

Recent Progresses in the Mechanistic Studies of Aggregation-Induced Emission-Active Boron Complexes and Clusters

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ABSTRACT

We herein review the recent progresses in the development of boron-containing compounds with aggregation-induced emission (AIE) properties. In particular, the contribution of boron to molecular motions in the excited state is mainly focused in this review. Initially, the series of boron complexes with bidentate ligands are surveyed. We will explain their optical properties by classifying into three groups having different types of the dative bonds, such as B–O and/or B–N. As an application, stimuli-responsive polymers and film-type sensors are introduced. Next, we recently found that the tridentate ligands are a promising platform for constructing AIE-active complexes. Influence of skeletal distortions on mechanical motions in the excited state followed by AIE behaviors are explained. Moreover, several examples on the application to near-infrared (NIR)-luminescent materials are described. Finally, we also mention aromatics-connected boron cluster compounds, *o*-carboranes. Because of preferable structural features of *o*-carboranes for avoiding aggregation-caused quenching (ACQ) and structural relaxation in the excited state, aryl-modified *o*-carborane dyads and triads often show not only AIE and crystallization-induced emission (CIE) but also stimuli-responsive luminochromic behaviors. From recent works, these unique luminescent properties and detailed mechanism in *o*-carborane materials are explained.

1. Introduction

Boron complexation with π -conjugated ligands is an effective strategy for constructing luminescent molecules. Molecular rigidity and planarity, which are essential for enhancing emission efficiencies, can be improved by boron complexation. Therefore, boron complexes can be regarded as a versatile “element-block”, which is a minimum functional unit containing heteroatom,[1–4] for constructing luminescent materials, such as polymers [5–8]. However, there are still several issues to be solved for practical applications of these luminescent organic dyes. The most critical problem is ACQ observed in the condensed state of organic dyes. Organic dyes generally exhibit intense emission only in the diluted solutions, and most of luminescent properties are usually spoiled in the solid state. To obtain luminescence in solid and film, we need to avoid ACQ. Although several strategies, such as introduction of bulky substituents and isolation of each luminophores [9–15], have been proposed for obtaining solid-state luminescent properties, these modifications to avoid ACQ next cause loss of stimuli responsiveness. Thus, the molecular design for simultaneously obtaining solid-state emission properties and stimuli-responsivity is still strongly challenging.

AIE is one of potential properties to be consistent with solid-state luminescence and stimuli-responsiveness. Basically, AIE-active dyes showed intense emission in the condensed state. This means that AIE-active dyes intrinsically have environment-sensitive luminescent properties.

Furthermore, as we introduce many examples in this review, solid-state luminescent properties, such as luminescent color, can be tuned depending on molecular morphology in aggregate and solid. Based on these variable luminescent properties, environmental sensors can be fabricated. Further luminescent materials with unique stimuli responsiveness can be expected from AIE-active boron complexes.

In this review, we survey recent progresses in the development of AIE-active boron-containing compounds. Particularly, we focused on mechanism of AIE behaviors and role of boron in the AIE behaviors are illustrated. Initially, boron complexes with the bidentate ligands possessing AIE and/or CIE properties are described. Tricoordinated boron has high reactivity, and unique sensitivity is often observed [16–18]. In contrast, AIE-active boron complexes have generally tetraordinated structures involving two dative bonds with the bidentate ligand and other substituents such as fluoride, alkyl or aromatic groups. Because of high stability and acceptability to chemical modification, the wide variety of molecular structures with intense emission have been reported, and some of them can present AIE properties. From these AIE-active boron complexes with the bidentate ligands, we classified into three groups according to the types of the dative bonds, such as B–O and/or B–N bonds. Moreover, we also mention conjugated polymers involving AIE-active boron complexes and their applications for environment-sensitive luminescent materials and stimuli-responsive film sensors are demonstrated.

Next, we illustrate AIE properties of boron complexes with the tridentate ligands. The boron complexes which can show larger degree of structural relaxation after photo-excitation exhibit poor luminescent properties in solution due to energy-consumable molecular tumbling. Meanwhile, some of them can show significant emission in solid, followed by AIE behaviors because loss of excitation energy should be inhibited accompanied by the suppression of molecular motions in the condensed state. In particular, structural relaxation is often observed from the boron complexes with the tridentate ligands for releasing structural distortion in the excited state. Thus, typical AIE and/or CIE behaviors have been discovered from the tridentate ligand-containing complexes. Previously, we explained the idea of “excitation-driven” boron complexes, which show mechanical motions in the excited state, and their usability for designing sensing materials [19]. In this review, further examples of “excitation-driven” tridentate boron complexes are demonstrated.

Finally, we explain AIE-properties of boron cluster compounds containing the *o*-carborane unit. Boron atoms can form various types of three-dimensional cluster compounds through three-center two-electron bonds [20]. In the perspective of the research field on AIE, *o*-carborane (1,2-dicarbado-*clos*o-dodecaborane, $C_2B_{10}H_{12}$), an icosahedral carbon-boron cluster, is a promising building block for efficient solid-state emission and stimuli-responsive materials. In most cases, AIE from *o*-carborane derivatives possessing a π -conjugated subunit connected to the carbon atom in *o*-

carborane is originated from the transition from the intramolecular charge transfer (ICT) state, where the *o*-carborane unit can act as an electron acceptor [21]. Interestingly, the distance between two carbon atoms on the *o*-carborane (l_{C-C}) drastically gets longer after photoexcitation. Recent researches have pointed out that the unique molecular motion plays an important role in emission quenching, and the restricted C–C elongation in the aggregates and crystals improves the radiative decay process, resulting in AIE behaviors. Comparison of 12-vertices regioisomers also supports the critical effect of C–C elongation: although *o*-carborane-based luminophores are generally AIE-active, *m*- or *p*-carborane-based isomers are AIE-inactive [22,23]. Hence, it can be said that *o*-carborane-based AIEgens also have the “excitation-driven” character, promising for various sensing applications [19].

2. Tetracoordinated boron complexes with bidentate ligands

Bidentate ligands that afforded AIE-active boron complexes are classified into three categories depending on the elements at binding sites: (1) N,N-type, (2) N,O-type, and (3) O,O-type ligands [24–28]. Therefore, in this section, we firstly show AIE-active boron complexes according to those classification, followed by other AIE dyes with related structures for each.

2.1. N,N-type ligands

2.1.1. Boron dipyrromethene and its analogs

Boron dipyrromethene (BODIPY, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) and its analogs are one of the most essential and practical luminescent dyes [29–36]. Their π -conjugated N,N-type ligands comprise two pyrrole units bridged by a methine group and can be considered as a half of porphyrins. BODIPYs typically show high molar extinction coefficients in the order of $10^5 \text{ M}^{-1}\text{cm}^{-1}$, remarkably efficient luminescence (Φ_{PL} up to 1.0) in solution states, and small Stokes shifts. In addition, their aza-analogs (Aza-BODIPYs) have attracted much attention because of their longer-wavelength absorption and emission properties [35,36]. However, ACQ is inevitable due to their highly planar π -conjugated structures resulting in strong intermolecular interactions. The ACQ of BODIPYs hampers their applications as solid-state emitters. Recent research has enabled us to switch their ACQ to AIE (Figure 1 and Table 1) [37]. The typical strategies for constructing AIE-active BODIPYs are classified into three types: (1) modulation of excited-state intramolecular rotations especially at the *meso*-position; (2) inducing an excitonic coupling enhancing emission probability in aggregation states; (3) decoration of a BODIPY skeleton with AIE moieties.

Figure 1 and Table 1

Firstly, it has been well known that the degree of rotational freedom of the *meso*-substituent of BODIPYs strongly affects their photophysical properties [38–48]. Rotatable aryl substituents at the *meso*-position lead to fast non-radiative deactivation of excited molecules. Theoretical calculations revealed that the oscillator strength for S_1 – S_0 transition is significantly small for the optimized structure of *meso*-phenyl BODIPY which has a dihedral angle of 0° between the BODIPY core and the *meso*-aryl group [42]. Consequently, BODIPY dyes have been utilized as local and micro viscosity probes in biological media [41,43,44,46,47]. In 2009, Peña-Cabrera and Tang *et al.* reported that BODIPYs **1–4** with an electron donor, triphenylamine, as a *meso*-substituent exhibited AIE (Figure 2) [49]. In this class of dyes, BODIPY units serve as an electron acceptor originating from the strong electron-withdrawing nature of nitrogen, boron, and fluorine atoms. Thus, a twisted intramolecular electron transfer (TICT) state would occur in their solutions, where the dihedral angle between donor and acceptor planes gets closer to 90° at the charge-transfer excited states. In dilute THF solutions, the chromophores weakly emit in the red region from the TICT state. Meanwhile, the aggregates formed in THF/hexane mixture (99 vol% of hexane) emit in the green region, because the intramolecular rotation which was responsible of TICT was hampered by aggregation. The green emission should be attributed to a locally-excited (LE) state, where the BODIPY moiety was selectively excited. The molecular structure of the LE states should be similar to that of the ground state. The results of single-crystal X-ray structure

analysis revealed that the bulky triphenylamine moieties repelled π – π interactions, resulting in the emission from the LE molecules. Since this report, some TICT-type AIE-active BODIPYs, such as **5** and **6**, have been developed [50,51].

In 2022, Xu and Liu *et al.* reported a new AIE-active azetidine-substituted BODIPY dye based on the accurate prediction of TICT [52]. They demonstrated that the time-dependent density functional theory (TD-DFT) calculations with the CAM-B3LYP/cLR-SMD level of theory were appropriate for quantitative prediction of LE, ICT and TICT states for typical organic fluorophores involving naphthalimide, rhodamine, coumarin, and BODIPY. The computational method was applied to a *meso*-phenyl BODIPY system and provided a reasonable potential energy surface (PES) along the dihedral angle between the BODIPY core of **7** and its phenyl planes. The results of the calculations showed that the S_1 state possessed the LE feature, where both electron and hole distributions were localized at the BODIPY moiety. The authors speculated that the incorporation of an electron-donating group into the *meso*-phenyl ring could stabilize the TICT state. The newly designed azetidine-functionalized BODIPY **8** was subjected to the TD-DFT calculations. The PESs were calculated along both rotational angles φ and θ . The PES along θ from the Franck–Condon (FC) structure ($\theta = 72^\circ$) to a TICT geometry ($\theta = 90^\circ$) was estimated to be barrierless. On the other hand, the PES along φ , where $\varphi = 0^\circ$ for the FC structure and $\varphi = 90^\circ$ for a TICT geometry, was calculated to be uphill. Therefore, it had been suggested that the

azetidine-substituted BODIPY dye could form a TICT state in polar solvents which has twisted structure at the BODIPY–aryl linkage rather than the aryl–azetidine one. Indeed, the synthesized azetidine-BODIPY dye showed almost no emission in 1,4-dioxane ($\Phi_{\text{PL}} \sim 0$), while its photoluminescence intensity enhanced as the water fraction of 1,4-dioxane/water solutions increased. The molecular aggregates would hamper the C–C rotation. Furthermore, its solid exhibited bright fluorescence with Φ_{PL} of 0.11. These results clearly showed the AIE property of this azetidine-BODIPY dye based on the restricted TICT.

As the second approach for achieving AIE-active BODIPY systems, many efforts have been devoted to controlling exciton coupling in aggregation states. Exciton coupling means interactions between electric transition dipole moments of neighboring molecules, leading to distinct electronic states or exciton bands. For the case of a dimer, the energy diagram for the exciton coupling is shown in Figure 3. When two dipoles interact, exciton states split into two states of in-phase ($|\Psi_{\uparrow\uparrow}\rangle$) and out-of-phase ($|\Psi_{\uparrow\downarrow}\rangle$) dipole arrangements. For the in-phase state $|\Psi_{\uparrow\uparrow}\rangle$, the sum of the transition dipole moments is nonzero. Therefore, the transition from the ground state to the in-phase state $|\Psi_{\uparrow\uparrow}\rangle$ is allowed, while the transition from the ground state to the out-of-phase state $|\Psi_{\uparrow\downarrow}\rangle$ is forbidden. Meanwhile, their energies depend on the slip angle θ between the two dipoles. For $\theta = \cos^{-1}(1/\sqrt{3}) \sim 54.7^\circ$, these two states showed no energy splitting, or degenerates. When θ is below 54.7° , the allowed in-phase state $|\Psi_{\uparrow\uparrow}\rangle$ is more stable. Such a

molecular arrangement is generally stated as J-aggregates. J denotes “Jelley” according to the name of E. E. Jelley, who observed the spectral change of a cyanine dye due to the aggregation [53,54]. J-aggregates absorb and emit lower-energy light than the corresponding discrete molecules. Absorption and emission spectra of J-aggregates tend to be sharp because of their allowed transition nature. On the other hand, when θ is over 54.7° , the forbidden out-of-phase state $|\Psi_{\uparrow\downarrow}\rangle$ becomes more stable than the other. In this case, the absorption band of the dimer appears in the higher-energy region than that of the monomer, because the lower-energy state $|\Psi_{\uparrow\downarrow}\rangle$ is forbidden. Hence, such a molecular arrangement is stated as H-aggregates (H denotes hypsochromic). According to the Kasha’s rule, emission occurs from the lowest-energy excited state in a multiplicity interested. Since H-aggregates involve a forbidden state as the lowest-energy excited state, their emission should be less efficient than that of monomers.

Figure 3

Typical BODIPY-based dyes form H-aggregates in the dense states due to their rigid π -planes and lose their efficient fluorescence. In contrast, some BODIPYs tend to form J-aggregates [55–61] and provide AIE properties in certain cases [62–69]. AIE-active BODIPY based on emissive J-aggregates have been achieved by *meso*-substitution [62,63]. Trifluoromethyl (**15**) and ester (**10**)

and **11**) functional groups at the *meso*-position of 1,3,5,7-tetramethyl BODIPY brought about the AIE property accompanied by the formation of J-aggregates in acetonitrile/water mixed solvents. On the other hand, the methyl (**16**), formyl (**12**), nitrile (**13**), and chloride (**14**) derivatives showed ACQ, although the nitrile and chloride ones assembled into J-aggregates. Furthermore, the 3,5-dimethyl derivatives (**17–24**) have not shown AIE with J-aggregation. These results suggested that an electron-withdrawing *meso*-substituent combined with the flanking methyl groups would be required for achieving AIE based on J-aggregation.

