Boron-Nitrogen Compounds in Luminescent Materials: A Review of Applications and Synthesis Methods

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Abstract. Boron-nitrogen compounds (B-N) have emerged as a promising material due to their unique electronic structure and excellent luminescent properties, showing great potential in organic light-emitting diodes (OLED) and electroluminescent devices. This paper systematically reviews the molecular structure, optical, and electronic properties of B-N compounds, discusses their applications in luminescent materials, and explores synthesis methods, including Friedel-Crafts-type reactions, borohydride reduction reactions, and olefin metathesis. Additionally, the paper analyzes key factors in controlling the performance of luminescent materials, investigating the impact of synthesis conditions, doping, and the preparation of composite materials on luminescent efficiency and stability. Despite significant progress in B-N compound research, challenges remain in synthesis precision, luminescent efficiency, and industrial production. Future research should focus on improving targeted synthesis capabilities, optimizing electronic structure and luminescent performance, and exploring more efficient, cost-effective production processes. With continued innovation, B-N compounds are poised to become a foundation for the next generation of high-efficiency luminescent materials, driving advancements in optoelectronic technology.

Keywords: Boron-nitrogen compounds, Luminescent materials, Synthesis methods, OLED.

1. Introduction

In recent years, boron-nitrogen (B-N) structures have replaced traditional carbon-based structures as a hot research topic in materials chemistry, particularly in the development of organic light-emitting diode (OLED) materials, showing great potential [1]. These boron-nitrogen compounds not only exhibit excellent luminescent properties but also have more easily adjustable energy levels and bandgaps, stronger intermolecular interactions, higher luminescence quantum efficiency, and superior air stability compared to carbon skeletons. In addition, B-N compounds possess excellent physical and chemical properties, such as remarkable ductility, allowing their use in various applications, including electronic device screens [2]. Despite these advantages, challenges remain in improving luminescent efficiency and reducing production costs. If B-N doped compounds can effectively replace the currently mainstream platinum-group metal-doped materials as the main structure of the luminescent layer, the production cost of OLED devices could be significantly reduced [3]. Research on B-N compounds can be traced back to the experiments of Stock and Pohland in 1926, but it has regained attention in recent years due to its potential applications in semiconductor devices. Particularly, the transition-metal-mediated [2+2+2] cycloaddition enabling non-fused 1,4-azaborine [4] has injected new vitality into research on B-N structure substitution.

Boron (B), as a Group III element, has a valence electron configuration of 2s2 2p1, with an empty pπ orbital on the atom, making it prone to coordination with the lone pairs of other atoms [2]. This characteristic allows nucleophilic reagents to attack it, forming tetra-coordinate boron compounds. For example, in HF, the lone pair on the F atom interacts with boron’s pπ orbital, generating BF4-. In recent years, boron-containing luminescent materials with π-conjugated frameworks have attracted widespread attention in the fields of organic electroluminescence and chemical sensors due to their unique photoelectric properties. OLEDs are devices that convert electrical energy into light, utilizing organic luminescent materials that have high luminescence efficiency, tunable emission colors, fast response speed, low driving voltage, thinness, light weight, and low cost. The emission principle is based on injecting carriers from the electrodes into the organic layer, where they move and recombine to form excitons. The radiative recombination of excitons leads to luminescence.

This study aims to systematically analyze the synthesis methods of B-N compounds as luminescent materials, including Friedel-Crafts-type reactions, borohydride reduction reactions, and olefin metathesis. By employing literature analysis to study the synthesis of these compounds, the paper presents and proposes some ideal synthesis strategies. The common Friedel-Crafts alkylation reaction involves removing halogens from alkyls through Lewis acids, generating a positively charged alkyl that then adds to an aromatic ring, achieving aromatization through base treatment. This paper will explore the advantages of B-N compounds' chemical properties, focusing on their research progress in low-carbon and environmentally friendly high-luminescence-efficiency applications, providing a new perspective and research basis for luminescent materials development.

