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# Controlling the Aggregation and Assembly of Boron-Containing Molecular and Polymeric Materials

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## Biography

Daisuke Shimoyama received his B.Sc. in 2015 and Ph.D. degree in 2020 at Hiroshima University, Japan, where he worked as a JSPS young researcher under the supervision of Prof. Dr. Takeharu Haino. After graduation, he worked as a Ph.D. Researcher in the Graduate School of Advanced Science and Engineering, Hiroshima University. He is currently a postdoctoral associate at Rutgers University in the group of Prof. Dr. Frieder Jäkle. His current research interests are focused on boron-doped macrocycles and chromophores as luminescence materials and for stimuli-responsive applications.

Frieder Jäkle is a Distinguished Professor in the Department of Chemistry at the Newark campus of Rutgers University. He received his Diploma in 1994 and Ph.D. in 1997 from TU München, Germany, under the direction of Prof. Wagner. After a postdoctoral stint with Prof. Manners at the University of Toronto he joined Rutgers University in 2000. His research interests revolve around main group chemistry as applied to materials and catalysis,

encompassing projects on organoborane Lewis acids, conjugated hybrid materials, luminescent materials for optoelectronic and sensory applications, stimuli-responsive and supramolecular polymers. He is the recipient of an NSF CAREER award (2004), an Alfred P. Sloan fellowship (2006), a *Friedrich Wilhelm Bessel Award* of the Alexander von Humboldt Foundation (2009), the ACS Akron Section Award (2012), the Boron Americas Award (2012) and the Board of Trustees Research Award at Rutgers University (2017). In 2019 he was named a *Fellow* of the American Chemical Society.

**Abstract:** Boron-containing molecules and polymers are attractive as powerful tunable Lewis acids for small molecule activation and catalysis, as luminescent materials for organic electronic device and (bio)imaging applications, and as smart chemical sensors. While the characteristics of the boron-containing building blocks are attractive in and of themselves, their assembly into higher order supramolecular materials offers access to unique properties and emerging functions. Herein we highlight recent achievements in the field of aggregated organoboron materials. We discuss how supramolecular interactions can be exploited to precisely control the structure of the assemblies and impact their functions as luminescent materials, recyclable and smart catalyst systems, chemical sensors, stimuli-responsive and self-healing materials.

## 1. Introduction

The development of advanced functional materials frequently takes advantage of organic-inorganic hybrids as they merge advantageous features and complementary properties of the respective organic and inorganic components.[1-4] Among inorganic components, boron is attractive because its compounds are inherently electron-deficient.[5-6] Having available one electron less for bonding interactions, boron compounds frequently feature low-lying lowest unoccupied molecular orbitals (LUMOs) and small band gaps, characteristics that are beneficial for creating conjugated π-systems that find applications in bio-imaging, organic photovoltaics (OPVs), field-effect transistors (OFETs), and light-emitting diodes (OLEDs).[7-11] Moreover, the Lewis acidic character of tricoordinate boron allows for reversible binding of neutral and anionic substrates, which has drawn significant attention for organocatalysis, chemical sensing applications, and the development of stimuli-responsive smart materials.[12-20]

While the molecular properties of boron species are advantageous in and of themselves, molecular aggregation and self-assembly into higher order structures frequently offer access to unique characteristics and novel functions.[21-22] With respect to luminescent materials, aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) are a topic of much current interest.[23] The advantageous photophysical characteristics of boron building blocks have inspired many researchers to explore them as AIEgens.[24] On the other hand, directed supramolecular assembly can more precisely organize molecular systems via noncovalent interactions.[25] Indeed, the past decade has witnessed dramatic improvements, which have enabled precise control over both the aggregation process and the structure of the final assemblies. The electron-deficient character and Lewis acidity of boron can be advantageously exploited to generate supramolecular systems with unusual properties and functions.

In this review we discuss the key strategies for generating aggregated organoboron materials while highlighting some of the most recent achievements. First, we will offer a brief introduction to organoboron compounds used as AIEgens. We will then illustrate the well-ordered assembly of boron chromophores into one-dimensional polymers and higher order structures, controlled by noncovalent interaction. We will show that this aggregation process efficiently utilizes boron compounds to control the association process, including the sequence of monomers, while also imparting the resulting assemblies with unique properties. Finally, we will discuss the self-assembly of boron-containing polymers into higher order architectures and their emerging applications as recyclable and smart catalyst systems, chemical sensors, stimuli-responsive and self-healing materials.

## 2. Aggregation of molecular boron chromophores

### 2.1. AIE of boron chromophores

Organoboron compounds frequently serve as powerful chromophores and luminophores. Composed of a π-conjugated system to which boron is attached or embedded into, their rigid structures favor large molar absorbance coefficients and high fluorescence quantum yields. However, the luminescence has a tendency to become weak or disappear in the aggregated state due to aggregation-caused quenching (ACQ), which limits their applications as luminescent materials for imaging and optoelectronic device applications. As demonstrated in seminal work by Tang and co-workers,[23, 26] this issue can be circumvented by careful molecular design that promotes AIE and avoids ACQ. Their discoveries have inspired the development of several boron-based AIEgens to generate new photoactive materials. Figure 1 illustrates some representative AIEgens based on boron-dipyrromethene (BODIPY), boron diketonate, tricoordinated organoborane, and carborane derivatives. Common to all these chromophores is the AIE effect, which relies on the suppression of intramolecular motions that are associated with non-radiative deactivation processes. Tang et al. reported that AIE-active donor-acceptor systems containing BODIPYs in combination with triphenylamine moieties show AIEE characteristics derived from a twisted intramolecular charge transfer process.[27-28] Other approaches include the direct incorporation of AIEgens into BODIPY and the formation of *J*-aggregates of BODIPY to achieve narrow and red-shifted transitions.[29] The positions of the substituents on the BODIPY skeleton greatly affect the AIE behavior. Boron diketonate complexes also tend to suffer from ACQ, but judicious molecular functionalization can yield AIE chromophores.[30] In addition, replacement of the oxygen atom by nitrogen leads to boron ketoiminates and diiminates, which display enhanced molecular flexibility, resulting in active molecular motions in the solution state but sterically restricted motion in the solid-state due to intermolecular interactions.[31-33] Related AIEgens derived from boron formazanates were introduced by Gilroy et al.[34-35] and boron difluorohydrazone (BODIHY) chromophores were reported by Aprahamian et al.[36-37] Aprahamian et al. found a strong dependence of the emission of BODIHY chromophores on the solvent viscosity. Further, theoretical calculations suggested that the emission efficiency is correlated with the rotation angle of pendent phenyl groups.