As the third simple strategy, incorporation of tetraphenylethene (TPE) units has deprived BODIPYs of efficient solution-state luminescence and installed solid-state emission [70–75]. Peña-Cabrera and Tang *et al.* reported that AIE property was obtained from BODIPYs, **25–27**, bearing TPE at the *meso*-position with various π -conjugated linkers [70]. These chromophores showed quite low Φ_{PL} values in solution states ($< 1\%$), while the efficiency enhanced up to 27% in solid states. Both LE and TICT emissions were observed in polar solvents, such as chloroform, ethyl acetate and THF. The spectral features and DFT calculations suggested that the LE and TICT states were assigned to the BODIPY moieties and CT from TPE to BODIPY, respectively. Interestingly, the LE emissions were weakened with increasing the volume fraction of water in THF/water mixture. On the other hand, the TICT emissions were intensified. Consequently, the LE and TICT states showed completely opposite properties, ACQ and AIE, respectively. The

impacts of substituent positions and numbers on the ACQ and AIE properties were also evaluated (**28–35**) [71,72]. Effective emission enhancement by aggregation was observed only for compounds with suitable packing structures where chromophores were taken apart from each other, even if solution-state emissions were quenched by the introduction of TPE moieties.

2.1.2 Boron β -diketimate complexes

β -Diketimate ligands have been widely utilized for isolating various metal complexes (Figure 4 and Table 2). Recently, AIE- and CIE-active complexes of these ligands have rapidly emerged. Gardinier *et al.* reported that emission intensity of **36–38** was enhanced by aggregation compared to their solutions [76]. After this report, new series of CIE-active boron complexes **39–48** have been developed [77–80]. These molecules emit more efficiently in their crystalline states than those in solutions and amorphous states (Figure 5a and 5b). The peripheral aromatic rings would be responsible for the fast non-radiative quenching even in the amorphous states, because their free volumes are larger than crystalline states. It was also demonstrated that the mechanochromic behavior was affected by the substitution position of halides **40–43** [79]. In addition, related diketimate complexes with fused structures were also developed as AIE-active chromophores [81]. Furthermore, π -conjugated polymers based on β -diketimate complexes have been extensively studied for constructing film-state sensors (Figure 5c) [78,82–85]. It should be worth

to note that other group 13 element complexes with β -diketiminato ligands also exhibited CIE properties [86,87]. Moreover, quantum chemical calculations for β -diketiminato aluminum complexes implied that an out-of-plane twisting vibrational mode of the central chelation ring could be responsible for the internal conversion paths in solutions as well as a rotational vibration of the peripheral rings [87].

Figures 4 and 5, Table 2

2.1.3. Pyridine-based complexes

Pyridine-based N,N-ligands have also enabled us to access AIE-active complexes (Figure 6 and Table 3). The pyridine moiety is occasionally referred to as a cyclic imine. Wang and Liu *et al.* reported AIE-active pyridylenamide complexes in 2015 [88]. Their viscosity-dependent emission and crystal structures without π - π interactions suggested that the restriction of the rotation of the phenyl ring and *N,N*-dimethylamino group should be responsible for their AIE behaviors. Tanaka and Chujo *et al.* also developed similar pyridylenamide complexes **53** and **54** with and without a fused structure [89]. Complex **53**, which has freely rotatable phenyl groups, showed typical AIE, while the corresponding complex **54** with the fused structure exhibited ACQ. The larger Stokes shift of **53** (3079 cm⁻¹) than that of **54** (337 cm⁻¹) implied a large structural change in the excited

state. TD-DFT calculations with the B3LYP/6-31G(d,p) level of theory suggested that the unfused complex exhibited a large structural relaxation with bending at the C–N bond of the enamine unit (Figure 7). The restriction of such a relaxation should be responsible for the AIE. In addition, the freely rotatable phenyl rings hamper intermolecular interactions in the solid states, leading to efficient solid-state emission. By introducing heteroatoms including nitrogen, various AIE behaviors were observed [90–94]. Meanwhile, such a structural relaxation should be restricted for the fused complex [95–101]. In these fused molecules, AIE was no longer observed, luminescence can be observed both solution and solid states. Especially, stimuli-responsive luminochromic behaviors were observed. Environmental sensitivity can be preserved in multiple phases.

Figures 6 and 7 and Table 3

2.1.4. Hydrazone-based complexes

Since the first examples of AIE-active hydrazone-based complexes, namely BODIHY, were reported by Aprahamian *et al.* in 2011 [102], this class of ligands has been emerged as facile scaffolds of AIE-active complexes (Figure 8 and Table 4) [103–110]. The first example of cyano-functionalized BODIHY **56** showed a typical AIE behavior. Its dichloromethane solution showed Φ_{PL} of 0.06, while the value dramatically enhanced to 0.24 and 0.52 for the crystals and the spin-

coated films, respectively. The lower quantum yield of the crystals suggested some intermolecular interactions in the packing structure. Indeed, the single-crystal X-ray structure analysis showed π – π stacking (3.494 and 3.675 Å) within the layered structure.

Figure 8 and Table 4

So far, two different mechanisms of the AIE phenomenon have been proposed: (1) Suppression of Kasha's rule [103] and (2) restriction of flip-flop motion [106]. The experimental and theoretical study by Aprahamian *et al.* focused on the degree of rotational freedom around the N–aryl bond of BODIHYs (Figure 9a). Quantum chemical calculations using time-dependent density functional theory (TD-DFT) with Perdew–Burke–Ernzerhof (PBE) functional suggested that their lowest excited singlet states (S_1) have significantly smaller oscillator strengths than higher excited states. Furthermore, the N–aryl bond rotations would be responsible for the internal conversion from S_n to S_1 . Therefore, these compounds emit fluorescence in high-viscosity solutions from the S_n states (anti-Kasha emission) while not in low-viscosity ones due to rapid quenching through the S_1 states. Hence, the restriction of N–aryl rotation in solid states would lead to the suppression of Kasha's rule, resulting in their AIE behavior [103].

The other mechanism was provided by Zhou *et al.* and focused on a thermally accessible

conical intersection, where the complexes possess bent structures (Figure 9b) [106]. In contrast to the results of TD-DFT calculations by Aprahamian, TD-DFT calculations with B3LYP or CAM-B3LYP and complete-active-space self-consistent-field (CASSCF) calculations revealed that the oscillator strength of S_1 of BODIHY **56** is not close to zero and it should be a bright state. Furthermore, two-root state-averaged CASSCF (SA2-CASSCF) calculations suggested the existence of a minimal-energy conical intersection (MECI) with a large distortion of the molecular plane. The ‘flip-flop’ motion from the planar S_1 -optimized structure to the MECI should be barrierless in low-viscosity solutions. Meanwhile such a large change of molecular shapes and volume would be restricted in high-viscosity solutions and in solid state [106]. In the polymer main-chain, AIE was not observed from BODIHYs, meanwhile luminescence can be observed in the NIR region although π -conjugated system is not large [111]. Relatively-longer wavelength emission of the BODIHY unit can be detected both in solution and film.

Figure 9

2.2. *N,O*-type ligands

2.2.1. Boron β -ketoiminate complexes

β -Ketoiminate ligands have been developed as a robust scaffold for constructing AIE-active boron complexes (Figure 10 and Table 5). First examples of AIE-active boron β -diketoiminate complexes, **76–78**, were reported in 2013 [112]. The synthesized complexes emitted efficient fluorescence only in the aggregation states, in contrast to the corresponding boron β -diketonate complex which exhibited typical ACQ (Figures 11a and 11b). A bond energy of a B–N bond ($\sim 445.6 \text{ kJ mol}^{-1}$ or less) is weaker than that of a B–O bond ($\sim 536 \text{ kJ mol}^{-1}$). Such a weak bond could facilitate intramolecular motions and accelerate non-radiative quenching of excitons in solutions. Consequently, β -ketoiminate ligands could provide AIE-active complexes when appropriate steric hinderance is employed for preventing undesired intermolecular interactions in solid states.

Emission behavior of some AIE-active β -ketoiminate complexes is sensitive to intermolecular interactions. In addition, intermolecular interactions in solid states could be modulated by mechanical stress. Hence, mechanochromic luminescence is often coupled with AIE behavior of β -ketoiminate complexes. For instance, bithiophene-bridged β -ketoiminate complexes exhibited mechanochromic luminescence accompanied with enhancement of photoluminescence efficiency (Figure 11c) [113]. Their emission quantum yields improved after mechanical grinding, for example, 0.28 to 0.42 for compound **80**. Interestingly, for some cases, the resulted quantum yields of ground samples were higher than those of the corresponding solutions (0.34 for compound **80**).

It was implied that the intermolecular interactions could be perturbed by mechanical stress. Furthermore, the complexes with the smaller substituents **79** and **80** exhibited hypsochromic shifts by the mechanical grinding, while the complexes with the larger ones **81–83** showed bathochromic shifts. In the crystalline states of **79** and **80**, intermolecular interactions would not be prohibited by the small end groups, leading to low-energy exciton bands compared to single molecules. When mechanical stress was applied to the crystals of **79** and **80**, such intermolecular interactions would be weakened. As a result, **79** and **80** showed the hypsochromic shifts. In contrast, the larger substituents of **81–83** would prohibit strong intermolecular interactions in their crystalline states. After grinding, amorphous states involving substantial intermolecular interactions would be formed, resulting in the bathochromic shifts of their emission. Based on mechanochromic luminescent properties, the thermally stable hybrid dye, [114] aggregation-induced luminochromism in hydrogels [115] and dissolved oxygen-dependent luminescent probes [116] have been developed recently.

Figures 10 and 11, Table 5

2.2.2. *Pyridylenolate-based complexes*

Pyridylenolates are often regarded as fused β -ketoiminates and have been utilized as a scaffold

for constructing AIE-active boron complexes (Figure 12 and Table 6) [117–121]. Their solution-state luminescence properties were dependent on the substituent positions of peripheral aryl groups. Two phenyl groups introduced into the enol unit of compounds **84** and **85** accelerate non-radiative quenching in their solutions, resulting in their typical AIE [117]. On the other hand, when one of the phenyl groups was shifted to the pyridyl moiety in compounds **86–89**, their solutions emit strongly as well as their solids [118]. In addition, the introduction of nitrogen atoms into the scaffold also affected the emission wavelengths and quantum yields [119]. It is worth to note that synthesis of pyridylenolate structures has been accomplished by copper-catalyzed oxidation of 2-vinylpyridine derivatives [120] and zinc-catalyzed alkenylation of *N*-oxides [121].

2.2.3. Azole-based *N,O*-ligand complexes

Azole-based *N,O*-ligands have been utilized for constructing AIE-active boron complexes with as well as *N,N*-ligands (Figure 13 and Table 7) [122–129]. Kubota and Matsui *et al.* firstly reported a series of AIE-active thiazole boron complexes with a rotatable phenyl group (compounds **102–105**) [122]. The restriction of intramolecular rotation was proposed as the mechanism of the typical AIE behavior. In addition, the absence of strong CH/F interactions for the crystals of BPh₂ complexes **103** and **105** could be responsible for their more efficient solid-state luminescence than BF₂ complexes **102** and **104**. An additional phenyl group at the α -position

of the enol moiety has often enhanced the ON/OFF contrast between the solutions and aggregates because of dramatic acceleration of non-radiative quenching, as shown in compounds **106–115** [123,124]. Electron donating groups of the aryl moiety in the enol have occasionally improved the efficiencies of the solution-state emission, such as compounds **118, 19, and 125**) [126,129].

Figure 13 and Table 7

2.2.3. Boranil-Based N,O-Ligand Complexes

Some boranils, boron complexes of Schiff bases with salicylaldehyde derivatives, have exhibited AIE behavior (Figure 14 and Table 8) [130–134]. AIE behavior from boranils has been reported occasionally such as compounds **143** and **145–150** [130–133]. Coumarin-based Schiff base complexes, **151** and **152**, which possess N,O-chelate structure like boranils, showed AIE property [134]. These coumarin complexes exhibited drastic solvent-dependent emission. They emit efficiently ($\Phi_{\text{PL}} = 0.15$ for **151**, 0.49 for **152**) in THF, while the efficiencies decreased remarkably in acetonitrile ($\Phi_{\text{PL}} < 0.01$ for both **151** and **152**). The more polar phenomenon in acetonitrile could result in significant non-radiative quenching. Addition of water to the acetonitrile solutions lead to dramatic enhancement of luminescence because of the formation of aggregates.

2.3. *O,O*-type ligands

2.3.1. Boron β -diketonate complexes

β -Diketonates boron complexes have been utilized for achieving various luminescent materials. However, they typically suffer from ACQ because of their planar π -conjugated structure. Nevertheless, it has been revealed that AIE-active systems can be obtained occasionally by using boron β -diketonate complexes. Since a comprehensive review of luminescent materials based on β -diketonates has been published [135], we will describe only selected important developments here.

Dimethoxy-substituted β -diketonate boron complex **153** exhibited variety of solid-state luminescent functions [136]. This dye exhibited interesting AIE behavior. Its emission color strongly depended on the way of the formation of aggregation probably because of the degree of conformational freedom of the methoxy groups in the solid states (Figure 16a). The acetonitrile solution hardly showed luminescence. Dropwise addition of water into the vigorously stirred acetonitrile solution resulted in suspensions with blue emission. Meanwhile, rapid addition of water lead to emission color change from yellow to green. Green and blue emission might be attributed to two distinct polymorphs involving different conformers derived from the two methoxy groups. The yellow-emissive transient phase would be originated from an amorphous-

like state. It should be noted that the emission intensity was also dependent on polarity of solvents.

The more polar situations gave rise to the less efficient emission. Therefore, the mechanism of its AIE behavior may not originated only from the typical restriction of intramolecular motions. For instance, charge-separated excited states might be involved in its excited-state electronic structure.

Fraser *et al.* reported the effects of α -substitution on AIE of β -diketonate complexes **154–157** [137]. Only compound **155** showed typical AIE property in DMSO/water mixtures (Figure 16b). The α -methyl group forced a highly twisted structure in pure DMSO which should be non-emissive. As water was added, the formed aggregation condition should restrict molecular rotations, leading to increasing emission intensity. Compound **154** showed quite low-intensity luminescence in pure DMSO ($\Phi_{\text{PL}} = 0.037$) because the intramolecular charge transfer state should be predominant in such a polar solvent. As increasing water fraction, the polar solvent effect should decrease because of aggregation. Therefore, its emission was intensified until a certain critical point (water fraction = 60%). Over the critical point, the much weaker emission emerged, attributed from the bulk solid emission. In stark contrast, compound **156**, decorated by an electron-donating anisyl group at the α -position, showed efficient TICT emission in pure DMSO. Formation of such a twisted structure could be restricted in the solid state. Thus, the luminescence intensity dropped until 50% of water content. On the other hand, intermolecular interactions would be hampered by the steric hinderance of aryl groups. Consequently, the

emission from compound **156** recovered over 50% of water fraction. Finally, the strapped compound **157** exhibited typical ACQ because of the locked planar conformation. It is worth to emphasize that ICT states play an important role in non-radiative quenching paths of the AIE-active boron β -diketonate complexes.