2. Structure and Properties of Boron-Nitrogen Compounds

2.1. Molecular Structure of Boron-Nitrogen Compounds

molecular structure of B-N compounds is highly tunable, making them widely applicable in luminescent materials. The electron push-pull effect between boron and nitrogen atoms is key to enhancing the quantum efficiency of light emission. In B-N compounds, boron acts as an electron acceptor, and nitrogen acts as an electron donor. This electron push-pull effect not only facilitates efficient electron transfer but also enhances the separation efficiency of holes and electrons [5]. The sp3 hybridization of nitrogen and its lone electron pairs lead to a typically non-planar three-dimensional structure in these molecules. This geometry not only strengthens van der Waals forces between molecules but also helps form stable luminescent states. For example, luminescent materials prepared with boron tri-coordinated heterocycles exhibit increased spatial hindrance between molecules, effectively weakening π-π interactions and thereby enhancing fluorescence emission [5]. B-N compounds also exhibit high thermal stability, and the functional groups at the boron center can effectively modulate the optical properties of luminescent materials, achieving strong fluorescence emission.

2.2. Optical Properties

The optical properties of B-N compounds are strongly influenced by their molecular structure and electron distribution. Due to their unique aromatic ring structure and electron distribution, these compounds exhibit excellent light absorption and emission properties. Specifically, the number and position of B-N bonds play a crucial role in determining the optical properties of the material. Spectral analysis reveals characteristic absorption peaks of B-N bonds in the UV-visible spectrum, with the position and intensity of these peaks depending on the molecular structure [7].

In OLEDs, triplet excitons typically do not participate in emission. However, B-N compounds can transfer the energy of these triplet excitons through intermolecular excitation energy transfer, converting it into photons for high-efficiency luminescence [8]. Moreover, the emission color and efficiency of B-N compounds can be finely tuned by adjusting the number and position of B-N bonds, providing great flexibility and potential for the design of luminescent materials.

2.3. Electronic Properties

In B-N compounds, the high electron density of nitrogen atoms results in a significant polarity in B-N bonds. Boron carries partial positive charge, while nitrogen carries partial negative charge. This charge distribution not only affects the internal electron distribution and orbital energy levels of the molecule but also plays an important role in intermolecular interactions. Through resonance stabilization, B-N bonds can significantly enhance the chemical stability of materials, ensuring that luminescent materials maintain stable optical performance even in high-temperature or complex chemical environments [9]. Additionally, since boron and nitrogen in B-N bonds act as electron acceptor and donor respectively, these bonds can serve as centers for electron migration or coordination in organic synthesis. This characteristic gives B-N compounds broad application prospects in the design and synthesis of luminescent materials [10].

3. Synthesis Methods of Boron-Nitrogen Compounds

The synthesis methods of B-N compounds are diverse, with each method providing a unique pathway for developing specific types of luminescent materials. Further research and optimization of these methods can enhance material performance and reduce synthesis costs.

3.1. Friedel-Crafts Electrophilic Substitution Reaction

The Friedel-Crafts alkylation reaction is a classic electrophilic substitution reaction that can introduce an alkyl group into an aromatic ring by replacing a proton on the ring. This method is widely used in both laboratory synthesis and industrial production. Dewar first applied this method to the synthesis of B-N compounds in 1960, as shown in Figure 1. The lone pair on the nitrogen atom reacts with boron trichloride to form a C-B bond. Subsequently, under the catalysis of Lewis acids such as aluminum trichloride, a boron cation is generated and adds to the aromatic ring, forming a stable boron-nitrogen heterocycle [6, 11]. Although this method is difficult to achieve with electron-deficient aromatic rings, its mild reaction conditions and good selectivity make it important in the synthesis of B-N heterocycles. With further study of the reaction mechanism, this method can be optimized by adjusting reaction conditions and catalyst types to improve reaction yield and selectivity.