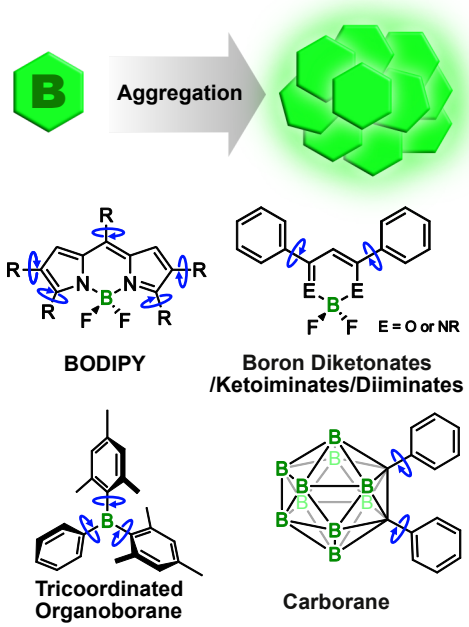


**Figure 1.** Molecular structures of representative borane chromophores.

Various tricoordinate organoboranes with sterically demanding mesityl or anthryl pendent groups also show AIEE characteristics.[38-42] These chromophores are frequently already emissive in solution because of restricted rotations due to steric effects. In addition, Chujo and co-workers discovered that *o*-carborane derivatives can serve as AIEgens.[43-46] *o*-Carboranyl moieties exhibit strong electron-acceptor properties when attached to organic π-conjugated systems.[47] In solution, the vibration of the C−C bond in *o*-carborane leads to fluorescence quenching. In contrast, in the aggregated state intramolecular vibrational modes and molecular motions are suppressed, while steric hindrance effectively inhibits intermolecular interaction.

These findings have inspired the synthesis of numerous new boron derivatives with AIE characteristics that have been explored in application fields ranging from bioimaging to chemical sensing, as described in detail in several recent reviews.[24, 48-49] As the development and methods for the functionalization of boron chromophores further widen in scope, we can expect to see the discovery of many new boron-based AIEgens with interesting properties and novel functions.

### 2.2. Well-ordered stacks of molecular boron chromophores

An effective approach to control the structure and function in the aggregated states is to apply more advanced supramolecular assembly techniques. When aggregation arises from complementarily intermolecular interactions between preorganized monomer components, stable supramolecular nanostructures with specific dimensions and directionality can be generated even in solution (Figure 2A).[50] The resultant supramolecular assemblies are dynamic, leading to stimuli-responsive soft materials such as gels, elastomers, and liquid crystals.[51-53] In particular, the assembly of planar molecules via π–π stacking interactions, as well as other directional noncovalent interactions such as hydrogen and halogen bonding, metal-metal, electrostatic, and hydrophobic interactions, has been widely utilized to construct advanced supramolecular materials.

Well-ordered assemblies derived from boron-containing building blocks have recently attracted attention, mainly because the unique structural features and photophysical characteristics offer an opportunity to generate new functional materials with exciting properties. For instance, BODIPY dyads were reported to form supramolecular stacks promoted by intermolecular hydrogen bonds.[54-55] Head-to-tail hydrogen bonding of **B1** (Figure 2B) gives rise to *J*-type aggregation of the BODIPY core, which is responsible for the observation of intense redshifted fluorescence. In the presence of suitable long alkyl chains, these one-dimensional assemblies can form bundled structures via hydrophobic interactions, resulting in formation of gels and liquid crystals. Numerous other boron chromophore-based supramolecular polymers have since been developed.[56-57] Importantly, molecular recognition events can enable control over the triggered assembly-disassembly of such stacked constructs. In one example, Maeda et al. attached two arylpyrrole units to boron diketonates (**B2**) and investigated their assembly-disassembly in response to anion recognition events.[58] The organoboron chromophore itself forms a supramolecular organogel that is highly luminescent. Efficient binding of guest anions through hydrogen bonding interactions, e.g., chloride complexation, induces a conformational change of the receptor. This process involves inversion of the pyrrole rings and planarization of the molecular geometry, which in turn triggers dissociation of the polymer into its monomeric building blocks. On the other hand, the monomeric anion complex of **B2** can be combined with planar π-conjugated cations, giving rise to supramolecular co-assemblies with alternating cations and anions, a process that is driven by ion-pairing interactions.[59-61] This controlled charge-by-charge assembly generates relatively more stable organogels with useful liquid crystalline properties.