Figure 16

3. Tetracoordinated boron complexes with tridentate ligands

When we prepare tetracoordinated boron complexes with tridentate ligands, the boron-fused ligand is slightly bent and a substituent at boron is perpendicularly protruded against the ligand surface due to the non-planar tetrahedral geometry (Figure 17) [138]. Those are different structural features from highly-planar boron complexes with the conventional bidentate ligands. Photoexcitation accompanied by elongation of the chemical bonds potentially induces further distortion of the bent scaffold because of the tightly ring-fused structure. When the large structural relaxation promotes faster non-radiative deactivation of the excited energy within pico-second order than radiative deactivation of that with nano-second one, the emission should be quenched such as in dilute solution state where the molecules are freely movable. In contrast, in condensed state such as aggregated or solid states, the emission should be recovered because of suppression

of energy-consumable structural relaxations. Additionally, the perpendicularly-protruded substituent at boron can restrict continuous π - π interaction even in the condensed state leading to emission quenching induced by exciton diffusion [139]. From those considerations, it is expected that boron-fused π -conjugated systems with tridentate ligands have a potential to show AIE and CIE properties. In this section, we will introduce the examples of AIE and CIE-active compounds by using the concept of the boron-fused tridentate ligands.

Figure 17

3.1. Azobenzene tridentate ligands

Azobenzene[140] is regarded as heteroatom-containing π -conjugated system with a nitrogen–nitrogen double (N=N) bond and the nitrogen atom is available for a coordination point (Figure 17). Pristine azobenzene is known to be a non-emissive scaffold due to fast internal conversion and excited deactivation through non-radiative deactivation processes accompanied by photoisomerization.[141–144] Moreover, the S_0 (ground state) to S_1 (the first excited state) transition is assigned to forbidden n - π^* transition, and that is another reason of no emission from azobenzene moieties. Recently, it was reported that azobenzene complexes with the coordination at the nitrogen atom showed intense emission by suppressing photoisomerization and alternating

the forbidden $n-\pi^*$ transition to the allowed $\pi-\pi^*$ transition [145]. Other studies suggested that the emission was observed from highly crystalline state of azobenzene derivatives [146,147]. Those behaviors strongly suggest that the azobenzene tridentate ligands is a promising scaffold for constructing AIE- and CIE-active compounds.

3.1.1. Boron-fused azobenzene complexes

Our research group found that boron-fused azobenzene complexes (BAz) with O,N,O-type tridentate ligands, such as 2,2'-dihydroxyazobenzene derivatives, worked as AIE-active platforms [148]. The fundamental structure, **BAz-H (158)**, can be synthesized by the one-step reaction from commercially-available 2,2'-dihydroxyazobenzene (**LAz**) and boron trifluoride diethyl ether complex ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) (Figure 18a). From a single crystal X-ray diffraction structural analysis, the complex had a tight ring-fused structure consisting of five and six membered rings around boron with a perpendicularly protruding fluorine atom from the π -surface (Figure 18b). The ligand was slightly bent (dihedral angle: $\varphi_{(\text{C}-\text{N}=\text{N}-\text{C})} = 165^\circ$) due to structural strain stem from the ring-fused tetrahedral geometry. In the diluted solution, **BAz-H** showed strong absorption around 479 nm attributable to the allowed $\pi-\pi^*$ transition according to the TD-DFT calculation (Figures 18c and 18d). This fact indicates that **BAz-H** has a potential to show emission unlike the pristine azobenzene moiety (e.g. **Az-H** in Figure 18c). However, contrary to the presumption, **BAz-H**

exhibited weak orange emission in the diluted solution and the PL lifetime was too short to detect (1.0×10^{-4} M in 1,4-dioxane; $\lambda_{\text{PL}} = 619$ nm, $\Phi_{\text{PL}} < 0.001$, $\tau < 0.10$ ns). Interestingly, the emission was observed in the aggregated state under water-rich solvent condition and the PL lifetime was detectable as nano-second order (1,4-dioxane/H₂O = 1/99 v/v; $\lambda_{\text{PL}} = 603$ nm, $\Phi_{\text{PL}} = 0.023$, $\tau = 1.09$ ns) (Figure 18e). This environment-sensitive emission behaviors were a typical AIE property. Theoretical calculation with TD-DFT supported that **BAz-H** was much more bent in the excited state (dihedral angle: $\varphi_{(\text{C-N=N-C})} = 141^\circ$) than in the ground state (dihedral angle: $\varphi_{(\text{C-N=N-C})} = 165^\circ$) (Figure 18f). This was mainly caused by elongation of N=N bond length at the excited state by ca. 0.1 Å compared to that at the ground state. It was presumed that the bending motion induced fast non-radiative deactivation of excited energy. The emission was also recovered and enhanced by extension of π -conjugation at 4,4' positions of the azobenzene moiety with oligomeric and polymeric approaches by using co-monomers, bithiophene and fluorine derivatives. This means that delocalization of π -electron through the elongated π -conjugated system also suppressed the bending motion. This research is the first discovery of AIE property from the BAz scaffold.

Figure 18

3.1.2. Substituent effects and functionalization

From the series of our research, it was found that almost all BAZ derivatives exhibited weak or no emission ($\Phi_{\text{PL}} < 0.01$) in the solution state and presented the emission in condensed state ($\Phi_{\text{PL}} > 0.01$) (Figure 19). Hence, it can be said that BAZ scaffold is useful for preparing AIE-active molecules. Furthermore, the emission property and functions can be tuned by chemical modification at the azobenzene moiety and at the boron atom (Figures 19b and 19d). Main substitution points and the molecular orbitals (MOs) are described in Figure 19a. **BAz-5Br (160)** showed the longest absorption wavelength among the BAZ derivatives [149]. Both experimental and theoretical data suggested that substitution at 5,5' positions were effective in narrowing energy gap resulting from selective reduction of LUMO or elevation of HOMO energy levels (Figure 19c) [149,150]. On the other hand, substitution at 3,3' positions hardly affect the energy gap. For example, **BAz-4Br (159)** and **BAz-4Br3F (162)** or **BAz-4Br5F (161)** and **BAz-4Br35F (163)** had similar λ_{abs} , respectively. Those different behaviors depending on the substitution points are attributed to the shapes of HOMO and LUMO (Figure 19a). There are orbitals only in HOMO at 5,5' positions and that indicates that a resonance effect worked only in HOMO [151–159]. Therefore, a lone pair of electrons of halogen increases HOMO energy level and cancels reduction of HOMO energy level by inductive effect of the halogen atoms. In contrast, 3,3' positions have orbitals both in HOMO and LUMO. Hence, the resonance and inductive effects equally work and there are little effects on energy gap of the π -conjugated system. In addition, 4,4' positions are

utilized for elongation of π -conjugation and enhancement of luminescent properties. Halogenation or connecting aromatic rings can improve photoluminescence quantum efficiencies. Introduction of substituents at boron is also beneficial for improving solid-state emission in AIE and CIE properties. The substituent at boron is vertically projected against π -conjugated system and would effectively inhibit intermolecular π - π interaction leading to excess diffusion of exciton.

A phenol group is simple but provides critical effects on solid-state emission properties (Figures 19d and 19e) [160]. **BAzPh-4Br (164)** showed good solid-state emission in the red region ($\lambda_{\text{PL}} = 659$ nm, $\Phi_{\text{PL}} = 0.12$) and the emission was effectively quenched in solution ($\Phi_{\text{PL}} < 0.01$). The substituent at boron enhanced inductive effect of boron. Pentafluorophenyl (**BAzC6F5-4Br (165)**) and mesityl groups (**BAzMes-4Br (166)**) increased and decreased accepting ability of the BAz unit, respectively. The BAz unit can be also used as a strong electron accepting unit because of electron-withdrawing ability of nitrogen and boron atoms in π -conjugated monomers. In particular, fluorination and introduction of the phenyl groups can vary emission wavelengths of the π -conjugated polymers even in NIR region ($\lambda_{\text{PL}} = 787\sim 980$ nm) and improve Φ_{PL} especially in film ($\Phi_{\text{PL}} = 0.01\sim 0.09$) (Figure 20) [150,160].

Figures 19 and 20

3.1.3. Application to biochemistry

Recently, the AIE property of the BAZ unit was used for biochemical application. Hori, Tomita, Sohma and Kanai groups developed photooxygenation catalyst (**167**) that permeated to pass the blood-brain barrier (BBB) and selectively and directly degrades an extracellular Alzheimer's disease-related undruggable protein, amyloid- β protein ($A\beta$) (Figure 21) [161]. When the catalyst is isolated in solution, the catalyst did not work due to excitation deactivation caused by vigorous molecular tumbling. On the other hand, when bound to $A\beta$, the catalyst is able to activate photooxygenation reaction of $A\beta$. In addition, the catalyst was designed for practically using *in vivo* application. Chemical modification at 4,4' positions and at boron provide bathochromic shift of maximum absorption wavelength and that was merit for activation by tissue-permeable long-wavelength light irradiation. Owing to the compact but light-absorbing ability in the orange and red color, the molecule can work as a visible light-activatable chemical catalyst. The catalyst activity can be switched on/off depending on binding/nonbinding to aggregated $A\beta$ where its molecular mobility was controlled. Theoretical calculation proposed that **10** also formed much more bent structure in the excited state compared to in the ground state. Therefore, it can be said that the BAZ scaffold is compact but can incorporate various functions to satisfy needs for applications.

Figure 21

3.1.4. Two six-membered rings with extension of π -conjugation

As a similar unit to BAZ, optical behaviors involved in planarity of π -conjugated system can be tuned by introduction of a methylene chain between benzene and oxygen moieties at the one side of the ligand. The structures are shown in Figure 22. Those units were synthesized from regioselective diazocoupling reactions with aniline and 2-hydroxynaphtyl derivatives [162]. The resulted chemical structure (BAzM) has two six membered rings around boron and much more planar π -surface in comparison to the structure composed of six and five membered rings (BAZ). The monoboron **monoBAzM (168)** showed weak emission among various states ($\Phi_{\text{PL}} < 0.01$), while it was enhanced at 77 K ($\Phi_{\text{PL}} = 0.77$) or in viscous states ($\Phi_{\text{PL}} = 0.01$). Therefore, BAZM has a potential to exhibit AIE property. Whereas, once the BAZM unit was extended to bisboron complexes (bisBAzM), both **bisBAzM-n (169)** and **bisBAzM-b (170)** showed good emission even in dilute solutions and slight loss of the emission in aggregate, which was opposite behavior of AIE, called ACQ. We experimentally revealed that the inversion of the AIE and ACQ properties should be caused by structural relaxation in the excited state from transient absorption spectroscopy (Figure 23a). After photoexcitation, monoBAzM showed large structural change leading to fast internal conversion within 20 ps and that was faster than the emission order of

fluorescence. On the other hand, there were small structural changes in bisBAzM, and the excited energy was emitted as fluorescence with ca. 0.5 ns. Theoretical calculations suggested that structural bent could be induced by elongation of N=N bond after photoexcitation in monoBAzM, whereas the elongation was restricted by extension of π -conjugated in bisBAzM (Figure 23. Interestingly, *anti*-conformation of bisBAzM exhibited an efficient CIE property even in the NIR region ($\lambda_{\text{PL}} = 643$ nm, $\Phi_{\text{PL}} = 0.06$ for ***anti*-169**, $\lambda_{\text{PL}} = 783$ nm, $\Phi_{\text{PL}} = 0.09$ for ***anti*-170**). This means that the direction of a perpendicularly protruded substituent at boron influences on solid-state emission properties and *anti*-form is suitable. From those results, we concluded that a compact and bendable structure with the single N=N bond is effective in showing AIE or CIE property.

Figures 22 and 23

3.2. Azomethine tridentate ligands

Azomethine (Schiff base) is the common name of the molecules containing a carbon–nitrogen double (C=N) bond. As a tridentate ligand, *o*-salicylideneaminophenol is structural analog of 2,2'-dihydroxyazobenzene (Figure 17). Similarly to azobenzene scaffolds, pristine azomethine scaffold hardly shows emission [163] despite the fact that various boron complexation enhances its emission property [164]. Although various types of complexes are developed, the example of

tridentate ones are still limited. C=N bonds can be obtained by the condensation reaction of amine and aldehyde derivatives and there are much more structural variations than azobenzene ones because of easiness of preparation [165]. In this section, we will illustrate AIE and CIE properties of boron-fused azomethine complexes (BAm) using the tridentate ligands.

3.2.1. AIE and CIE properties with thermosalient effect

We developed the BAm complex (**BAm-Et2N (171)**) from *o*-salicylideneaminophenol with a diethylamino group (Figure 24a) [166]. The complex **171** showed weak emission in the diluted solution state ($\Phi_{\text{PL}} = 0.001$, 1.0×10^{-5} M in chloroform) and the slight emission enhancement was detected in amorphous ($\Phi_{\text{PL}} = 0.003$). Additionally, the emission was enhanced under dispersion condition in a polymer film ($\Phi_{\text{PL}} = 0.011$) where the molecular motion should be partially restricted. From the theoretical calculation, elongation of the C=N bond length and bending of dihedral angle of C–C=N–C in the excited state (1.42 Å and 114°, respectively) occurred in comparison to those in the ground state (1.30 Å and 161°, respectively) (Figure 24b). Because of larger structural strain and longer elongation C=N bond than N=N one, the proposed bending motion of the BAm complex seemed to be more vigorous than that of the BAz one. The “flexible and bendable” molecular motion should induce non-radiative deactivation of the excited energy.

Interestingly, recrystallization in THF under hexane atmosphere provided two polymorphic

crystals, a yellow needle-like crystal (α) and an orange block crystal (β). Both crystals of **171** showed distinct CIE properties because of dramatical emission improvement in the crystalline states ($\Phi_{\text{PL}} = 0.39$ for crystal α and $\Phi_{\text{PL}} = 0.34$ for crystal β). From the PL lifetime measurement, large enhancement of k_r in the crystalline states ($k_r = 10^8 \text{ s}^{-1}$) was detected from that in amorphous state ($k_r = 10^5 \sim 10^6 \text{ s}^{-1}$). Therefore, the highly-ordered crystalline packing structure should be responsible for acceleration of the radiative process. Furthermore, we observed a thermosalient effect (Figure 24c), where the crystal is jumping or fragmented during a crystal–crystal phase transition triggered by heating and cooling [166]. In particular, the phase transition was visualized by emission color change owing to the CIE property. The $\alpha \rightarrow \beta$ phase transition was induced by heating at around 80 °C, and the $\beta \rightarrow \alpha$ phase transition was promoted by cooling at around –50 °C with sawtooth-like phase transition peaks which are often observed in thermosalient-active crystals [167]. It is proposed that these mechanical behaviors should be associated with a very fast phase transition accompanied by anisotropic deformation (Figure 24d) [168]. Thermosalient-active crystals are still rare in addition to the fact that few examples were reported with emission color change [169,170]. Those unique functions should be derived from the tightly-fused but “flexible and bendable” scaffold.

