new class of boron-based acceptors, with a substituent which maintains good electronic coupling between boron and the other substitutes on boron, without sacrificing the overall stability of the compound and to investigate their photophysical properties and applications. This thesis contains six chapters. The contents of individual chapters are described below.

Chapter-1 The first chapter provides an overview of the basic concepts of photoluminescence and highlights the challenges and opportunities associated with the design and development of novel luminescent materials. An assessment of the fundamental characteristics of triarylboron based donor-acceptor systems and their applications in various fields such as chemical sensors, aggregation induced emission, mechanochromism, thermally activated delayed fluorescent materials, organic radicals and optoelectronics are presented. This chapter also outlines the importance and scope of the work presented in this thesis.

Chapter-2 The second chapter describes the general experimental techniques and synthetic procedures followed in this thesis.

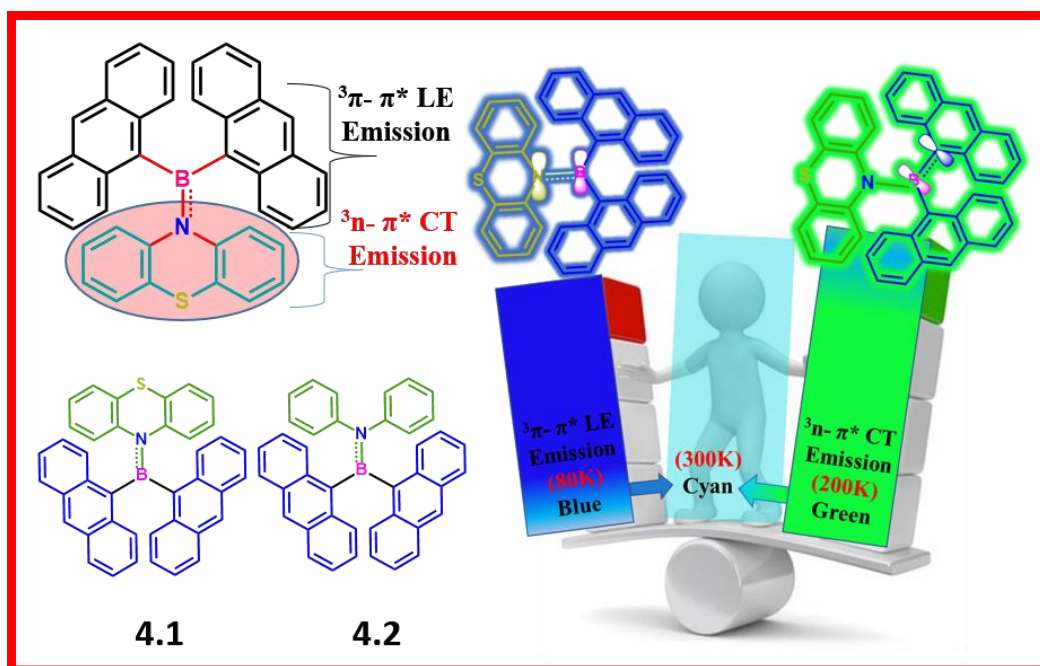
Chapter-3 describes the design and successful synthesis of di(anthryl)boryl “An₂B-” acceptor moiety. Two donor-acceptor dyads **3.1** and **3.2** were prepared by covalently linking the novel acceptor “An₂B-” with aniline and N,N-dimethylaniline respectively. A model compound An₂BPh (**3.3**) devoid of amine donor was also prepared to rationalize the effect of donor amine groups on the optical properties of dyads **3.1** and **3.2**. Molecular structures determined by single crystal X-ray diffraction method revealed that, the phenyl group of the aniline donor moiety in **3.1** and **3.2** assumes a quinonoid structure; however, such a quinonoid arrangement is absent in **3.3** without the amine donor. These results clearly indicate that there is a strong “through-bond” charge transfer interaction in **3.1** and **3.2**. This inference is well supported by UV-vis and photoluminescence (PL) characteristics of these compounds in solvents of different polarities and time resolved PL studies and together with computational calculations. These compounds are weakly emissive in solution state, but strongly emissive in viscous media, solid and aggregated states.