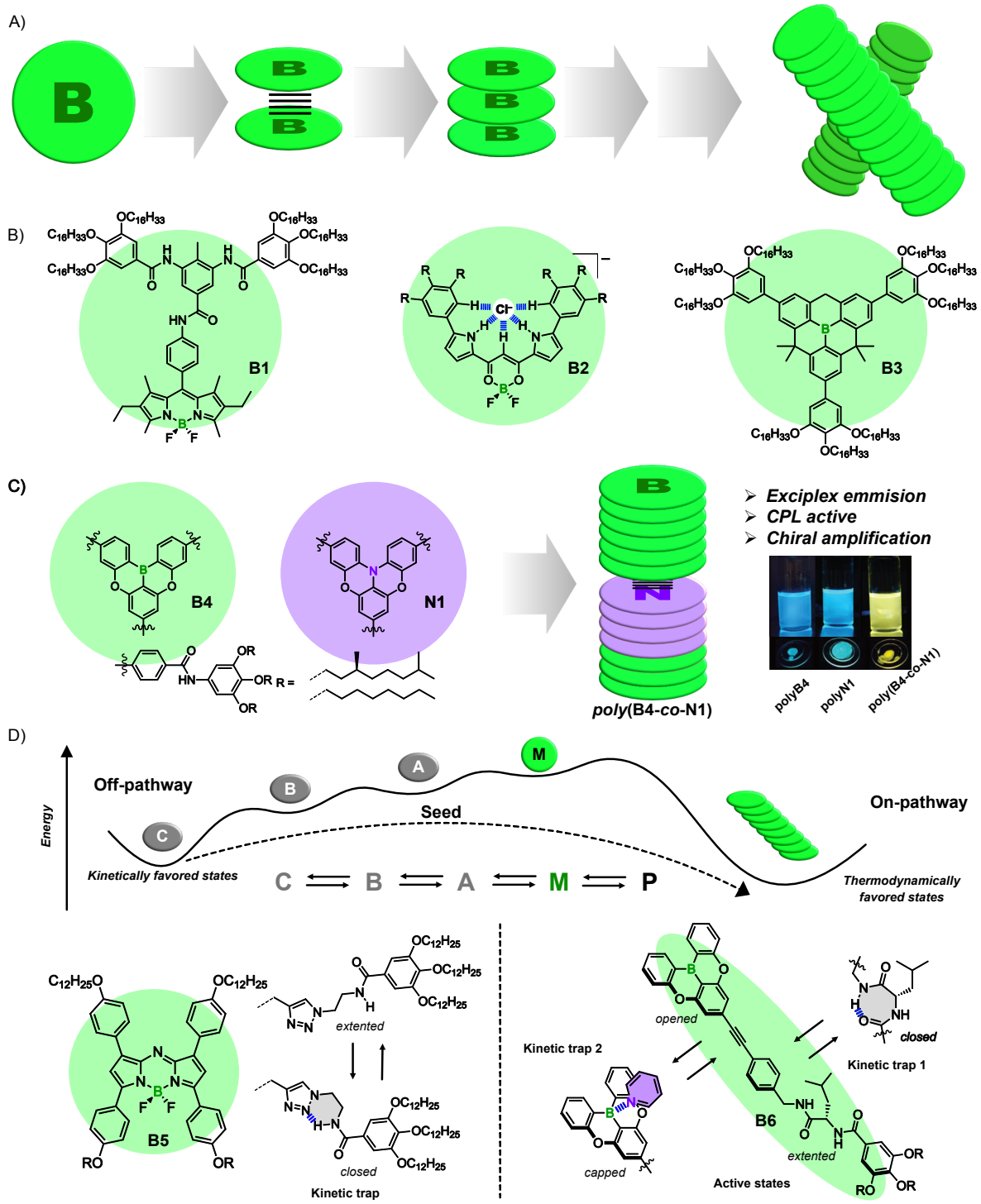


**Figure 2.** A) Well-ordered supramolecular polymerization of molecular boron chromophores; B) Building blocks for supramolecular homopolymerization. C) Supramolecular copolymerization via B−N interactions. Adapted with permission from [62] Copyright © 2020 American Chemical Society. https://pubs.acs.org/doi/10.1021/jacs.0c06921 D) Seeded polymerization controlled by a kinetic trapping system.

Tricoordinate organoboranes also serve as promising building blocks for assembled structures. They are not only luminescent, but the empty p-orbital on boron can also promote electron-transport when stacked in a face-to-face fashion. However, the stabilization of reactive boron centers commonly requires the introduction of bulky protective groups. This steric

hindrance typically suppresses interactions between monomers. In 2012, Yamaguchi et al. introduced a compact triarylborane platform by structurally constraining boron in a rigid planar framework.[63] The first planarized triphenylborane with three dimethylmethylene bridges did not form columnar π-stacked supramolecular polymers, but removal of the methyl groups on one of the bridges allowed for more efficient intermolecular interaction. As a result, hexagonal columnar assembly of **B3** was achieved to afford air-stable discotic liquid crystals at room temperature.[64] In the liquid crystalline phase, the triarylborane units are well-organized. Due to the short distance between boron units ambipolar charge transport with charge-carrier mobilities of $10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$ for electrons and $3 \times 10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$ for holes could be realized.

Very recently, the Meijer and Yamaguchi groups realized supramolecular random block-like copolymers **poly(B4-co-N1**) that are comprised of discotic chiral triarylborane and triarylamine monomers (Figure 2C).[62, 65] The supramolecular homopolymerization of related triarylamine monomers had previously been studied.[66-68] The individual borane and amine homopolymers displayed a blue emission. However, when the triarylborane and triarylamine monomers were mixed, a change in the emission color to yellow was detected even by naked eye. The yellow fluorescence was assigned to the formation of B-N excited-state complexes (exciplexes). In addition, attachment of chiral groups to these building blocks induced the formation of supramolecular structures with preferred handedness. This chiral amplification effect is indicative of the formation of supramolecular copolymers via B···N interactions; circularly polarized luminescence[69-70] with a large anisotropic factor ($g_{lum}$) at the exciplex emission band, and a sergeant-and-soldier phenomenon[71-72] were observed, ruling out the possibility of simple dimer formation. Interestingly, in the bulk, the supramolecular copolymers showed B-N exciplex emission without the presence of emission bands for the homopolymers, suggesting an increased number of B-N contacts due to well-ordered structures. The unusual bulk material properties that are achieved provide a motivation to further pursue precisely controlled systems, such as alternating boron-nitrogen arrays, by applying complementary preprogrammed supramolecular self-assembly approaches.