Figure 24

3.2.2. AIE and CIE properties with chiral boron

A tetracoordinated boron can be a stereogenic center. BAm derivatives have a stereogenic boron center, and racemic and homochiral crystals can change molecular arrangement in the solid state leading to different AIE and CIE behaviors. We separated the enantiomers of **BAm-Et2N-Cl (172)** and investigated their optical properties [171]. Optical resolution was carried out by using chiral high performance liquid chromatography (HPLC) (Figure 25a). The single crystal X-ray diffraction analyses revealed that the racemic crystal formed dense dimeric structures between the (*R*)- and (*S*)-enantiomers, whereas the homochiral crystal had loosely stacked in the helical-shaped molecular motifs (Figure 25b). These structural differences had a significant influence on the emission properties in the crystalline state. Indeed, these crystals displayed different optical properties accompanied by a CIE property ($\lambda_{\text{PL}} = 585$ nm and $\Phi_{\text{PL}} = 0.37$ for *rac*-**172**, $\lambda_{\text{PL}} = 568$ nm and $\Phi_{\text{PL}} = 0.29$ for (*R*)-**172**), meanwhile those showed the same absorption and emission behaviors in the diluted solution ($\lambda_{\text{abs}} = 464$ nm, $\lambda_{\text{PL}} = 526$ nm, $\Phi_{\text{PL}} = 0.002$, 1.0×10^{-5} M in chloroform) (Figure 25c). In addition, circularly polarized luminescence (CPL) properties were detected from the homochiral crystals. The detectable dissymmetry factor, $g_{\text{CPL}} = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$ (I_{left} , I_{right} : PL intensities of left and right-handed CPL, respectively) was not so high ($g_{\text{CPL}} \sim 10^{-4}$). However, since CPL from a single crystal is technically difficult, there are room for

further investigation. It is known that a stereogenic boron center potentially shows chiral inversion [172,173]. Interestingly, the heat-initiated homogeneous racemization without any solvents was observed in the molten state of the homochiral crystal. This dynamic stereochemical behavior in homogenous media would be a promising candidate for constructing the solid-state stimuli-responsive materials.

Figure 25

Except for our research, chiral boron complexes with tridentate ligands were reported and their properties were investigated. Harriman *et al.* synthesized enantiomerically-pure boron complexes through the condensation reaction with three components phenylboronic acid, aldehyde derivatives, and optically active *tert*-leucine (Figure 26) [174]. As the aldehyde derivatives, salicylaldehyde and 2-methylamino-benzaldehyde provided a N,O,O-chelate (**LB(O)** (**173**)) and N,N,O-chelate (**LB(N)** (**174**)) complexes, respectively. The single diastereomer was obtained from the reaction because the *cis*-formation was more stable than *trans*-formation due to the bulky *tert*-butyl group at leucine. Those complexes showed weak emission in 2-methyltetrahydrofuran ($\lambda_{\text{PL}} = 510 \text{ nm}$ and $\Phi_{\text{PL}} = 0.009$ for **173**, $\lambda_{\text{PL}} = 610 \text{ nm}$ and $\Phi_{\text{PL}} = 0.017$ for **174**) and the emission was gradually enhanced via cooling process. **174** is significantly more fluorescent when prepared

in the form of a thin film, cast with the CHCl_3 solution ($\lambda_{\text{PL}} = 600 \text{ nm}$, $\Phi_{\text{PL}} = 0.19 \pm 0.04$). This is also the AIE behavior from chiral boron complexes with a tridentate ligand and a solid-state CPL property should be expected. Pischel and Campaña groups reported CPL from enantiopure boronic acid-derived salicylidenehydrazones (BASHY) complexes. Salicylidenehydrazones were used as a tridentate ligand for constructing much more planar π -conjugated systems with intense emission even in solution ($\Phi_{\text{PL}} = 0.5 \sim 0.6$) with moderate CPL intensity ($g_{\text{CPL}} \sim 3 \sim 5 \times 10^{-4}$) [175]. The complexes have two six-membered rings around the boron atom, and therefore planarity and ligand strain strongly affect optical behaviors in solution and solid states. The field of CPL chemistry with the luminophores having stereogenic boron centers has been just started and achievement of increasing the value of g_{CPL} is strongly expected by constructing unique structures originating from boron complexes.

Figure 26

3.2.3. Design strategy for AIE and CIE-active molecules

We mentioned that structural strain around boron had a significant influence on the optical behavior in solution and solid states. Herein, we demonstrate the new design strategy for controlling ACQ and AIE molecules based on quinoline-based boron complexes [176]. We

synthesized two types of the quinoline-based boron complexes (Figure 27a). **BPhQ (175)** and **BPhQM (176)** were obtained from the tridentate quinoline ligand and the methylene-inserted one, respectively. The results of single-crystal X-ray diffraction analyses are shown in Figure 27b. **175** had a relatively distorted conformation ($\varphi = 154.7^\circ$) due to the tightly-fused structure composed of five and six membered rings around tetracoordinated boron. On the other hand, **176** had a relatively planar structure ($\varphi = 168.8^\circ$) because of the loosely-fused two six-membered rings by the inserted methylene group. **175** exhibited typical AIE and CIE properties ($\Phi_{\text{PL}} = 0.008$ in solution, $\Phi_{\text{PL}} = 0.014$ in aggregation, $\Phi_{\text{PL}} = 0.017$ in crystal). In contrast, **176** showed intense emission in solution and ACQ in solid ($\Phi_{\text{PL}} = 0.21$ in solution, $\Phi_{\text{PL}} = 0.072$ in aggregation, $\Phi_{\text{PL}} = 0.051$ in crystal). From the comparison of the crystal packing structures, the different optical behaviors were probably caused by the difference in molecular planarity between **175** and **176**. In **175**, continuous intermolecular π - π interactions were restricted by steric hindrance imposed by the distorted π -conjugated system (Figure 27b). Whereas, the high planarity of **176** induced densely packed molecular columns which formed continuous face-to-face π - π interactions. The results clearly showed that AIE and CIE or ACQ should be designed with or without structural distortion.

Figure 27

3.2.4. Highly-efficient film-state emission with AIE-active monomer

As a π -conjugated co-monomer for polymer synthesis, it is useful for introduction of long alkyl chains to improve solubility to common solvents. Therefore, we designed new boron complexes (BAmM) which had two six membered rings with two long alkyl chains at the methylene moiety [177]. The **BAmM** (**177**) showed weak emission in the dilute solution ($\Phi_{\text{PL}} = 0.016$) (Figure 28). The quantum efficiency was almost same degree with those of BAm derivatives with five and six membered rings around boron. Meanwhile, the emission efficiencies can be highly enhanced by constructing π -conjugated polymers with fluorene (**P-BAmM-Fl** (**178**): $\lambda_{\text{PL}} = 542$ nm, $\Phi_{\text{PL}} = 0.24$, 1.0×10^{-5} M in chloroform) and bithiophene (**P-BAmM-BT** (**179**): $\lambda_{\text{PL}} = 627$ nm, $\Phi_{\text{PL}} = 0.46$, 1.0×10^{-5} M in chloroform) (Figure 28). Surprisingly, the similar levels of emission efficiencies were detected even in the film state (**178**: $\Phi_{\text{PL}} = 0.29$, $\lambda_{\text{PL}} = 553$ nm; **179**: $\Phi_{\text{PL}} = 0.30$, $\lambda_{\text{PL}} = 637$ nm). In general, wide π -surfaces of π -conjugated polymers are unfavorable for obtaining solid-state emission due to ACQ caused by π - π interaction. The unique structure of BAmM composed of the perpendicularly protruded fluorine atom and two alkyl chains contributes to suppression of interchain π - π interactions in film state.

In addition, the alkyl chains at the boron complex and bithiophene units can play a significant role in enhancing film-state emission intensity [178]. Almost all donor-acceptor type π -

conjugated polymers from BAmM and bithiophene units with various lengths of alkyl chains showed highly-efficient emission in film in red to deep red regions. In particular, the polymer consisting of BAmM with two ethyl chains (C2) and bithiophene with two dodecyl chains (C12) exhibited clear stimuli-responsiveness accompanied by red-shifted emission during solvent vapor annealing processes. Those results indicate that the BAm unit has a potential to be a versatile “element-block” for realizing solid-state luminescent π -conjugated polymers including stimuli-responsiveness.

Figure 28

3.2.5. Bisboron complex for solid-state NIR emission

The effect of extension of π -conjugation on AIE and CIE properties was evaluated in BAm derivatives. To increase solubility and crystallinity, the BAmM scaffold with diphenyl substituents at the methylene chain was selected [179]. Monoboron complex (**monoBAmM (180)**) was obtained as racemic mixtures with two enantiomers, whereas bisboron complex (**bisBAmM (181)**) was synthesized as a mixture of diastereomers (*syn*- and *anti*-**181**) because of the two stereogenic boron centers (Figure 29). Fortunately, the diastereomers can be successfully separated with a reprecipitation method owing to solubility difference. Insoluble *anti*-**181** was

selectively reprecipitated into diethyl ether from the chloroform solution of mixture of the diastereomers. Afterwards, soluble **syn-181** was collected from the filtrate. Owing to the robust fully-fused structure of the bisboron complex, efficient emissions of **syn-** and **anti-181** in solution were observed in the NIR region ($\lambda_{\text{PL}} = 731 \text{ nm}$, $\Phi_{\text{PL}} = 0.035$ and $\lambda_{\text{PL}} = 729 \text{ nm}$, $\Phi_{\text{PL}} = 0.038$, $1.0 \times 10^{-5} \text{ M}$ in chloroform, respectively) with dramatical bathochromic shifts in the emission spectra from **180** ($\lambda_{\text{PL}} = 522 \text{ nm}$, $\Phi_{\text{PL}} = 0.003$, $1.0 \times 10^{-5} \text{ M}$ in chloroform). Furthermore, it was revealed that **181** inherited solid-state emissive properties in BAm derivatives having a perpendicularly-protruded substituent at boron. The solid-state NIR emissions of **syn-** and **anti-181** were measured to be $\lambda_{\text{PL}} = 757 \text{ nm}$ ($\Phi_{\text{PL}} = 0.035$) and $\lambda_{\text{PL}} = 745 \text{ nm}$ ($\Phi_{\text{PL}} = 0.052$), respectively, and especially *anti*-conformation showed a clear CIE behavior. It was proposed that three bulky phenyl groups around boron should effectively prevent the chromophore unit from π - π stacking, followed by ACQ.

Figure 29

3.2.6. Salicylaldehyde-based acylhydrazone

As described previous topics, boron complexes with the tridentate ligands have the potential to show AIE and CIE properties. The structural strain in the complexes plays a key role in

emission annihilation in solution as well as solid-state emission. Recently, Jia *et. al.* reported unique AIE properties of boron complexes with salicylaldehyde-based acylhydrazone [180]. The chemical structures are shown in Figure 30a. It is presumable that the scaffold could be relatively bent because of six and five membered rings around tetracoordinated boron. Two types of boron complexes, **DPDP (182)** and **DPDN (183)** having benzene and naphthalene moieties, respectively were synthesized. The PL spectra to investigate AIE features at good solvent (DMF) with incremental addition of poor solvent (H₂O) are shown in Figures 30b and 30c. The PL intensity of both dyes was weak in pure DMF. On the other hand, the intensity began to increase with a gradual increase of water content. As the water fraction (f_w) reached 40%, the intensity was elevated to the maximum for **182** ($\Phi_{PL} = 0.25$). In contrast, continuous increase of the water content from 40% to 90%, the emission spectra of **182** showed a distinct decrease in the intensity (ca. $\Phi_{PL} = 0.05$). The unique behavior having a peak top might be attributed to generation of ordered crystalline aggregates in middle water content and that of amorphous agglomerates with random stacking structure under water-rich situation. In addition, **182** and **183** showed solid-state emission with mechanochromism. The boron complex created by tridentate ligand with salicylaldehyde-based acylhydrazone should be a new candidate for a AIE or solid-state stimuli-responsive scaffold.

Figure 30

As other examples of boron complexes with tridentate ligands, the molecular rotor showing viscosity-dependent emission was reported from the dimer of BAm derivatives [181]. The molecular rotor is expected as a candidate for AIE or CIE-active molecule. BODIPY with tridentate ligand was also reported [182]. The complex showed intense emission in the solution state because of high planarity and rigidity of the BODIPY structure similarly to conventional complexes. In particular, the tridentate ligand-modified BODIPY showed solid-state emission despite the fact that conventional BODIPY dyes often show critical ACQ. It is presumed that the perpendicularly-protruded substituent might be effectively increase in solid-state emission by disturbing intermolecular motions.

In summary, we explained multiple functions of the tridentate ligand. Except for the above researches, we accomplished to develop unique polymers having light-absorption and emission in the NIR region, [183] and stimuli-responsiveness [184]. Moreover, by employing hypervalent tin atom, we obtained emission bands in much longer regions [185,186]. Thus, it can be said that the tridentate ligand should be a scaffold to design solid-state luminescent and stimuli responsive materials.

4.o-Carboranes

o-Carborane is another attractive boron-based compound with “flexible” character triggered by photoexcitation. In 2020, the comprehensive review about *o*-carborane-based AIEgens was published, focusing on their potential for stimuli-responsive materials [21]. Although only two years have passed after the review, there have been some important progresses in the development of *o*-carborane-based luminophore, especially in molecular design strategy and mechanistic insight. Here, we mainly treat the newly reported compounds not included in the previous review. We first summarize some novel scaffolds and concepts of *o*-carborane-based AIE-active molecules. Afterwards, several representative examples showing stimuli-responsivity are listed. Finally, recent works on the molecular motions including steric effect and C–C elongation are summarized, suggesting some mechanistic insights.