Promising AIEE (aggregation-induced emission enhancement) features were observed in these compounds upon formation of FONs (fluorescent organic nanoparticles). The AIE studies clearly indicate that the free rotation of $C_6H_5-NH_2/C_6H_5-NMe_2$ moiety is the major deactivation pathway for quenching the luminescence of **3.1** and **3.2** in solution state.



Apart from the above-mentioned investigations, other functional characteristics of these D-A dyads were also explored. Both the compounds show mechano-luminescence behaviour. Compound **3.1** shows turn-on PL response while compound **3.2** shows turn-off mechano-luminescence characteristics. Furthermore, the molecular conformation dependent optical characteristics of these compounds were exploited for detecting micro/macro characteristics of the environment such as viscosity and temperature of the medium.

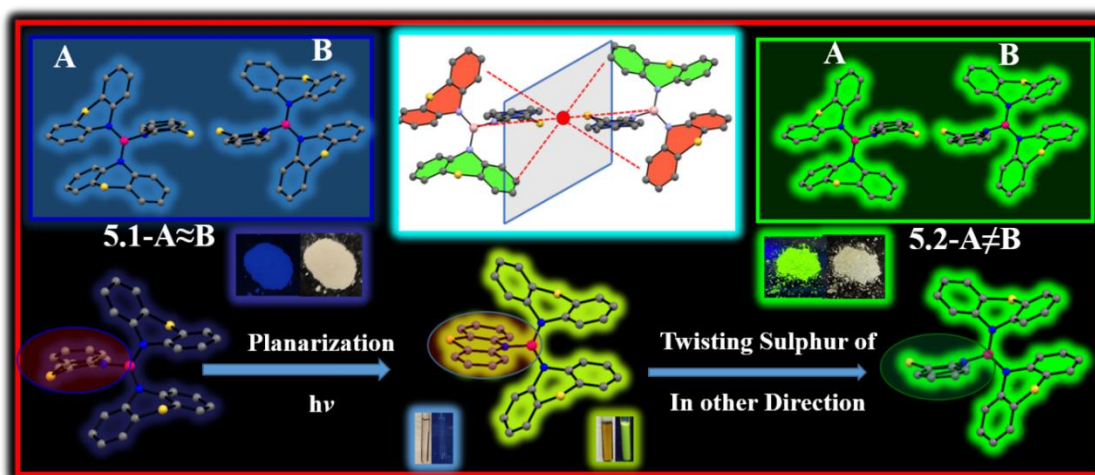
Chapter-4: The di(anthryl)boryl ((An)₂B-) moiety developed in chapter-3 was successfully employed for synthesizing a new class of aminoboranes **4.1** and **4.2**. Synthesis and intriguing low temperature delayed fluorescence characteristics of these aminoboranes are described in this chapter. Finetuning the temperature dependent delayed fluorescence characteristics of organic/organometallic compounds is a highly contemporary area of research. Systematic structural and electronic perturbation was used to fine-tune and to understand the luminescence properties of aminoboranes **4.1** and **4.2**. Computational study was carried out to gain an insight into the DF and luminescence mechanisms in bis(anthryl)boryl based compounds