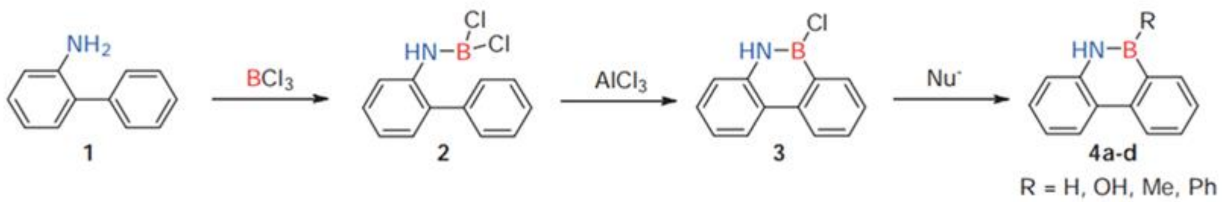

Fig. 1 Synthesis route of B-N substituted phenanthrene [6].

3.2. Borohydride Reduction Reaction

The borohydride reduction reaction is an effective method for synthesizing B-N heterocycles. White used oleylamine as a substrate in 1963, adding borane to form a B-N bond, and using a borohydride reduction reaction to construct a C-B bond. Finally, a dehydrogenation reaction catalyzed by palladium-carbon was performed to aromatize the heterocycle, forming a B-N substituted heterocyclic benzene. The advantage of this reaction lies in its high selectivity, allowing target products to be synthesized by modifying the substrate structure [12]. However, a major limitation of this reaction is the stringent reaction conditions, particularly the requirement for high-temperature dehydrogenation, which limits its use in practical production. To overcome this issue, researchers are exploring new catalysts and reaction conditions to improve the efficiency and feasibility of the reaction.

3.3. Olefin Metathesis Reaction

The olefin metathesis reaction is an effective method for constructing aromatic rings. In 2000, Ashe et al. successfully constructed a closed six-membered ring structure using a transition metal reaction and olefin metathesis, followed by aromatization treatment. Later, in 2017, Liu et al. further refined this method by introducing alkylation reagents and DDQ, successfully synthesizing 1,9-B-N substituted naphthalene [13]. Although this method has good selectivity and mild conditions, the requirement for two double bonds in close proximity within the substrate limits its wider application. Future research may focus on expanding the substrate scope and optimizing reaction conditions to enable broader application of this method.

4. Applications of Boron-Nitrogen Compounds in Luminescent Materials

4.1. OLED (Organic Light-Emitting Diodes)

OLED technology, as an important display and lighting technology, relies on the injection, movement, and recombination of carriers in the organic layer to form excitons, which emit light through the radiative recombination of excitons. The application of B-N compounds in OLEDs is mainly reflected in their excellent luminescence quantum efficiency and unique electronic structure. By introducing B-N compounds into the organic layer, the energy gap between the HOMO and LUMO levels can be effectively reduced, thereby enhancing electron transition efficiency [8]. Moreover, to optimize the luminescence efficiency of OLEDs, electron transport layers and hole transport layers are typically introduced between the cathode and the luminescent layer and between the anode and the luminescent layer, respectively. These transport layers balance the injection rates of carriers, preventing space-charge effects from negatively impacting luminescence efficiency. B-N compounds, as luminescent layer materials, can play a key role in this structure, significantly improving OLED luminescence efficiency and stability through their unique molecular structure and electronic properties [9].

4.2. LEC (Light-Emitting Electrochemical Cells)

LEC is a new type of organic electroluminescent technology characterized by its thin, lightweight, and easy-to-manufacture structure. Compared to OLEDs, LECs do not require additional electron and hole injection layers or output layers, instead balancing electron injection through their electrochemical properties. This simplified structure gives LECs a competitive edge in the field of luminescent materials [10]. In the selection of LEC materials, polymeric host materials such as benzothiophene (BDT) and benzotriazole (BTz) are widely used. By doping these polymers with boron compounds, the solubility and performance of the devices can be significantly improved [7]. In addition, thermally activated delayed fluorescence (TADF) materials, used as primary luminescent materials, can further enhance LEC efficiency by finely tuning the relative positions and quantities of boron and nitrogen atoms, allowing for color-tuning of luminescence [10].