4.1. Survey of recent works

Recently, various novel *o*-carborane-tethered AIEgens based on tetraphenylethene,[187–190] perfluorophenyl,[191] imidazole,[192] and arylazide[193] have been reported (Figure 31, Table 10). Sha, Yan, Li, and coworkers reported a remarkable PL red-shift by introducing the electron-withdrawing substituent on the carbon atom in *o*-carborane (C_{cage}) [190]. Especially, **189** with pentafluorobenzene unit showed its PL peak at 678 nm in the solid state, retaining high Φ_{PL} value

(0.59).

In addition to surveying AIE-active scaffolds, some novel achievement and concept have also been demonstrated. Nuñez *et al.* reported efficient luminescence from water-dispersed nanoparticles [194]. “Remote effect” from the *o*-carborane unit,[195] excitation-wavelength dependent PL color,[196] clustering-triggered emission,[197] two-photon absorption,[198] thermally activated delayed fluorescence (TADF),[199] and excimer emission [200] were demonstrated, proving a great potential of *o*-carborane as advanced luminous materials.

Figure 31, Table 10

4.2. Stimuli-responsiveness

As summarized in the previous review,[21] *o*-carborane can induce environment-sensitivity to the tethered luminogens by wide variety of mechanisms (Figure 32, Table 11). For example, Peng and Fang *et al.* established the sensing system of volatile organic compounds (VOCs) utilizing the sensitivity for polarity of the ICT emission band [202]. *o*-Carborane is also widely known to react with nucleophiles, forming a deboronated cluster called as *nido*-carborane [203]. Utilizing this unique chemical reaction, fluorine sensors were developed based on carbazole [204].

Figure 32, Table 11

The ICT band of *o*-carborane-based luminophore is highly sensitive to surrounding temperature because of the following two reasons. First, an energy barrier between LE and ICT states prevents the excitons from reaching the ICT state at lower temperature. Second, larger structural relaxation is induced at higher temperature, resulting in longer PL wavelength. Guo *et al.* reported anthracene-tethered *o*-carborane derivatives showing thermochromic luminescence [205]. We developed several concepts for realizing thermochromic luminescence based on *o*-carboranes. Bis(thienylethynyl)benzene-substituted *o*-carborane was dispersed into amorphous polystyrene films and the change of LE/ICT ratio was observed by thermal annealing [206]. A different approach for modulating the LE/ICT ratio is the introduction of the intramolecular interaction site between *o*-carborane and aryl moiety [207]. More recently, the cooperative PL character of ICT and excimer emission was also achieved [208].

Mechanochromic luminescence is another attracting stimuli-responsiveness observed from limited numbers of solid-state luminescent materials. Generally, *o*-carborane has globular shape and few strong intermolecular interactive sites, resulting in a loose packing structure sensitive for external stimuli. Lu and Yan *et al.* developed polymorphs-dependent mechanochromic luminescence. When ground, one polymorph showed red-shift and another showed blue-shift in

PL spectra [209]. We reported a series of aryl-*o*-carboranes with an ethynylene spacer unit. They all showed a mechanochromic property, and especially, **228** had two-step color change by different mechanical stimuli [210].

Fang *et al* developed sensing devices that trace the change in PL character. *o*-Carborane-based alkynyl-gold(III) complex showed highly selective ketone sensing with great repeatability [211]. They also constructed a trichloroacetic acid sensing system based on the intramolecular hydrogen bond [212].

4.3. Mechanistic insight

Although *o*-carborane-based emitters are vigorously investigated, the detailed relationship between a chemical structure and a PL efficiency is still unclear. As the last topic, the recent works related with mechanistic insights are summarized (Figure 33, Table 12).

Figure 33, Table 12

Lee *et al.* have systematically investigated the effect of substitution position based on regioisomers of pyrene,[213] spiro[acridine-fluorene],[214] and fluorene [215]. Those works showed that the structurally more fluctuated isomer tends to emit more efficiently. They also

pointed out the effect of the (1) dihedral angle between the *o*-carboranyl appended aryl plane and the bonding axis of the *o*-carborane cage (Ψ) [216,217] and (2) electronic state [218,219] based on the substitution position. In addition to the investigation about the steric effect just around the carbon-carbon bonds in *o*-carborane, various works treated planarity [220,221] and substituent effect [222–224] on the aryl group itself. Totally, these works showed the importance of the geometric effect in the *o*-carborane-relating photophysical events.

Finally, the precisely-designed works investigating the dynamics in the photophysical events are briefly summarized. We reported two types of biphenyl-substituted *o*-carboranes in which the neighboring carbon and boron atoms of *o*-carborane are fused by a biphenyl ring [225]. The allowed structural relaxation is only the elongation of l_{C-C} in the structure, and the AIE phenomenon was observed in both compounds. Thus, PL annihilation through the C–C elongation can be experimentally proved. More recently, the importance of C–C elongation was also explored by computational methods. Ji, Curchod, Lambert, Marder and coworkers conducted comprehensive investigation of 1-(pyren-2'-yl)-*o*-carborane and mainly focused on the thermodynamic equilibrium character between LE and CT states [226]. In the research, they pointed out the third optimized structure with large l_{C-C} (2.62 Å) in addition to LE (1.63 Å) and CT (2.34 Å) geometry at S_1 states with prohibited transition character ($f = 0.0000$). Alkan *et al.* also found the “dark” state of the anthracene-tethered system [227]. In addition to the dynamics

around the C–C bond, they simultaneously investigated the effect of the dihedral angle Ψ and correlated the geometry and the electronic character at the S_1 state. Geng, Su, and coworkers computationally investigated the thermochromic behavior and substituent effect based on the anthracene-based compounds, pointing out the relevance between l_{C-C} and the PL property [228]. Thus, exploration about molecular motions at the S_1 state have gradually been achieved in these two years and should bring fruitful insight into the field of *o*-caraborane-based AIE-active molecules.

5. Perspective

We introduced applications of AIE-active boron compounds as a platform for developing stimuli-responsive luminochromic materials. One of next steps for creating advance functional luminescent materials should be to realize much complicated stimuli-responsiveness. In the above examples, such as mechano-, vapo- and thermochromic luminescent materials, molecular environmental alterations play a key role in luminochromic behaviors. Meanwhile, boron intrinsically has unique reactivity and electronic properties. From this viewpoint, tricoordinate boron complexes are a potential scaffold for coexisting environmental sensitivity and elemental properties. According to the recent reports, AIE-active molecules containing the tricoordinate boron have been discovered [229]. In these compounds, boron mainly works as an electron

acceptor unit. Although it is still challenging to stabilize the tricoordinate state of boron and utilize it as a robust material [16], highly-sensitive and multi-responsive properties are expectable from the tricoordinate boron compounds.

6. Conclusion

We herein survey recent studies of AIE-active boron compounds. Particularly, we mainly explain the mechanism on AIE behaviors of these boron compounds. Basically, in order to obtain intense emission from organic molecules, molecular motions should be suppressed as much as possible. Indeed, boron complexation is regarded as an attractive candidate for obtaining luminescent dyes because of molecular rigidity. In contrast, by introducing weak dative bonds to boron and distortion into boron-containing conjugated system, AIE behaviors can be realized. In the case of *o*-carborane dyads and triads, excitation-driven bond extension in the cluster unit should be responsible for emission annihilation in solution in AIE behaviors. These results mean that if we can appropriately control molecular motions in the excited state, which were the major processes for excitation deactivation, unique stimuli-responsiveness can be obtained. These properties are applicable for constructing superior sensors and molecular probes with much higher sensitivity than conventional materials originating from environmental sensitivity of excited molecules. Thus, we can say that such “flexible” boron compounds are promising platforms for

realizing advanced sensing technologies.

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6. References

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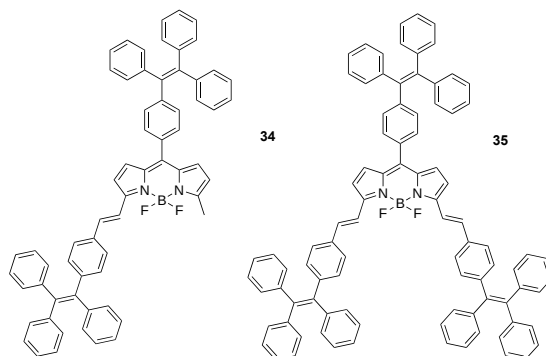
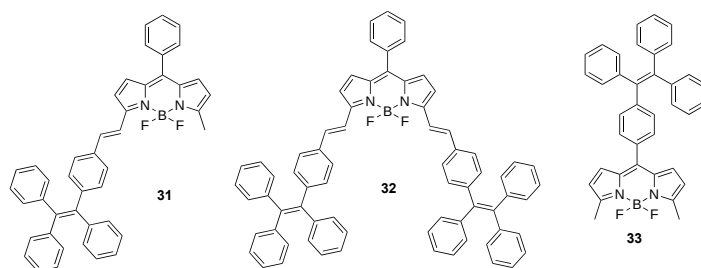
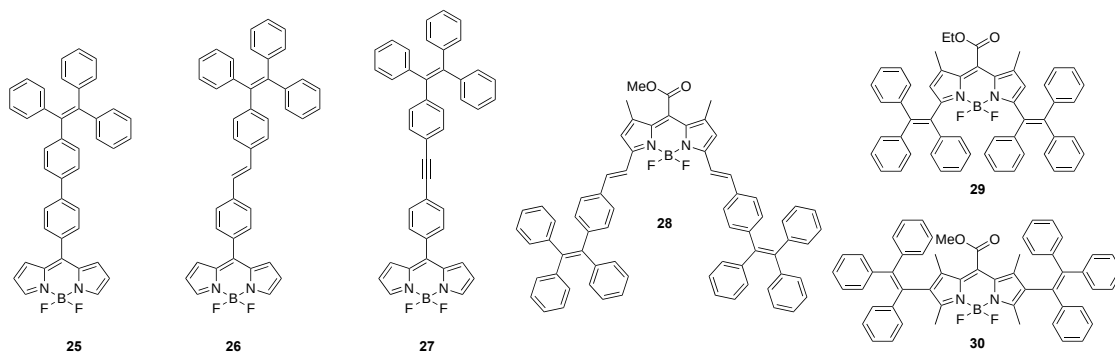
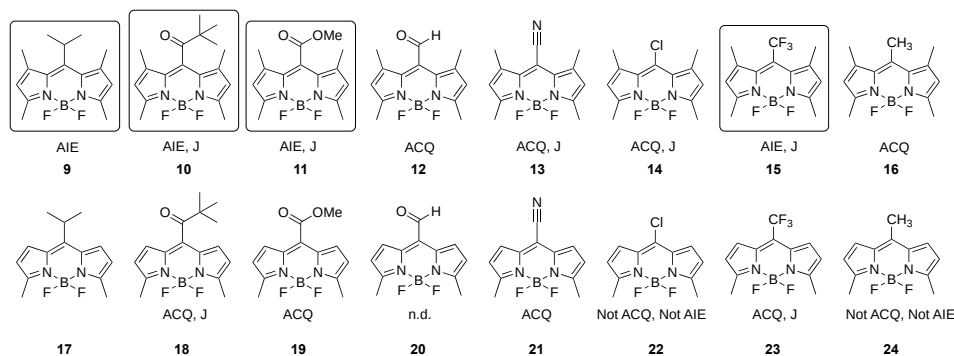
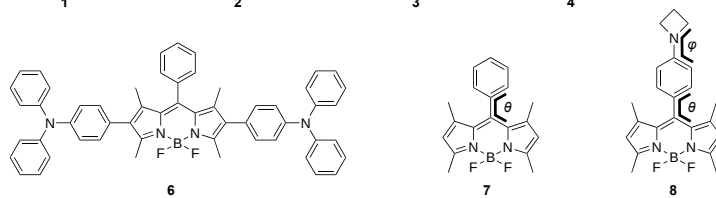
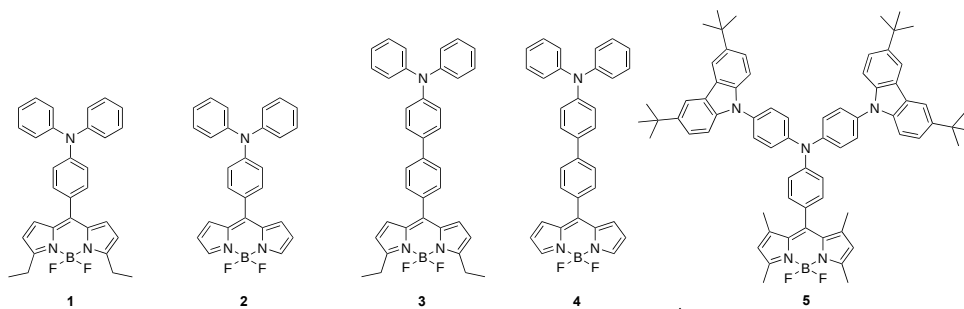


Figure 1. Chemical structures of BODIPY-based AIE-active complexes and related ACQ-dyes. "J" denotes J-aggregation.

Table 1. Photophysical properties of BODIPY-based AIE-active boron complexes and related

ACQ-dyes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
1	663	0.061	643	—	[49]
2	—	—	—	—	
3	688	0.011	658	—	
4	—	—	—	—	
5	520, 656	—	633	—	[50]
6	412, 668	0.003	665	—	[51]
8	—	—	~600	0.11	[52]
9	545	0.014	557		[62]
10	544	0.007	594		
11	543	0.005	587		
12	545	0.002	—		
13	585	0.50	579, 637		[62,63]
14	527	0.51	573		
15	622	0.008	625	0.06	
16	520	1.0	—	—	
17	528	0.90	522		[62]
18	600	0.52	~600		
19	604	0.44	601		
20	632	0.34	—		
21	586	0.60	584		
22	535	0.84	530		
23	564	0.94	~555		
24	526	0.99	~525		
25	524, 650	0.002	618	0.050	[70]
26	640	0.003	640	0.270	
27	529	0.001	600	0.075	
28	691	0.047	—	0.0020	[71]
29	697	0.064	—	0.0232	

30	630	0.0031	~650	0.039	
31	610	0.746	~625	0.017	[72]
32	690	0.420	~720	0.013	
33	530, 620	0.038	530, 616	0.489	
34	612	0.619	~700	0.015	
35	685	0.503	—	0.007	

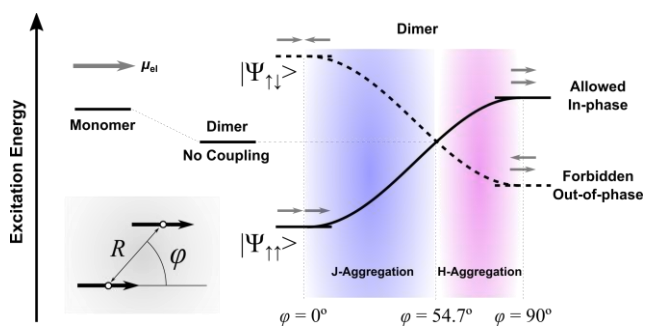


Figure 3. Schematic representation of exciton couplings in a dimer.