As discussed above, supramolecular polymers are frequently associated with well-organized structures, including size, polydispersity, geometry, monomer sequence, and so on. Pioneered by Manners et al, living and seeded supramolecular polymerizations have recently emerged as attractive techniques to control the primary structures.[73-74] This approach requires the existence of kinetically accessible metastable and/or inactive species, besides the monomers and final thermodynamically favored assembled state (Figure 2D).[75] Certain stimuli can then be used to trigger the transformation from metastable into the thermodynamically favored aggregated states. The design of such systems often involves a conformational change between folded and extended structures that is enabled by formation of intra- and intermolecular hydrogen bonds.[76] In a recent example, amide-functionalized aza-BODIPYs **B5** were prepared through click reactions.[77] This boron chromophore formed two different types of aggregates through on- and off-pathways, respectively. At low temperatures, the monomers in the closed form aggregated into kinetically metastable nanoparticles. Upon temporary heating, the closed conformers were converted to extended conformers, promoting the growth of a thermodynamically more stable supramolecular polymer via intermolecular interactions. The thermodynamically stable aggregates were then added as seeds to the solution containing the metastable aggregates, inducing well-controlled seeded supramolecular polymerization. Ogi and Yamaguchi et al. very recently introduced a seeding method based on a dual kinetic trap system using both hydrogen bond-induced folding and Lewis pair complexation.[78] They functionalized Hatakeyama's planarized triarylborane[79] platform with chiral hydrocarbon side chains that are attached via a chiral amino acid-based diamide spacer (**B6**). The monomers are kinetically trapped in a folded structure by hydrogen bonding, while intermolecular axial coordination of pyridine leads to capped inactive states. Taking advantage of the ensuing multiple-equilibrium system with folded/unfolded diamide (kinetic trap 1) and

complexed/uncomplexed boron (kinetic trap 2), seed-initiated supramolecular polymerization could be achieved at unusually high millimolar-level concentration. These studies demonstrate that the formation of well-ordered supramolecular polymers can be accomplished by installing boron into the molecular building blocks, suggesting a bright future for next generation supramolecular hybrid polymers.

## 3. Assembly of boron polymers and block copolymers

While we have focused on the aggregation and deliberate assembly of molecular boron compounds into supramolecular materials in the previous section, the bulk and solution state assembly of polymers into higher order structures is an important field of research with many implications on everyday life. We will discuss recent advances where assembly of boron-containing polymers is exploited for applications as luminescent materials, smart sensors, nanocatalysts, as well as dynamic and healable materials. Boronic acid-functionalized polymers and their assembly have also been extensively studied, but this topic is beyond the scope of this review.[80]

### 3.1. Assembly of luminescent boron polymers

Not unlike molecular boron chromophores, boron-containing polymers offer many advantageous attributes, including efficient luminescence, stimuli-responsiveness, sensing ability, and so on.[5, 16, 81] Biocompatible boron polymers have been widely explored for applications in the biomedical field. In a landmark study, Fraser et al first reported polylactides that are functionalized with boron diketonate complexes at the chain end as multi-emissive oxygen sensing biopolymers (Figure 3A).[82-83] In solution and in the solid-state, boron diketonate complexes normally exhibit strong fluorescence, but their phosphorescence cannot be detected at room temperature. In contrast, boron diketonate polymers **PB7** display long-lived room-temperature phosphorescence (RTP) in the film state under oxygen-free conditions. The phosphorescence is promoted by the rigid polymer medium that restricts the thermal decay pathways of the boron chromophores. Interestingly, the ratio of the fluorescence and phosphorescence intensities depended on the degree of lactide polymerization due to differences in intersystem crossing rates, allowing for tuning of the emission color from cyan to greenish yellow. The phosphorescence was quenched by oxygen providing an effective oxygen sensor for tumor hypoxia imaging applications.

Extension of the π-conjugation length is a common approach to tune the emission color of conjugated materials. Over the past decades, boron-containing conjugated π-systems have frequently been employed to construct color-tunable π-conjugated polymers.[84-87] In a different approach, Wang, Li and co-workers demonstrated that multicolor emission that is dependent on the degree of polymerization can be achieved by chromophore assembly of non-conjugated side-chain functionalized polymers **PB8** (Figure 3B).[88] They utilized a stimulus-responsive boron chromophore that exhibits different emission colors in its closed (red, tetracoordinate boron) and open conformation (blue, tricoordinate boron).[89] The emission color change of this chromophore can be modulated by external stimuli, e.g., changes in pressure, temperature, and solvent effects. When attached to polymethacrylate, conversion of the blue-emitting tricoordinate to the red-emitting tetracoordinate boron chromophores was observed with increasing polymer chain length (2.22–83.8 kDa) in solution. In contrast, all polymers exhibited red emission due to tetracoordinate boron centers in the film state. This suggests that the assembly of boron chromophores in solution contributes to the high proportion of the red-emitting closed-form at higher molecular weights. In further support of the proposed mechanism, boron-containing random copolymers **PB8j** and **PB8k**, containing *tert*-butyl

methacrylate (*t*-BMA) as a comonomer to space out the boron units, showed white and blue emission in the film state respectively.