5. Performance Control of Boron-Nitrogen Luminescent Materials

5.1. Influence of Synthesis Conditions on Luminescence Performance

The luminescence performance of B-N compounds is largely affected by synthesis conditions, including the choice of precursors, reaction temperature, reaction time, and the use of catalysts. Small adjustments in synthesis conditions can significantly alter the optical and electronic properties of the material.

In the improvement of Friedel-Crafts reactions, the use of butyllithium to remove hydrogen from amine enhances the nucleophilicity of nitrogen, making it easier to form B-N bonds. This method improves reaction efficiency, and according to Nakamura et al., using toluene, a higher boiling, more polar, and less toxic solvent, increases the reactivity between nitrogen and boron reagents while reducing the toxicity of the solvent, making the synthesis process more environmentally friendly [6]. In terms of catalyst selection, research has shown that CuI performs better than traditional Cu powder in coupling reactions, yielding better results. Additionally, the applied voltage has a significant impact on luminescence brightness. As the voltage gradually increases, the brightness of the luminescent device increases until it reaches a maximum, providing an important reference for optimizing the application of luminescent materials [8].

Controlling reaction temperature and time is also crucial. For instance, higher reaction temperatures may lead to decreased thermal stability, affecting luminescence performance, while excessively long reaction times may result in by-product formation, reducing product purity and performance. Therefore, optimizing these synthesis conditions can significantly improve the luminescence efficiency and overall performance of B-N compounds.

5.2. Doping and Composite Material Preparation

Doping and composite material preparation can further optimize the luminescent properties of B-N compounds. Yang Chuluo et al. reported two B-N-based luminescent materials, 2PXZBN and 2PTZBN. Due to the heavy atom effect of sulfur, these materials exhibited stronger spin-orbit coupling and higher reverse intersystem crossing rates [10]. This effect helps improve the luminescence efficiency of the materials, particularly in spontaneous emission processes, where energy transfer and exciton lifetime are significantly enhanced.

Additionally, study introduced sulfur and selenium atoms into the CzBN multi-resonance framework, significantly increasing the reverse intersystem crossing rate of the materials, allowing CzBSe luminescent devices to emit sky-blue light at 481 nm [10]. This study demonstrates that through reasonable element doping and structural design, the luminescent color and efficiency of materials can be effectively tuned, expanding the potential applications of B-N compounds in various fields.

Doping can also enhance the thermal and optical stability of materials. For example, doping with bulky groups not only inhibits molecular stacking but also reduces non-radiative energy losses, significantly improving luminescence efficiency. Additionally, by combining B-N compounds with other luminescent materials to form multifunctional composite materials, more complex luminescence control can be achieved, providing new avenues for the development of novel optoelectronic devices.

5.3. Optimization of Luminescence Efficiency and Stability

Optimizing luminescence efficiency and stability is a key issue in the practical application of B-N compounds. In 2016, a study introduced diphenylamine into the para position of boron, enhancing the resonance effect of the molecule. The introduction of diphenylamine not only effectively increased the radiative emission rate but also significantly improved the triplet exciton rate, ultimately achieving high-efficiency luminescence in the device [10]. Other research teams have successfully suppressed luminescence quenching caused by molecular stacking by introducing bulky groups like tert-butyl, achieving narrow-spectrum luminescence with a full width at half maximum (FWHM) of only 27 nm. These experimental results demonstrate that adding bulky groups can effectively inhibit intermolecular interactions and concentration quenching effects, resulting in narrower FWHM and higher luminescence efficiency [9].

In addition, the choice of molecular structure and groups has a profound impact on the performance of luminescent materials. Introducing resonance structures such as carbazole can effectively reduce structural relaxation in the excited state, resulting in higher luminescence efficiency and device efficiency. At the same time, introducing donor and acceptor groups into the molecular structure allows precise control of the HOMO-LUMO energy gap, enabling luminescence color adjustment. These optimization measures not only improve luminescence efficiency but also expand the range of applications, showing great potential in the development of highly efficient green and even red luminescent materials [10].

