

# Boron-doped acenes and their emissive properties

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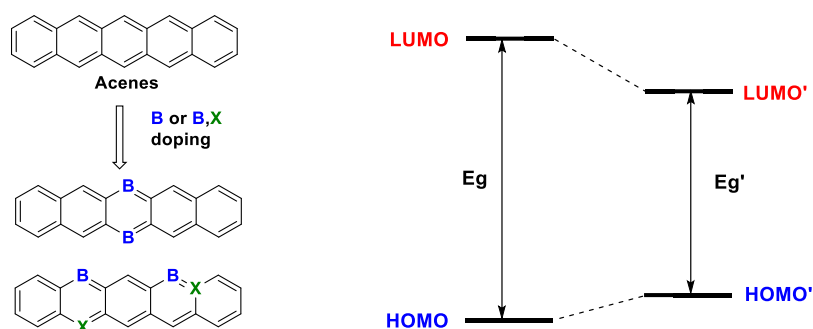
Literature Seminar

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Acenes, polycyclic aromatic hydrocarbons, made up of linearly  $n$ -annulated benzene rings are useful building blocks for light-emitting materials, organic semiconductors, and singlet exciton fission-based solar cells.<sup>1-2</sup> The presence of extended, planar conjugated  $\pi$ -systems makes them excellent conductors of electrons and enables them to absorb and emit light across various wavelengths. For example, 9,10-diphenyl anthracene has been utilized in organic light-emitting diodes with stable blue emission and pentacene is a prototypical semiconductor for organic field-effect transistors.<sup>3</sup>

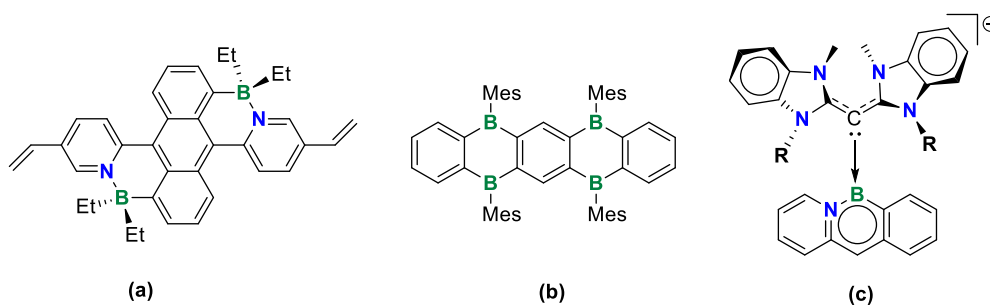
However, they have limitations such as reduced fluorescence in the crystalline state and photo-induced dimerization and/or oxidation due to the presence of narrow band gaps and energetically low triplet states. Extending the  $\pi$ -conjugation length is a simple way to tune the HOMO-LUMO gap and achieve low band gap materials by raising the HOMO and lowering the LUMO levels. While this technique reduces band gaps, increasing the HOMO can harm the oxidative stability of organic  $\pi$ -conjugated materials.<sup>4</sup>

Recently, the incorporation of main group elements like boron into the acene backbones has offered a viable approach to obtain stable heteroatom-containing acenes. Such complexes have been shown to facilitate extension of  $\pi$ -conjugation via overlap of the unoccupied  $p_z$  orbital on boron with antibonding  $\pi^*$  orbitals of adjacent organic  $\pi$ -systems. This offers intriguing features, such as Lewis acidity, reduced band gaps, stimuli-responsivity, and tunable physical properties.<sup>5</sup>



**Figure 1.** Boron-Containing Acenes: Reduced band gap and intriguing physical properties

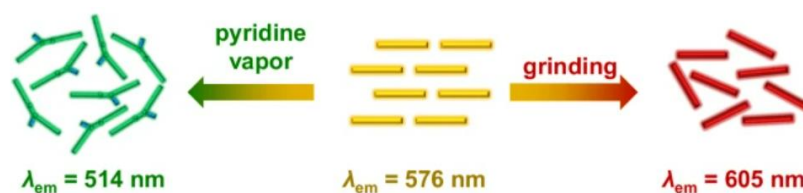
In 1971, Van Veen and Bickelhaupt incorporated one boron atom in the backbone of anthracene, opening the chemistry of boron-doped acenes. In 2008, Ashe and co-workers reported the first synthesis of dihydrodiborapentacene, and Wagner and workers further optimized the synthetic method in 2017, leading to significantly improved yields.<sup>6-7</sup>



**Figure 2.** Varying degrees of boron incorporation in boron-doped acenes: (a) B–N Lewis pair-substituted anthracenes (b) Quadruply doped tetrahydrotetraboro-acenes (c) Cationic B–N doped acenes stabilized by carbodicarbene ligands

Replacing C=C bonds with two isoelectronic B–N units leads to functionalized anthracenes that can achieve stable near IR(NIR) emission due to selective LUMO extension, as reported by Jakle et al. (Figure 2a). Synthesis of monomer, vinyl bridged dimer, and polymers, followed by Single-Crystal X-ray analysis, electrochemical, UV/Vis, and time-resolved fluorescence spectroscopy measurements and DFT calculations aid in the detailed investigation of the electronic structure, optical properties, and reactivity toward oxygen upon selective extension of the LUMO conjugation. According to photokinetic studies, the compound's ability to generate and release singlet oxygen is one of its most intriguing properties.<sup>8</sup>

The Wang group realized the highest doping level in boron acenes by increasing the number of boron atoms and expanding the number of aromatic rings (Figure 2b). These boron-doped acenes exhibit stronger Lewis acidity than their diborane analogs, as revealed by photophysical and electrochemical studies. The compounds become highly sensitive to environmental factors such as solvent polarity and pH, resulting in a dynamic shift of emission colors from green to red, providing versatile materials for sensing applications as confirmed by titration experiments with Lewis bases like pyridine and dimethylaminopyridine. Moreover, the boron complex with 9 aromatic rings shows mechanochromic luminescence properties due to its loose lamellar packing.<sup>9</sup>



**Figure 3.** Shift in emission wavelength in stimuli-responsive multicolor emission of quadruply doped boron acenes<sup>9</sup>

A recent study from the Gilliard Jr. group explores novel azaboracene molecules that integrate carbodicarbene ligands, enhancing both stability and luminescent properties (Figure 2c). This system differs significantly from the previous three studies on boron-doped acenes by employing a cationic carbodicarbene-azaboracene structure, which brings notable stability even under air and light exposure conditions that typically destabilize other B–N doped acenes.<sup>10</sup>



**Figure 4.** Boremium ions emitting in water under UV light<sup>10</sup>

These ions show both solution-phase and solid-state luminescence with strong resistance to degradation (Figure 4). These molecules' cationic nature lowers the optical gap, increases quantum efficiency, expanding the potential uses in fields like biological imaging and optoelectronics.

The systematic investigation of boron-doped acenes provides a promising pathway for developing stable, tunable, and highly emissive materials in the visible to NIR range. These findings show considerable advances in environmental responsiveness, color tunability, and molecular stability, critical for growing applications in optoelectronics, bioimaging, and environmental sensing.

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