

SYNOPSIS

A New Class of Boron-Nitrogen Compounds: A Rational Approach for the Design and Development of Smart Materials

Replacing nonpolar homodiatomic C=C unit in a fully carbon π -conjugated system with an isoelectronic polar heterodiatomic B-N fragment is an active area of research. The first BN/CC isosterism was demonstrated seven decades ago. In the following decades, a significant amount of research effort has been devoted to understand the nature of chemical bonding between boron and nitrogen. Although, BN/CC isosterism is known for seven decades, surprisingly, the knowledge about the solid-state structure and optical properties of aminoboranes are scarce in literature. In modern days luminescent materials find numerous applications in display and lighting technologies, security systems, sensing and biological investigations. Thus, the main goal of this thesis is the design and development of novel aminoborane based organic materials that exhibit bright luminescence in the solid state. By exploiting BN/CC isosterism, we have developed new materials which are prototypes and exhibit interesting properties such as aggregation-induced emission and stimuli-responsive luminescence characteristics. Boron-nitrogen chemistry not only provides a rational design for smart materials but also enhances our understanding of the structure-property correlations in the solid state. This thesis contains 7 chapters and the content of each chapter is described below.

Chapter 1

The first chapter provides an introduction to the theme of the thesis and presents a general review of boron based donor-acceptor systems with special emphasis on BN/CC isosterism. Replacement of C=C units by an isoelectronic B-N units in acyclic/cyclic π -systems and their potential applications in various fields are discussed. In addition, advances in the new frontier areas, such as aggregation-induced emission, mechanochromism and triboluminescence are discussed in brief.

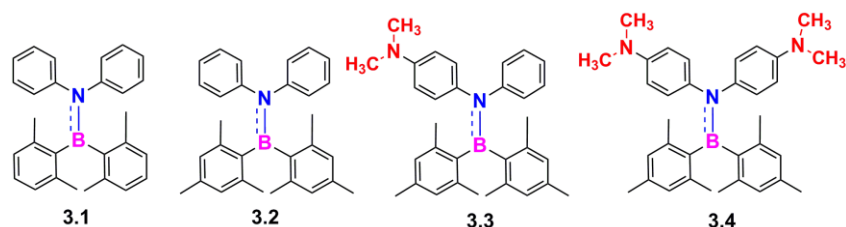
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Chapter 2

The second chapter deals with the general experimental techniques and synthetic procedures utilized in this work.

Chapter 3

Replacing homodiatomic C=C in polyaryl systems with an isoelectronic heterodiatomic



B–N unit is a powerful strategy for rational design and construction of novel materials with versatile properties. In chapter 3, we

uncover for the first time the intriguing aggregation-induced emission enhancement (AIEE) properties of four tetra-arylamino-boranes (TAAB) **3.1-3.4** in which the C=C fragment of the tetra-arylethene molecule is replaced by the isoelectronic B–N unit. The dipole moments of these compounds are fine-tuned by judiciously placing amine donor(s) on the aryl groups attached to nitrogen. The optical properties are greatly influenced by the number of amine donor(s) on the B–N fragment. Compounds **3.1-3.4** are weakly emissive in dilute solutions, but are strongly emissive in aggregated/condensed state. Compounds with strong amine donor(s) on B–N fragment exhibit reversible mechanofluorochromism. The experimental observations are corroborated by quantum mechanical calculations.

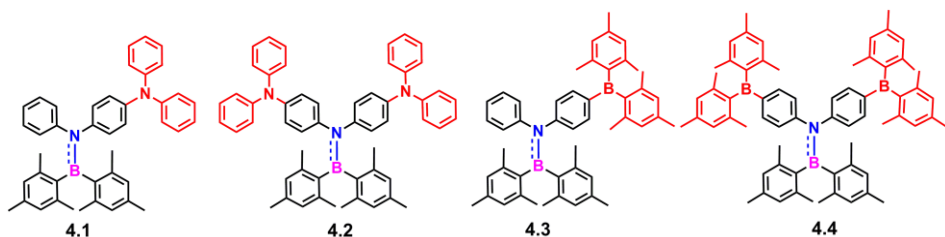
Chapter 4

The synthesis, structure and intriguing optical characteristics of four new polyaromatic aminoboranes (**4.1-4.4**) bearing bis(mesityl)boron (Mes₂B) as electron accepting unit(s) and diphenylamine (Ph₂N) as electron donating unit(s) are reported in this chapter. These compounds are strongly fluorescent in the solid state. Crystalline samples of **4.1** and triarylborane decorated aminoboranes **4.3** and **4.4** were found to be blue emitters in the solid state. Compounds **4.1** and **4.2** showed aggregation-induced emission (AIE) and

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aggregation-induced emission color switching, respectively, while **4.3** and **4.4** exhibited aggregation-induced emission enhancement. Compounds **4.1** and **4.2** showed fascinating mechanofluorochromism upon grinding and such fluorescence changes are due to a crystalline–amorphous phase transition, as confirmed by powder X-ray diffraction studies (PXRD).