6. Challenges and Future Directions

Despite significant progress in the research of B-N compounds in recent years, many challenges remain. First, synthesis precision is a major challenge in current research. How to perform precise reactions at specific positions to achieve the desired structure remains a key focus for scientists. Recent studies have shown that increasing the length of the carbon backbone may lead to local anti-aromaticity within the molecule, thereby enhancing reaction selectivity [10]. This discovery provides new ideas for future industrial production and may promote the development of more efficient and precise synthesis methods.

Moreover, improving luminescence efficiency remains an urgent issue. Introducing heteroatoms such as sulfur and selenium into the periphery of the molecule can enhance luminescence efficiency to a certain extent [6]. Theoretical calculations have shown that the introduction of B-N bonds facilitates intermolecular charge transfer, significantly improving the efficiency of luminescent devices. However, due to the structural complexity of these molecules, even the simplest B-N compounds, such as boron-substituted naphthalene, may still exist in multiple isomeric forms (Figure 2). Although various post-processing methods have been proposed in recent years to reduce the generation of isomers, no method has yet been developed to completely solve this problem [6]. Therefore, how to design and synthesize these compounds more effectively to minimize isomer formation will be an important direction for future research.

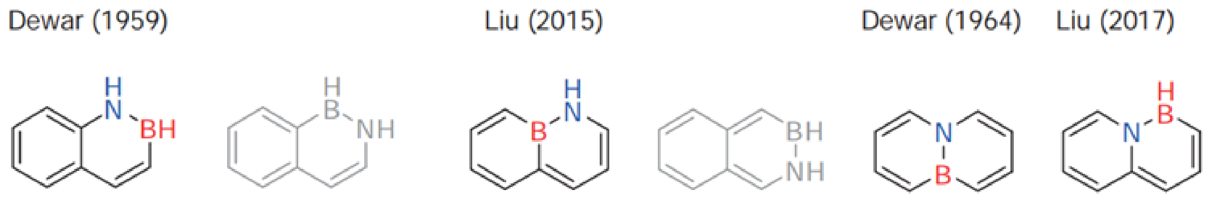

Fig. 2 Isomeric structures of B-N substituted naphthalene [6].

At the same time, while many methods have been developed for synthesizing B-N doped aromatic rings, most of these methods have high substrate requirements, limiting their application in industrial production. Currently, industrial production still relies mainly on Friedel-Crafts alkylation reactions. However, the limitations of this reaction restrict the further research and application of B-N compounds. In the future, function-oriented synthesis of specific molecules will become a mainstream research direction. Particularly in the development of highly efficient luminescent materials, new material design strategies need to be explored to achieve higher luminescence performance and broader application scenarios.

7. Conclusion

In summary, B-N compounds exhibit great potential in OLED and electroluminescent devices due to their unique electronic structure and excellent chemical stability. Currently, industrial production mainly uses Friedel-Crafts alkylation to synthesize these materials, with nitrogen and boron sources primarily provided by ammonia and borane. Although these methods are mature and widely used, challenges remain in reducing production costs, improving production efficiency, optimizing product structures, and achieving greater synthesis precision in targeted synthesis.

Furthermore, as research continues, increasing evidence shows that B-N doped aromatic rings not only offer advantages in luminescence efficiency but can also be further optimized by introducing other heteroatoms. Future research may focus on developing new synthesis routes to achieve more efficient luminescent devices while exploring the potential applications of these materials in other high-tech fields. Theoretically, further research will help elucidate the relationship between the electronic structure and optical properties of B-N compounds, providing guidance for material design. We look forward to ongoing research and innovation to find simpler, more efficient synthesis methods, promoting the application of B-N compounds in luminescent materials. As technology advances and research deepens, the prospects for B-N compounds will become broader, providing new momentum for the development of modern optoelectronic technology

Authors Contribution

All the authors contributed equally, and their names were listed in alphabetical order.

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