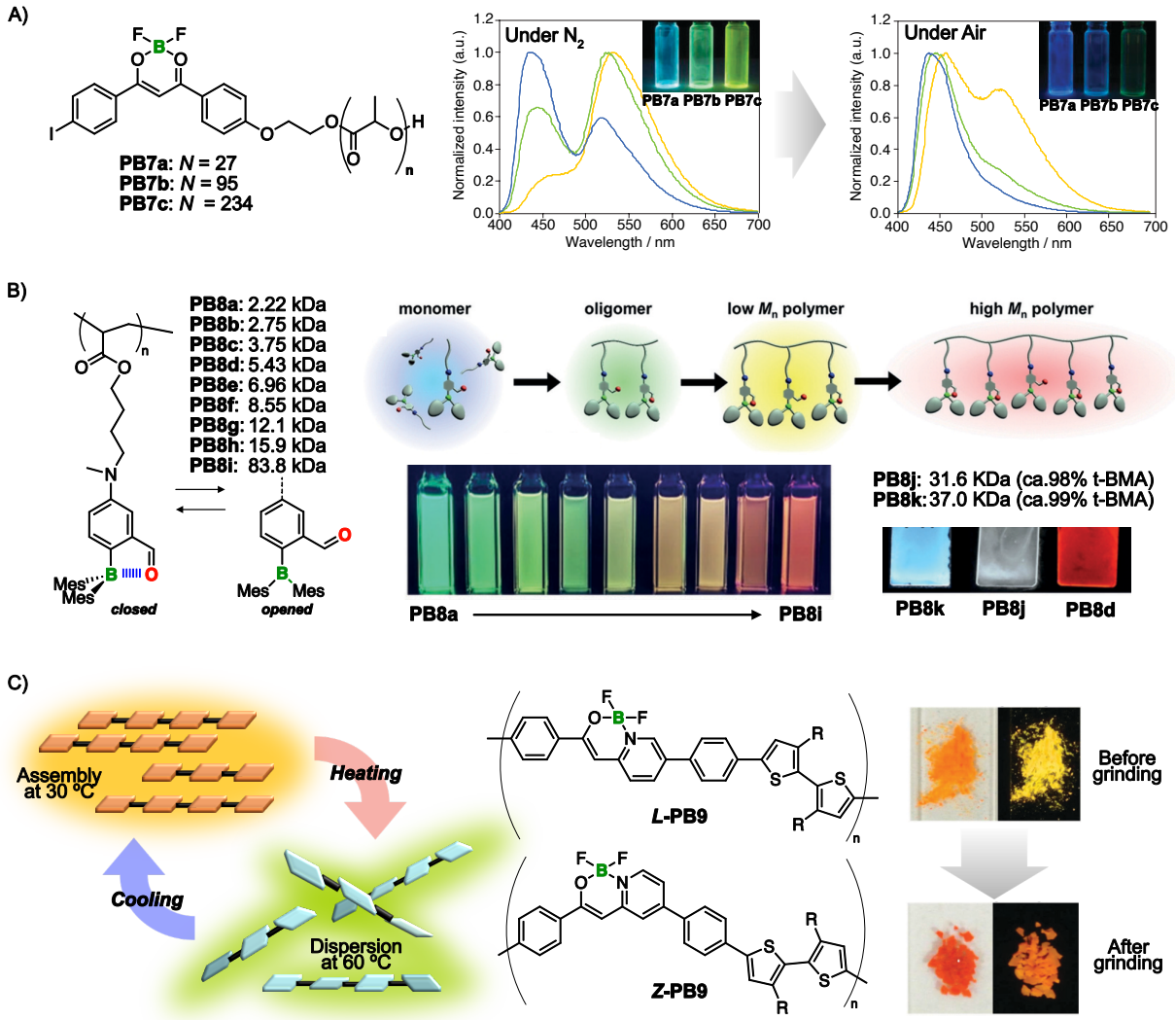


**Figure 3.** Aggregation state-dependent luminescence of boron-containing polymers. A) Oxygen sensing of dual-emissive boron diketonates polymers. Adapted with permission from [83] (Copyright © 2009 Springer Nature). B) Tunable multicolor emission of switchable organoboron polymers. Adapted with permission from [88] (Copyright © 2019 Wiley-VCH). C) Stimuli-responsive behavior of π-conjugated polymers with boron ketoiminate groups. Adapted with permission from [90] (Copyright © 2020 The Royal Society of Chemistry).

The incorporation of organoboron AIEgens into the backbone of polymers offers an attractive approach to potential AIE-active materials. Chujo and co-workers developed a series of π-conjugated organoboron polymeric systems with boron ketoiminate,[91-93] boron diiminate,[94-95] azobenzene-boron complex[96-98] and carborane[99-100]. Modulating the polymer chain length and sequence in a π-conjugated system allows for tuning of the AIE properties. More recently, Tanaka and Chujo demonstrated that the geometry of an organoboron polymer could influence the emission in the aggregated state, as shown in Figure 3C.[90] *L*- and *Z*-type alternating copolymers with a boron ketoiminate skeleton were prepared by palladium-mediated coupling reactions. The difference in the linkage and shape of the polymer chains has a pronounced influence on the optoelectronic properties, as evidenced by cyclic voltammetry and optical spectroscopy. With increasing temperature, the emission color of ***L*-PB9** changed from orange to green in chloroform solution, whereas ***Z*-PB9** did not display any

thermochromic behavior. This effect was correlated with the presence of larger sized particles at 20 °C than at 50 °C in solutions of ***L*-PB9**. The results suggest that the thermochromic luminescence depends on intermolecular interactions that are related to the shape of the polymer. On the other hand, ***Z*-PB9** exhibited mechanochromism in the solid-state. The luminescence color of a powder sample of ***Z*-PB9** changed from orange to yellow upon grinding. Grinding may weaken the intermolecular interaction, leading to the observed blue-shift in the emission.

### 3.2. Amphiphilic organoboron polymeric Lewis acids

In another approach, amphiphilic polymers are used to achieve solution self-assembly into higher order architectures. In polar solvents amphiphilic block copolymers are known to spontaneously form nanostructures to reduce energetically unfavorable hydrophobic segment-solvent interactions.[101] Nowadays, the requisite well-defined block copolymers are readily accessible owing to the remarkable advances of controlled/living polymerization techniques. They can be assembled into various nanostructures (Figure 4A).[102-103] The resulting self-assembled micelles, vesicles, nanotubules, and so forth, offer promise for applications ranging from drug delivery to nano-confined catalysis. Furthermore, in recent years the introduction of stimulus-responsive moieties that respond to, e.g., pH, light, molecular binding, and redox events, has been explored to achieve control over the block copolymer assembly.[104] As powerful Lewis acids, tricoordinated organoboranes are capable of selective binding of neutral Lewis bases such as amines or phosphines, as well as anions such as cyanide or fluoride. The binding process not only provides control over the aggregation state but also a means to achieve selective chemical sensing of such analytes.