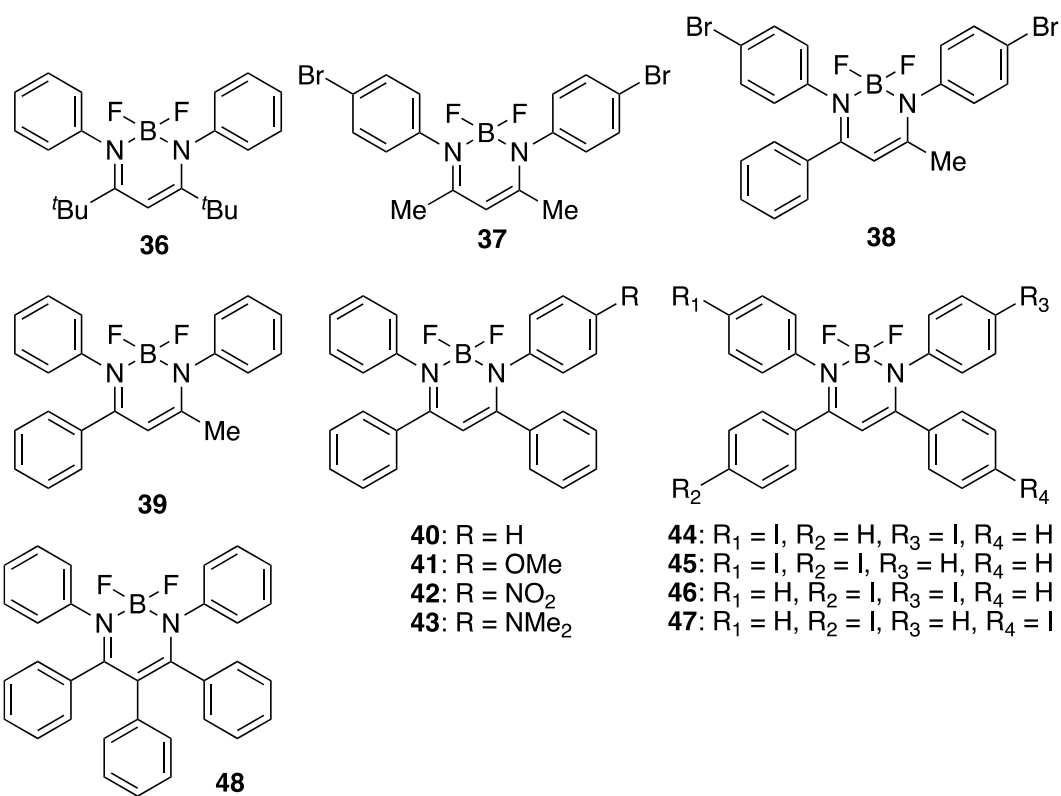


Figure 4. Chemical structures of β -diketiminato-based boron complexes

Table 2. Photophysical properties of β -diketiminato-based boron complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
36	365	—	—	—	[76]
37	419	—	—	—	
38	440, 470	—	399	—	
39	—	< 0.01	448	0.11	[77,78]
40	—	< 0.01	473	0.49	
41	—	< 0.01	470	0.59	
42	—	< 0.01	509	0.04	
43	—	< 0.01	602	0.08	
44	473	< 0.01	474	0.04	[79]
45	480	< 0.01	490	0.04	
46	480	< 0.01	489	0.04	
47	478	< 0.01	495	0.04	
48	465	< 0.01	443	0.66	[80]

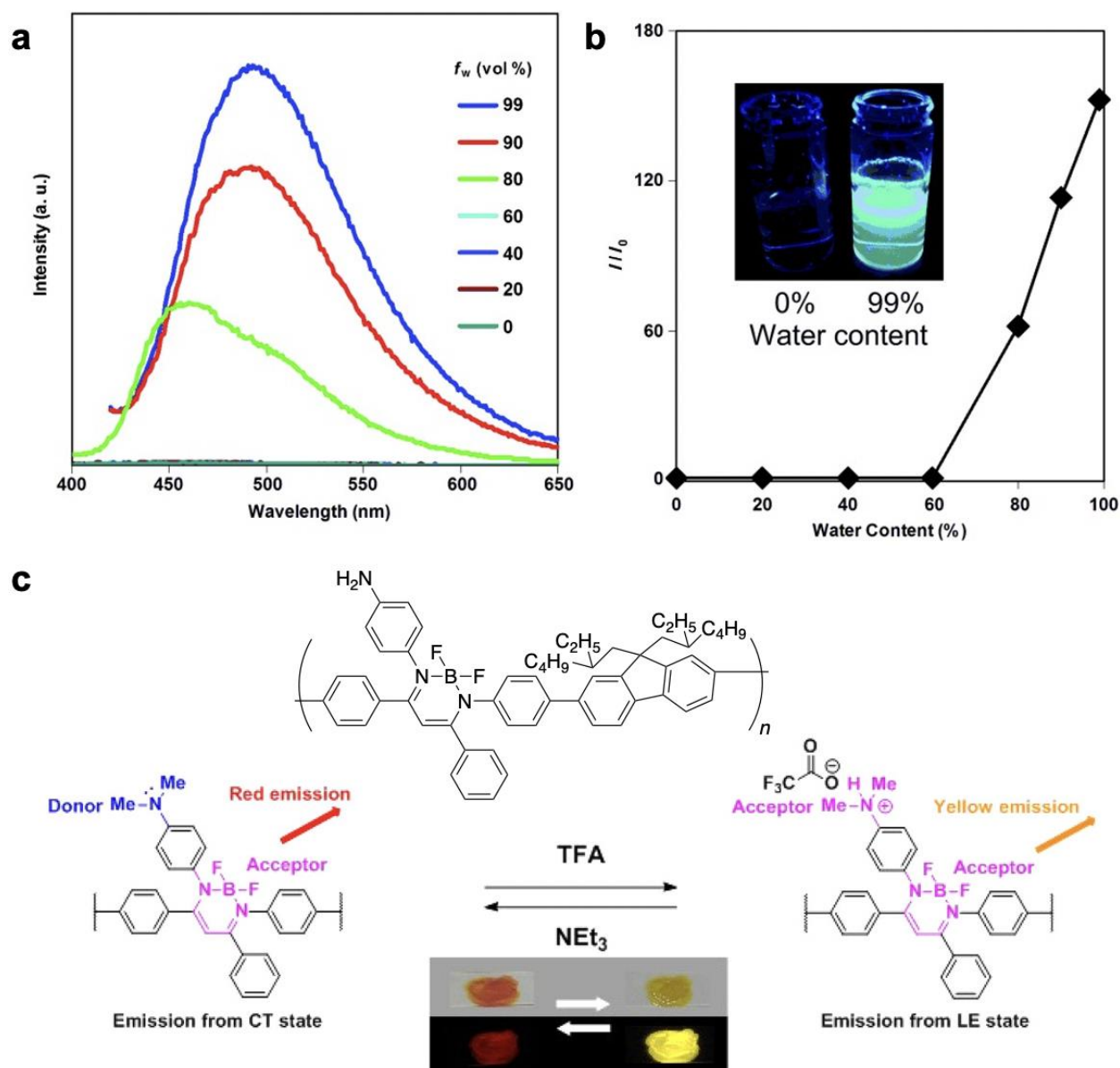


Figure 5. (a) Photoluminescence spectra of **40** in acetonitrile/H₂O mixture (5×10^{-5} M) with different fraction of water (f_w). (b) Photoluminescence intensity ratio of **40** relative to $f_w = 0\%$. (c) Selected example of a stimuli-responsive fluorescent film sensor composed of a conjugated polymer of a β -diketiminato complex. TFA: trifluoroacetic acid. (a,b) Reprinted with permission from ref [77]. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Reprinted with permission from ref [78]. Copyright 2014 American Chemical Society.

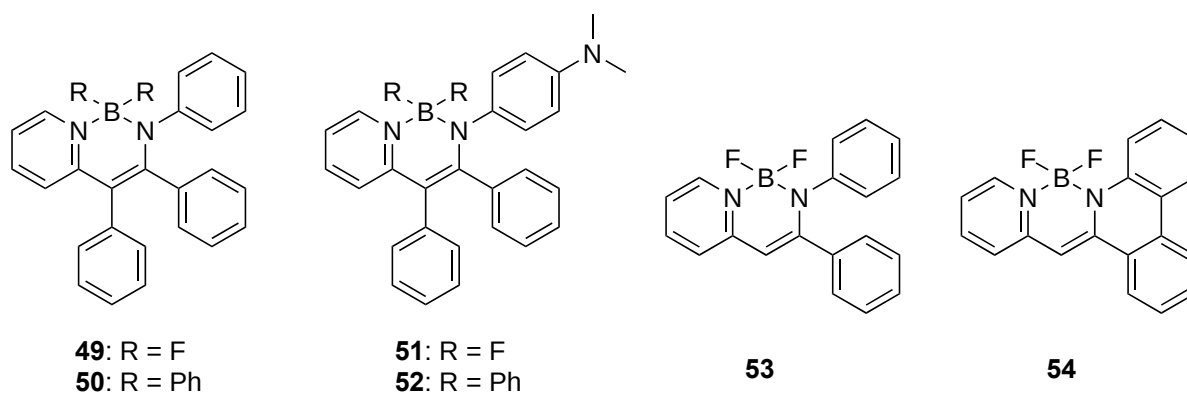


Figure 6. Chemical structures of pyridylenamine-based AIE-active boron complexes.

Table 3. Photophysical properties of pyridylenamine-based boron complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
49	471	0.004	481	0.12	[88]
50	464	0.013	534	0.20	
51	522	0.015	538	0.26	
52	513	0.038	577	0.10	
53	464	0.01	497	0.58	[89]
54	491	0.69	560	0.07	

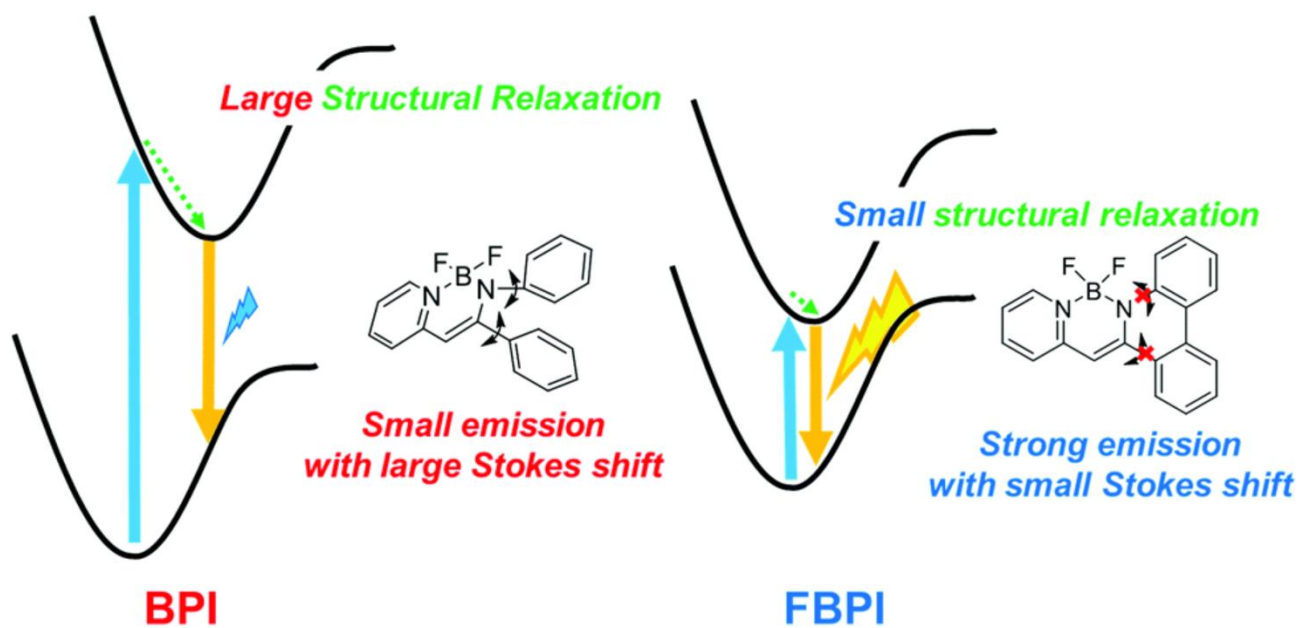


Figure 7. Mechanism of switching between AIE for **53** (BPI) and ACQ for **54** (FBPI) of pyridylenamide complexes. Reprinted with permission from ref [89]. Copyright 2017 Royal Chemical Society.

Table 4. Photophysical properties of hydrazone-based boron complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
55	538	0.07	525	0.20	[102]
56	512	0.06	497	0.52	
57	497	0.04	508	0.19	
58	506	0.04	491	0.05	
59	545	0.03	515	0.06	
60	636	—	—	—	[103]
61	488	—	—	—	[103]
62	500	—	—	—	
63	493	0.013	—	—	
64	505	—	—	—	
65	551	—	—	—	
66	552	—	—	—	
67	547	< 0.01	525	0.18	[105]
68	550	< 0.01	568	0.05	
69	577	< 0.01	578	0.01	
70	517	0.01	548	0.13	
71	561	0.05	572	0.05	
72	557	0.01	562	0.03	[108]
73	586	< 0.01	592	0.02	
74	533	0.02	539	0.02	
75	583	< 0.01	580	0.02	

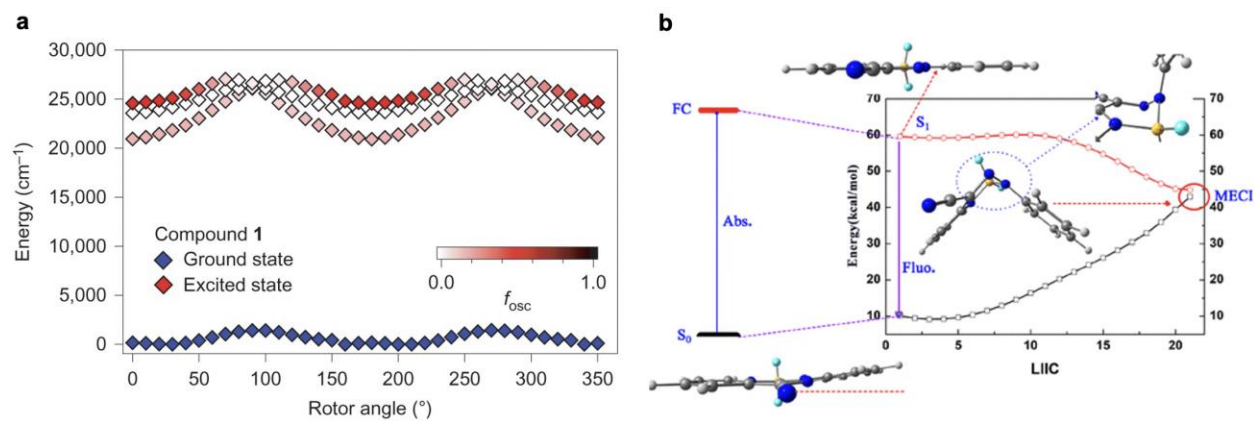


Figure 9. Proposed mechanisms of AIE behavior of BODIHYs. (a) Potential energy surfaces of S_0 – S_3 states of compound **56**. f_{osc} represents oscillator strength. Reprinted with permission from ref [103]. Copyright 2016 Nature Publishing Group. (b) Linearly interpolated internal coordinate (LIIC) from the S_1 geometry to a minimal energy conical intersection (MECI) of compound **56**. Reprinted with permission from ref [106]. Copyright 2019 American Chemical Society.