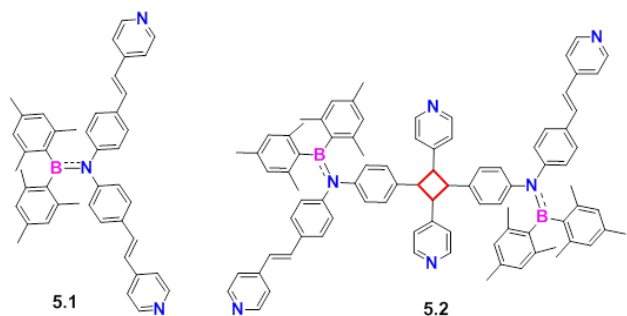
Interestingly, a ground sample of **4.2** was found to be stable and did not



revert back upon removal of external stress even after the sample was kept over a long period of time under ambient conditions (more than 6 months). “IPC” was written on a substrate of **4.2**, and the part that was touched showed fluorescence different from the rest of the substrate, which could be erased by heating. This result opens up the possibility of using **4.2** for rewritable data storage devices. The effect of steric and electronic factors on the optical properties of molecules was corroborated by DFT computational studies.

Chapter 5

Development of metal-free room temperature organic phosphorescent materials is emerging as highly attractive technology; however, several challenges remain in this area.



We report in this chapter a new BN system, tetraarylamino borane tethered with vinylpyridene units (**5.1**) and its corresponding photodimerized product (**5.2**) obtained by [2+2] cycloaddition of olefinic bonds in a single crystal to single crystal (SCSC) transformation upon

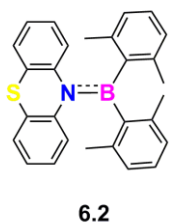
exposure to sun light within a very short time span of 1 hr. The reaction occurs in the solid state with complete conversion; however, there is no reaction in solution. The photodimerization is highly regioselective and irreversible under thermal conditions.

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Compounds **5.1** and **5.2** show distinct optical features in the solid state with contrast emission colours under UV light illumination and room temperature phosphorescence as confirmed by TRF measurements. DFT and TD-DFT calculations were performed to support the experimental observations.

Chapter 6

This chapter deals with the synthesis of the molecular siblings **6.1** (10-(dimesitylboryl)phenothiazine) and **6.2** (10-(bis(2,6-dimethylphenyl)boryl)phenothiazine)



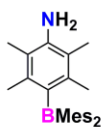
with multifunctional characteristics such as aggregation-induced emission (AIE), triboluminescence (TL), mechanofluorochromism and temperature sensing. Though **6.1** and **6.2** are structurally similar, their optical characteristics are quite different. The emission

characteristics of aggregates of **6.1** in 1:9 THF-water mixtures are sensitive to temperature while the aggregates of **6.2** are not so. Compound **6.1** showed luminescence color changes with mechanical stress, whereas **6.2** was insensitive to mechanical grinding. Relatively loose packing of **6.1** in the solid state makes it prone to mechanical forces and this could be a possible reason for its mechanofluorochromic properties. Crystals of **6.2** exhibited greenish yellow color triboluminescence (TL) when they were crushed with mild force. The polar non-centrosymmetric space group ($R3c$) of crystal **6.2** may be responsible for its TL behavior. No TL was observed for the crystals of **6.1**

Chapter 7

Design, synthesis and structural characterization of borylated aryl amines, Mes_2BAr {Ar = $\text{C}_6(\text{CH}_3)_4\text{NR}_2$ (**7.1**, **7.4**); $\text{C}_6\text{H}_4\text{NR}_2$ (**7.2**, **7.5**); $\text{C}_6\text{H}_3(\text{NR}_2)_2$ (**7.3**, **7.6**); R=H or CH_3 } and their optical properties are reported in this chapter. In these compounds, bright solid state emission with emission color tunability has been realized. The solid state luminescence characteristics of **7.1** and **7.3** are sensitive to mechanical stress with distinct emission color changes. Multiple strong intermolecular hydrogen bonds ($\text{N-H}\cdots\text{N}$ and $\text{N-H}\cdots\pi$)

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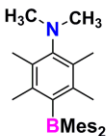
7.1



7.2



7.3



7.4



7.5



7.6

accompanied by subtle conformational changes play a significant role in the piezochromic response. PXRD and FT-IR spectroscopic studies and insensitivity of substituted derivatives to mechanical stress support the above inference. Interestingly, compound **7.3** crystallized in two different polymorphic forms **7.3BP** and **7.3GP**, which showed distinct luminescence, i.e., green and blue color under UV light. Such changes are due to their distinct hydrogen-bond network assembly in the solid state. Quantum mechanical calculations are performed in order to corroborate the optical properties.