Mild radical polymerization[105] and facile post-polymerization functionalization[106-107] protcols offer access to Lewis acid-functionalized block copolymers and their stimulus-responsive self-assembled materials.[108] Jäkle and co-workers have developed a wide range of block copolymers containing pendant boron moieties through controlled free-radical polymerization, and investigated their nanostructures.[22, 109-114] Among them are amphiphilic block copolymers **PB10** with well-defined chain architectures that consist of luminescent triarylborane Lewis acid-functionalized styrene and N-isopropylacrylamide (NIPAM) (Figure 4B).[115] In a mixture of DMF/THF = 99/1, these strongly blue fluorescent block copolymers formed micellar aggregates as confirmed by dynamic light scattering (DLS) measurements and transmission electron microscopy (TEM). Upon the addition of fluoride anions, the particle sizes reduced from 93 to 10 nm, indicating disassembly of the block copolymer micelles. This result suggests that anions were captured at the triarylboron units on the polymer side chains, which led to an increase in the affinity of the boron block for DMF. The higher affinity for DMF then triggered nanostructure dissociation into single chains. During the dissociation process, the fluoride binding also induced visible fluorescence quenching that is readily observed by naked eye, enabling the polymer to function as a dual-responsive fluoride ion sensor. Additionally, the introduction of cationic pyridinium moieties along the copolymer chain enhanced the anion binding constant and sensor performance, allowing for highly sensitive anion detection even in aqueous solution.

As with classical Lewis acid-base pair (LP) formation, frustrated Lewis pairs (FLPs) are also potent scaffolds for stimuli-responsive micellar systems. Yan and co-workers reported responsive self-assembled nanosystems **PB11** that are based on intermolecular interactions of Lewis acid and Lewis base-functionalized block copolymers with $CO_2$ (Figure 4C).[116] Lewis acidic bis(pentafluorophenyl)borane and sterically hindered Lewis basic dimesitylphosphine moieties do not interact with each other, but spontaneously bind carbon dioxide to drive the formation of micelles that are ca. 40 nm in size. The binding process is reversible in that heating causes the release of $CO_2$ gas, enabling dynamic control over the assembly-disassembly processes. Furthermore, these micelles were shown to be highly effective as nanocatalysts for

the formylation of amines, enabled by the dissociative generation of active Lewis acid/base sites. The reversible micellation was exploited to recycle the catalyst which retained high activity for at least eight cycles. Subsequently, the Yan group introduced $CO_2$-responsive FLP units into a single polymer chain, and employed them as recyclable carboxylation nanocatalysts.[117] Thus, the stimuli responsive behavior of the classical LPs and FLPs offers not only control over the assembly-disassembly processes but also directly impacts the function of the nanostructures. These examples demonstrate that the incorporation of LP and FLP motifs into polymeric materials is a very promising approach for applications that take advantage of stimuli-responsive properties. Their utility to serve as responsive units in bulk materials will be discussed in the following section.

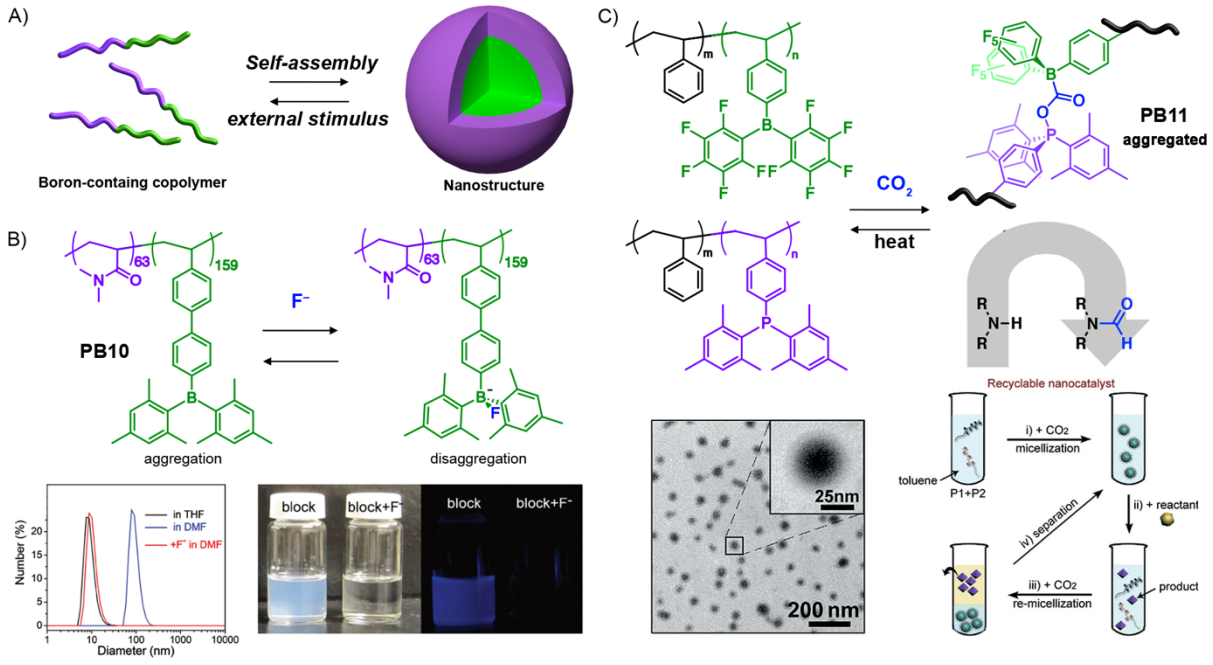


**Figure 4.** A) Nanostructure formation by block copolymer assembly. B) Stimulus-responsive self-assembled micelles derived from triarylborane block copolymers and their sensory properties. Adapted with permission from [115] Copyright © 2013 American Chemical Society. C) $CO_2$-responsive block copolymer assemblies based on FLPs and their use as nanocatalysts. Adapted with permission from [116] Copyright © 2018 Wiley-VCH.