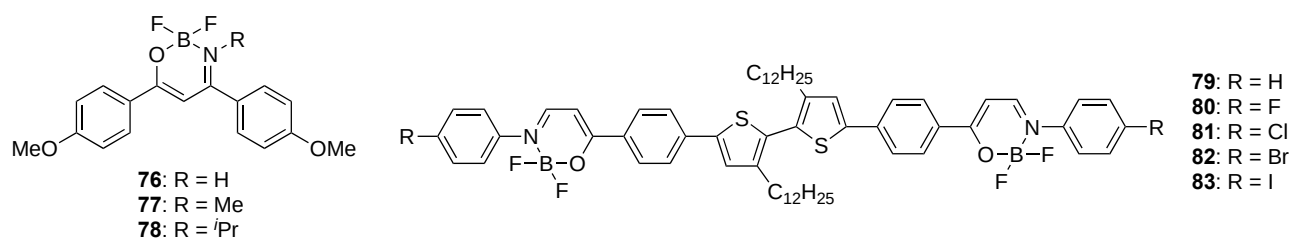


Figure 10. Selected AIE-active boron complexes based on β -diketoiminate ligands.

Table 5. Photophysical properties of AIE-active boron complexes based on β -ketoiminate ligands

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
76	426	0.01	471	0.76	[112]
77	424	< 0.01	470	0.42	
78	425	< 0.01	443	0.30	
79	564	0.35	619	0.33	[113]
80	565	0.34	626	0.42	
81	572	0.39	635	0.48	
82	578	0.40	639	0.47	
83	578	0.39	656	0.29	

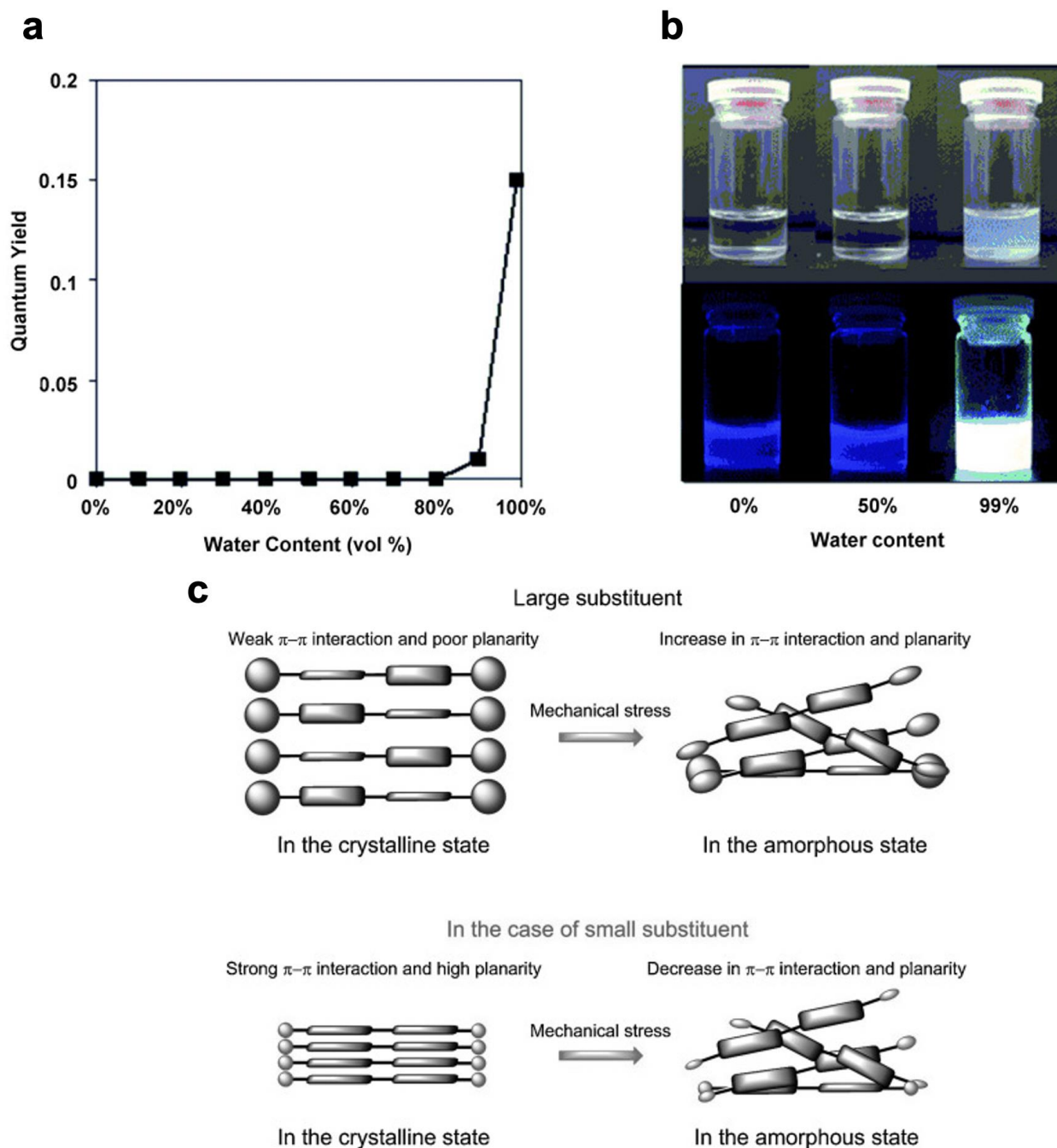


Figure 11. (a) Dependency of photoluminescent quantum yield of compound **76** on the water content of THF/water mixtures. (b) Photograph of compound **76** in THF/water mixtures with different compositions. Reprinted with permission from ref [112]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Proposed mechanism of the shift-direction dependency of mechanochromic luminescence on the substituents of compounds **79–83**. Reprinted with permission from ref [113]. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

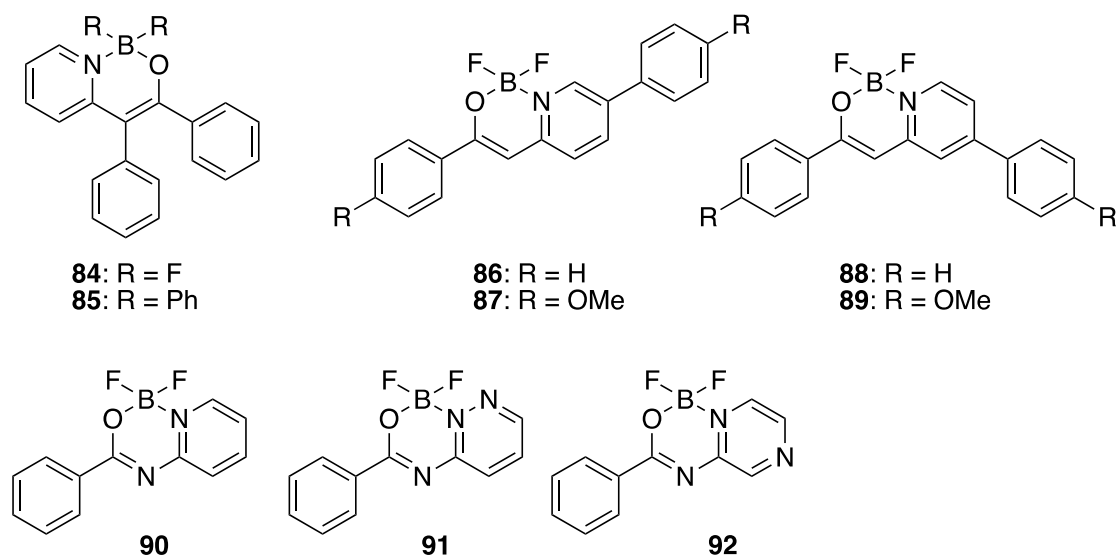


Figure 12. Chemical structures of pyridylenolate-based boron complexes.

Table 6. Photophysical properties of pyridylenolate-based complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
93	450	< 0.01	460	0.53	[117]
94	471	< 0.01	494	0.46	
95	450	0.17	497	0.25	[118]
96	468	0.58	488	0.68	
97	460	0.35	543	0.38	
98	463	0.80	500	0.81	
99	—	—	415	0.66	[119]
100	392	0.05	397	0.18	
101	403	0.13	426	0.16	

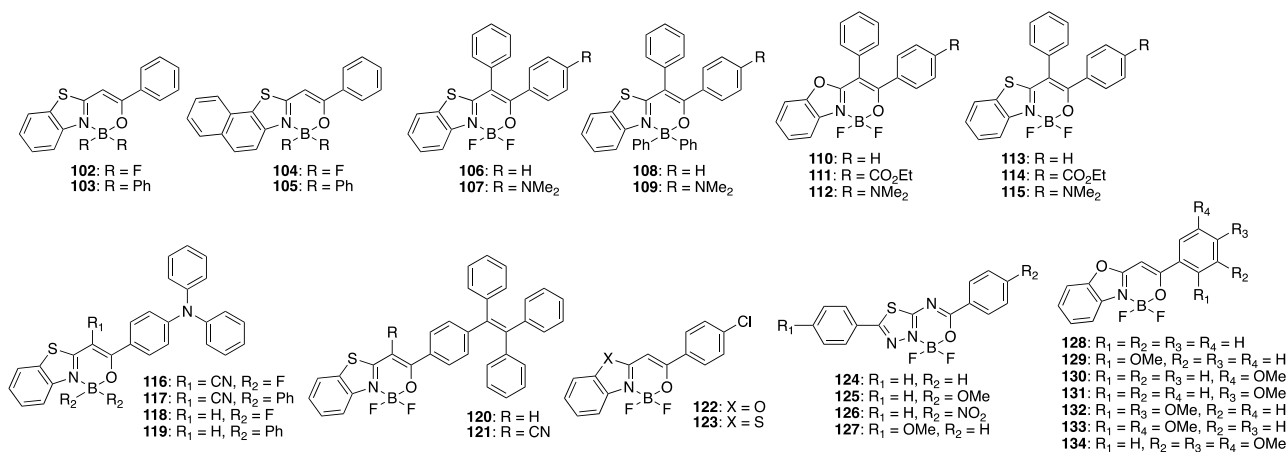


Figure 13. Chemical structures of boron complexes with azole-based N,O-ligands.

Table 7. Photophysical properties of azole-based N,O-ligand complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
102	440	< 0.01	495	0.26	[122]
103	499	0.41	503	0.60	
104	459	0.04	508	0.23	
105	510	0.49	527	0.50	
106	449	< 0.01	519	0.18	[123]
107	512	< 0.01	567	0.43	
108	473	< 0.01	524	0.23	
109	510	< 0.01	562	0.14	
110	389	0.013	494	0.061	[124]
111	400	0.011	540	0.048	
112	476	0.011	505	0.154	
113	446	0.014	499	0.065	
114	482	0.011	535	0.056	
115	507	0.010	531	0.142	
116	596	0.026	580	0.86	[125]
117	564	0.142	~550	0.79	
118	526	0.420	~530	0.37	
119	506	0.475	~500	0.55	
120	508	0.004	513	0.2355	[126]
121	565	0.003	553	0.2082	
122	439	0.04	447	0.24	[127]
123	454	0.08	460	0.20	
124	410	0.06	429	—	[128]
125	414	0.29	446	—	
126	409	< 0.01	—	—	
127	436	0.16	456	—	
128	425	0.01	468	—	[129]
129	425	0.01	436, 459	—	
130	427	0.01	471	—	
131	430	0.02	480, 550	—	

132	431	0.03	476	—
133	453	0.08	476	—
134	442	0.04	500	—

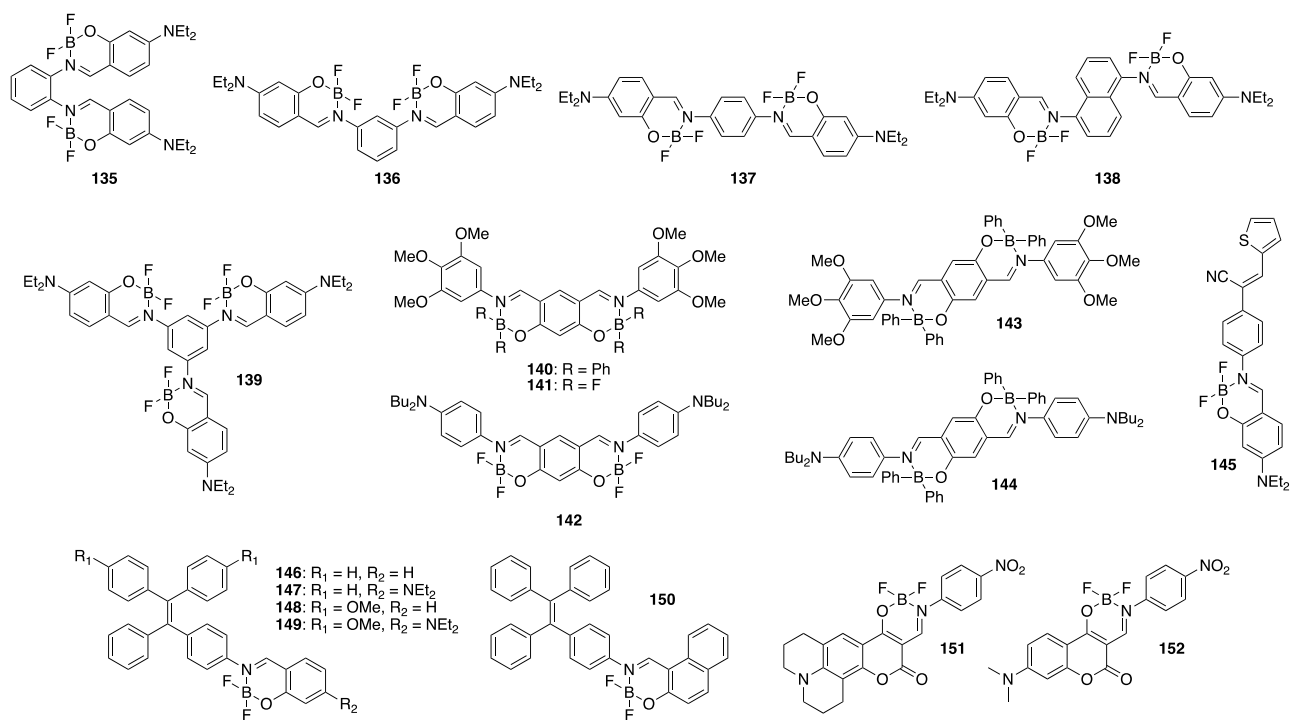


Figure 14. Chemical structures of boron complexes with boranil-based N,O-ligands.