Bonding parameters obtained from single crystal X-ray diffraction studies and DFT optimized structures indicate that $(An)_2B-$ is better acceptor than the Mes_2B- unit. Compound **4.1** and **4.2** show absorption features similar to that of anthracene; however, the absorption bands of **4.1** and **4.2** are 50 nm red shifted compared to the spectrum observed for simple anthracene. Both the compounds show dual emission features involving both LE and CT excited states. To understand whether the molecular flexibility plays a role in controlling the PL characteristics of **4.1** and **4.2**, aggregation dependent emission studies on both the compounds were carried out in THF- H_2O mixture. Compound **4.1** did not show aggregation dependent emission. However, compound **4.2** showed 26-fold stronger luminescence in aggregated state compared to its molecularly dispersed solutions. This result clearly indicate that the molecular flexibility indeed plays a role in controlling the PL characteristics of these compounds. Both the compounds exhibit delayed fluorescence characteristics in the temperature range 77K to 300 K. Interestingly, irrespective of the temperature, smooth overlap of prompt and delayed spectra of **4.1** and **4.2** was observed. However, the spectral shape and position of the peak maxima for **4.1** and **4.2** were highly sensitive to temperature at which the measurements were made. Based on steady state, time resolved experiments together with computational studies it was established that these molecules adopt different molecular conformation at different temperatures and consequently exhibit emission bands with different shapes and different energies. Further an asymmetric geometry perturbation of di(anthryl)boron unit in the excited state aids

effective coupling of singlet S_1 and triplet T_1 states, thus facilitating reverse intersystem crossing (RISC) and reduce the role of temperature in this process.

Chapter-5 describes visible light driven radical mediated molecular conformation switching and room temperature phosphorescence (RTP), thermally activated delayed fluorescence (TADF) and radical emission in tris(N-phenothiazinyl)borane (**5.1**). Compound **5.1** was synthesised by lithiation of phenothiazine followed by trapping the N-centred anion with 0.3 eq of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Compound **5.1** is a weakly blue emissive solid. Upon irradiation (5 minutes) of **5.1** with sunlight generates a radical cation, which was confirmed by electron paramagnetic resonance (EPR), line broadening of ^1H NMR resonance and near IR-radical absorption. This radical intermediate exhibit intense orange emission. The reduction of cation radical with ethanol gave a new conformer **5.2** which emits intense green light in the solid state.



A careful analysis of crystal structures of **5.1** and **5.2** divulges the presence of strain induced chirality in solid state of these two conformers. In solution state, both the conformers show similar ^1H -NMR pattern, UV-vis absorption and photoluminescence patterns. In contrast, the powder x-ray diffraction pattern for **5.1** and **5.2** are strikingly different. These results clearly indicate that the conformers are stable in solid state but interconverts rapidly in solution state. In the solid state, both **5.1** and **5.2** exhibit room temperature phosphorescence in distinct energy region of the electromagnetic spectrum. The molecular conformation of polymorphs in S_0 , S_1 , D_0 and D_1 and T_1 were optimized using DFT and TD-DFT methods. From the structural parameters obtained from optimized geometries in both ground and excited states together with steady-state and time-resolved photophysical studies, we have proposed a possible mechanism for luminescence and molecular conformation switching

in these molecules. To the best of our knowledge, this is the first report where the DF, RTP and radical emission is reported from the same organic emitter under various conditions.

Chapter-6 deals with synthesis and temperature dependent optical properties of dixylylborylnaphthalenediimide (**6.1**) and dimesitylboryl-naphthalenediimide (**6.2**) conjugates. These conjugates were synthesised by condensation of respective borylanilines with naphthalenetetracarboxylic anhydride. The UV-Vis absorption features of these compounds show weak CT band at the red end of the spectrum confirming the electronic coupling between diarylboryl and naphthalenediimide moieties. Because of weak electronic coupling, the HOMO and LUMO of these molecules are highly localized. This leads to a decrease in energy difference between the singlet and triplet excited states; consequently, these compounds exhibit delayed fluorescence characteristics. At ambient conditions, these compounds show only DF, however, at low temperatures, because of suppression of non-radiative decay of $T_1 \rightarrow S_0$, these compounds exhibit dual DF and phosphorescence features. Apart from the investigation of luminescence properties, other functional application of these conjugates was also explored. We made prototypes of coin battery using **6.1** and Li metal. Preliminary studies reveal that these molecules are potential candidates for battery applications.