### 3.3. Smart polymer networks with Lewis pair crosslinks

The remarkable stimuli responsiveness of Lewis pairs (LP) discussed above was recently also exploited in the reversible formation of dynamic polymer architectures, an area of intense current interest in view of the unusual bulk physical properties that can be achieved.[18] Many different types of dynamic recyclable, rehealable or shape-changing materials have recently been constructed by applying dynamic covalent and noncovalent bonding motifs.[118-120] Hydrogen bonding,[121] metal-ligand coordination,[122] ion pairing,[123] and host-guest interactions[124] all serve as essential tools to access reversibly crosslinked polymer networks. Tuning of the dissociation rates of these reversible interactions affects the dynamic behavior, enabling the formation of transient polymer networks (TPNs). While still in its infancy, the use of Lewis pair interactions is highly appealing because they can provide a wide range of binding affinities as illustrated in Figure 5A. This enables effective tuning of the physical properties of the resulting supramolecular polymers.

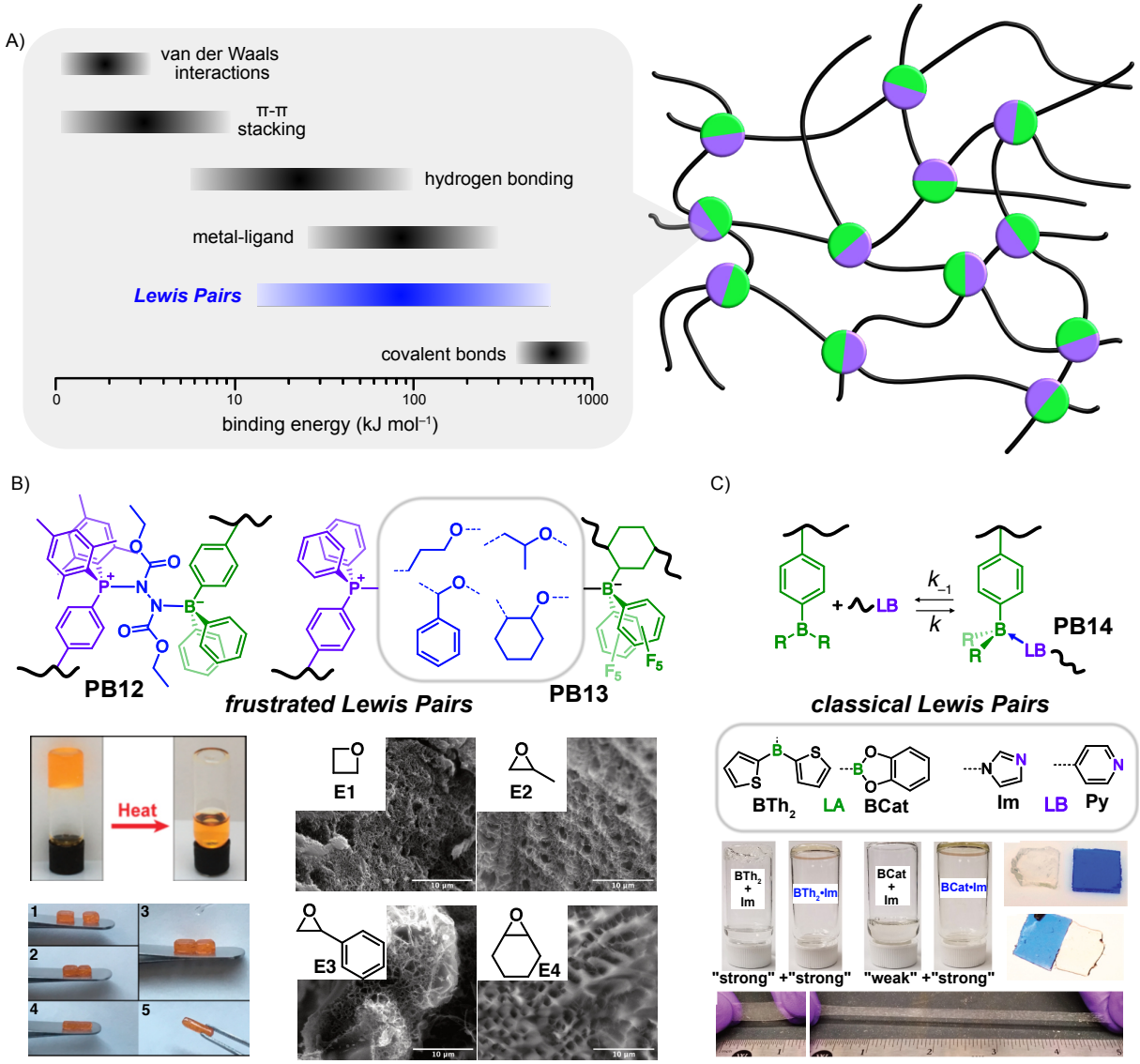


**Figure 5.** A) Network polymers based on supramolecular interaction. B) FLP-type network polymers. Adapted with permission from [125] Copyright © 2017, American Chemical Society. Adapted with permission from [126] Copyright © 2021 American Chemical Society. C) Classical LP-type network polymers. Adapted with permission from [127] Copyright © 2019 American Chemical Society.

First efforts toward FLPs type network polymers started only a few years ago. In a landmark study, Shaver and co-workers demonstrated that small molecule activation by FLPs could be used to generate polymer networks **PB12** with self-healing ability (Figure 5B).[125, 128] They prepared diarylborane- and dimesitylphosphine-functionalized styrenic random copolymers where the steric bulk of the phosphine groups prevents direct attack at the electron-deficient organoboron moieties. Upon addition of diethyl azodicarboxylate (DEAD), the B and P atoms were bound to the nitrogens of the linker to form dynamic FLPs crosslinks, as evidenced by gel formation. Importantly, the binding between FLPs and DEAD was found to be reversible. When the temperature exceeded 100 ºC, the boron-nitrogen dative bonds were cleaved, and the gel disassembled. The gels also showed self-healing properties in toluene. Very recently, the Shaver group introduced a new class of boron-containing polymeric Lewis acids that are derived from hydroboration of poly(styrene-*co*-cyclohexadiene).[126] When combined with diphenylphosphine-functionalized polystyrene, FLP-type polymer networks **PB13** could be generated by ring-opening of cyclic ethers, i.e., 1,3-propylene oxide (**E1**), 1,2-propylene

oxide (**E2**), styrene oxide (**E3**), and cyclohexene oxide (**E4**). The cross-linked morphology was confirmed by scanning electron microscopy (SEM), which showed network structures with different pore sizes (**E1** < **E2** < **E3** and **E4**). Rheological studies revealed that the mechanical properties of the materials are more akin to those of covalently crosslinked polymeric networks, in contrast to the dynamic DEAD-crosslinked networks described above. The crosslink density and materials' bulk physical properties could be controlled by the basicity (**E1** < **E2** < **E3** < **E4**) and steric hindrance of the cyclic ethers. The Yan group reported dynamic $CO_2$-bridging FLP system that exhibit stimuli-responsive self-recovery function.[129] They synthesized tris(4-vinylphenyl)borane and 4-styryl-dimesitylphosphine as two complementary FLP monomers and generated permanently covalent polymer networks via RAFT polymerization. Addition of $CO_2$ led to formation of additional dynamic crosslinks. The crosslinking density and the mechanical performance of the FLP network polymers, such as the strength and toughness could be tuned by varying the amount of $CO_2$ added. In addition, healing of broken gels was achieved by $CO_2$ purging.

As in the case of most dynamic covalent networks (e.g., dioxaborolane metathesis, Diels-Alder reactions, etc.), FLP-type polymer networks require elevated temperatures or catalysts to induce the stress relaxation needed for reorganization. In contrast, supramolecular forces can be weak enough to reversibly form and dissociate rapidly at ambient temperature. This allows for self-healing functions even without external stimuli. Supramolecular polymers based on classical Lewis pairs were initially investigated by Severin and co-workers.[130-131] Small molecule boronate esters connected with pyridines served as the monomers.[132] The specific viscosity dramatically increased with concentration, which proved that the monomers formed Lewis pairs to give supramolecular polymers at high concentrations. The degree of polymerization was postulated to also depend on the strength of the interactions between Lewis acid-base pairs. Subsequently, Brook et al. reported the first example of a thermoreversible LP-type polymer networks that consist of boronate ester-functionalized polydimethylsiloxane (PDMS) and multifunctional primary alkylamines.[133] More recently, Jäkle and co-workers prepared TPNs **PB14** with tunable bulk physical properties via classical LP interactions.[127, 134] Polystyrene (PS) with LA side chains was adopted as a multifunctional crosslinker and telechelic PDMS with LB end groups served as flexible bridging strands in the formation of the crosslinked TPNs (Figure 5C). The mechanical properties of the polymer networks were tuned through variations in the Lewis acid and base strength, which affect the corresponding association constants. They attached catecholboronate (BCat, *weaker acidity*) or di(thienyl)borane ($BTh_2$, *stronger acidity*) to PS, and pyridine (Py, *weaker basicity*) or imidazole (Im, *stronger basicity*) to PDMS. A wide range of association constants from $10^2$ to $10^8$ $M^{-1}$ could be achieved, with $BTh_2$•Im forming the strongest complex, followed by $BTh_2$•Py, BCat•Im, and BCat•Py. A kinetic study confirmed that lower association constants also lead to faster crosslink dissociation processes. Importantly, this difference in the binding behavior translated to the gelation process on the macroscale. Mixing of solutions of poly$BTh_2$ and polyIm resulted in immediate formation of a gel. On the other hand, polyBCat and polyIm remained as a homogeneous, free-flowing solution. Annealing and solvent evaporation afforded homogeneous and transparent organogels. Rheological studies revealed that the zero-shear viscosities $\eta^0$ increased from polyBCat•Py to poly$BTh_2$•Im with higher values correlating well with the larger binding constants. Moreover, the complex viscosities $\eta^*$ scaled with the dissociation rate constants, which indicated that crosslink dissociation controls the relaxation dynamics. The dynamic nature of the LPs was exploited in applications as self-healing materials and to generate reprocessible silicone elastomers (Figure 5C, bottom).

## 4. Conclusion

In this review, we have briefly demonstrated advances in the aggregation and assembly of functional materials that incorporate organoboron moieties. Well-ordered supramolecular assembly of precisely arranged boron-containing building blocks leads to desirable luminescence properties, such as multicolor tuning, sensing, and stimuli-responsiveness. On the other hand, the unique characteristics of boron, including its electron-deficient nature and Lewis acidity, can be exploited to achieve control over the assembly of supramolecular architectures. Thus, the combination of organoboron building blocks and supramolecular assembly produces a synergistic effect. Hence, we anticipate that well-controlled organoboron-based assembled material will be put into practical use in a wide range of fields in the near future.

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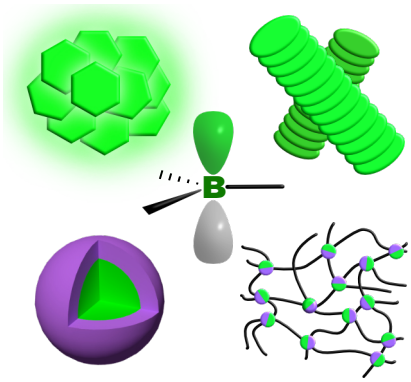
# Controlling the Aggregation and Assembly of Boron-Containing Molecular and Polymeric Materials




This review summarizes the key strategies for precisely controlling the structure and function of aggregated organoboron materials while introducing some of the most recent advances in the field. Molecular aggregation and self-assembly processes lead to well-ordered structures with unique properties and functions. The electron-deficient characteristics of the organoboron building blocks are exploited to develop fascinating new materials.

**Keywords**: boron, luminescent materials, self-assembly, nanostructure, polymer network