Table 8. Photophysical properties of boranil-based N,O-ligand complexes

	λ_{em} (solution) / nm	Φ_{PL} (solution)	λ_{em} (aggregation) / nm	Φ_{PL} (aggregation)	ref.
135	–		601	0.05	
136	457	0.43	525	0.10	
137	507	0.78	560	0.22	
138	474	0.12	588	0.05	
139	460	0.49	534	0.07	
140	558	0.09	541	0.18	[130]
141	556	0.04	–	–	
142	571	0.35	642	0.10	
143	–	–	720	0.30	
144	665	0.31	789	–	
145	486	0.26	542	0.33	[131]
146	640	–	–	ACQ	
147	525	0.35	–	ACQ	
148	515	0.22	–	AIE	[132]
149	610	0.53	–	AIE	
150	586	0.08	571	AIE	[133]
151	565	< 0.01	647	0.137	
152	545	< 0.01	620	0.153	[134]

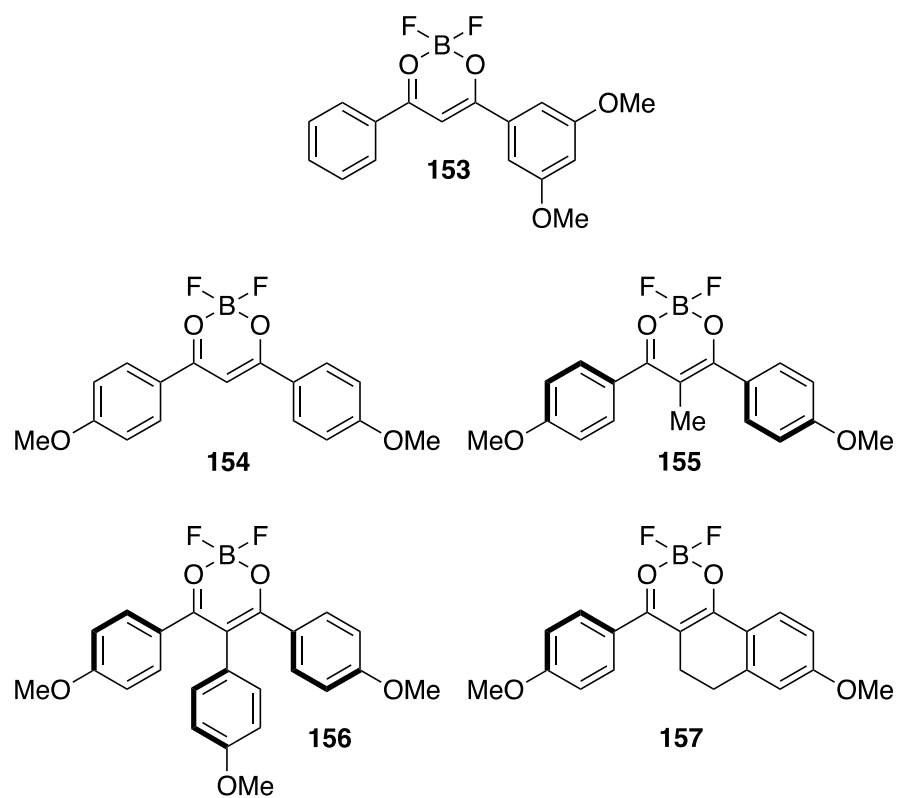


Figure 15. Chemical structures of selected β -diketonate boron complexes.

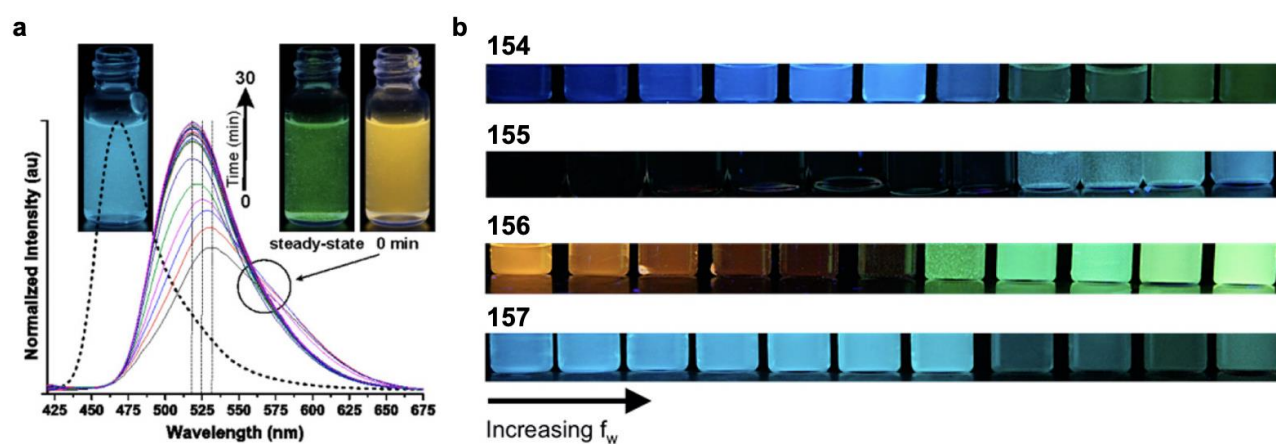


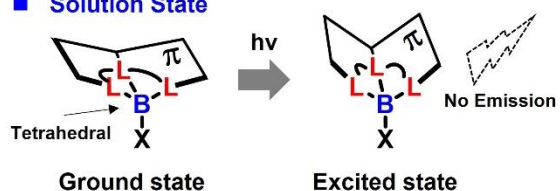
Figure 16. (a) Emission color dependence of compound **153** on the way of aggregation formation in CH₃CN/water mixtures. Reprinted with permission from ref [136]. Copyright 2014 American Chemical Society. (b) AIE and ACQ behavior of compounds **154–157** with increasing water fraction (f_w) in DMSO/water mixtures. Reprinted with permission from ref [137]. Copyright 2016 American Chemical Society.

Table 9. Optical properties of boron complexes with tridentate ligands displaying AIE or CIE

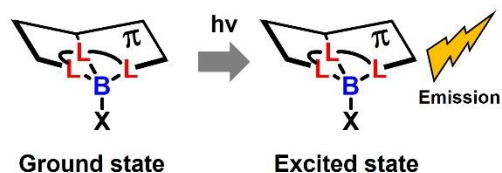
Cmpd.	$\lambda_{\text{PL,solution}}/\text{nm}$	$\Phi_{\text{PL,solution}}$	$\lambda_{\text{PL,AIE}}/\text{nm}$	$\Phi_{\text{PL,AIE}}$	Ref.
158	619	<0.01	603	0.023	[157]
159	621	<0.01	645	0.07	[159]
160	636	<0.01	674	0.02	[158]
161	654	<0.01	637	0.06	[159]
162	644	<0.01	613	0.02	[159]
163	688	<0.01	644	0.02	[159]
164	635	<0.01	659	0.12	[160]
165	628	<0.01	644	0.07	[160]
166	651	<0.01	662	0.02	[160]
167	616	—	615	—	[161]
168	589	<0.01	641	<0.01	[162]
anti-169	588, 624	0.05	651	0.03	[162]
syn-169	590, 624	0.05	649	0.02	[162]
anti-170	674, 722	0.03	756	0.02	[162]
syn-170	675, 722	0.04	755	0.02	[162]
171	510	0.001	540 ^[a] , 549 ^[a]	0.39 ^[a] , 0.34 ^[a]	[166]
rac-172	526	0.002	585 ^[a]	0.37 ^[a]	[171]
(R)-172	526	0.002	568 ^[a]	0.29 ^[a]	[171]
173	510	0.009	—	—	[174]
174	610	0.017	600	0.19±0.04	[174]
175	550	0.008	537	0.014	[176]
176	493	0.21	460	0.072	[176]
177	473	0.016	—	—	[177]
178	542	0.24	553 ^[b]	0.29 ^[b]	[177]
179	627	0.46	637 ^[b]	0.30 ^[b]	[177]
180	522	0.003	551 ^[a]	0.007 ^[a]	[179]
anti-181	729	0.038	745 ^[a]	0.052 ^[a]	[179]
syn-181	731	0.035	757 ^[a]	0.035 ^[a]	[179]
182	466	—	476	0.25	[180]
183	516	—	527	—	[180]

^[a] in crystalline state. ^[b] in film state.

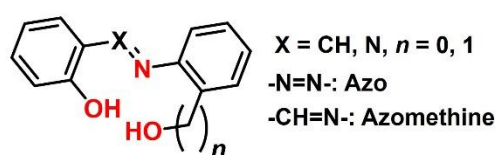
■ Solution State



■ Aggregated or Solid States



■ Tridentate Ligand for AIE or CIE



2,2'-Dihydroxyazobenzene ($X = \text{N}, n = 0$)

o-Salicylideneaminophenol ($X = \text{CH}, n = 0$)

Figure 17. Structural features of a π -conjugated system with a boron-fused tridentate ligand for AIE and CIE-active molecules.

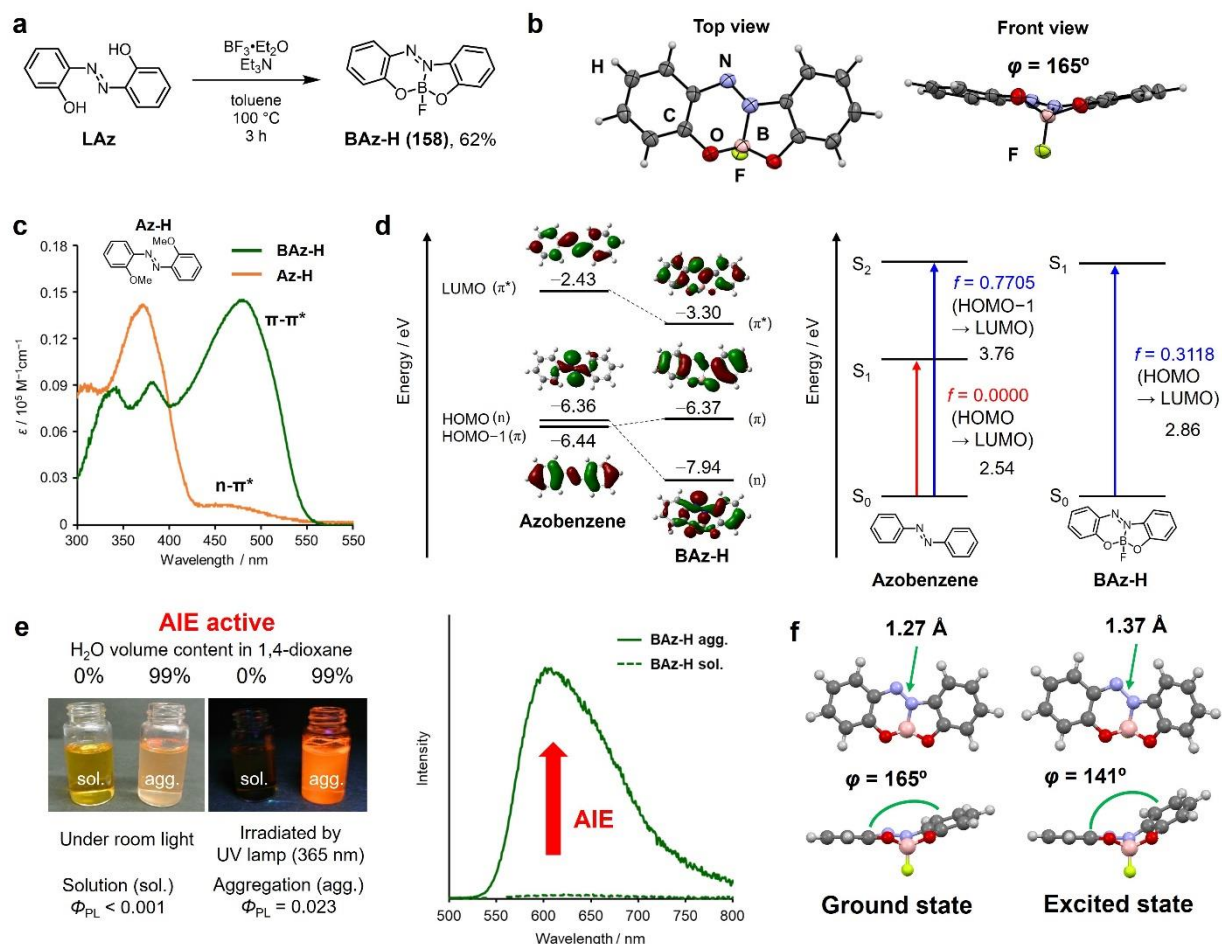


Figure 18. The features of **BAz-H (158)**. (a) Synthesis of **BAz-H** from **LAz**. (b) ORTEP drawings of **BAz-H** from results of single crystal X-ray structural analysis. (c) UV-vis absorption spectra of **BAz-H** and **Az-H** in toluene (1.0×10^{-5} M). (d) Energy diagram and selected MOs of azobenzene and **BAz-H** with TD-DFT calculation. (e) AIE properties of **BAz-H**. (f) Optimized structures in the ground and excited states of **BAz-H** with DFT and TD-DFT calculations, respectively. Reprinted with permission from ref 148. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

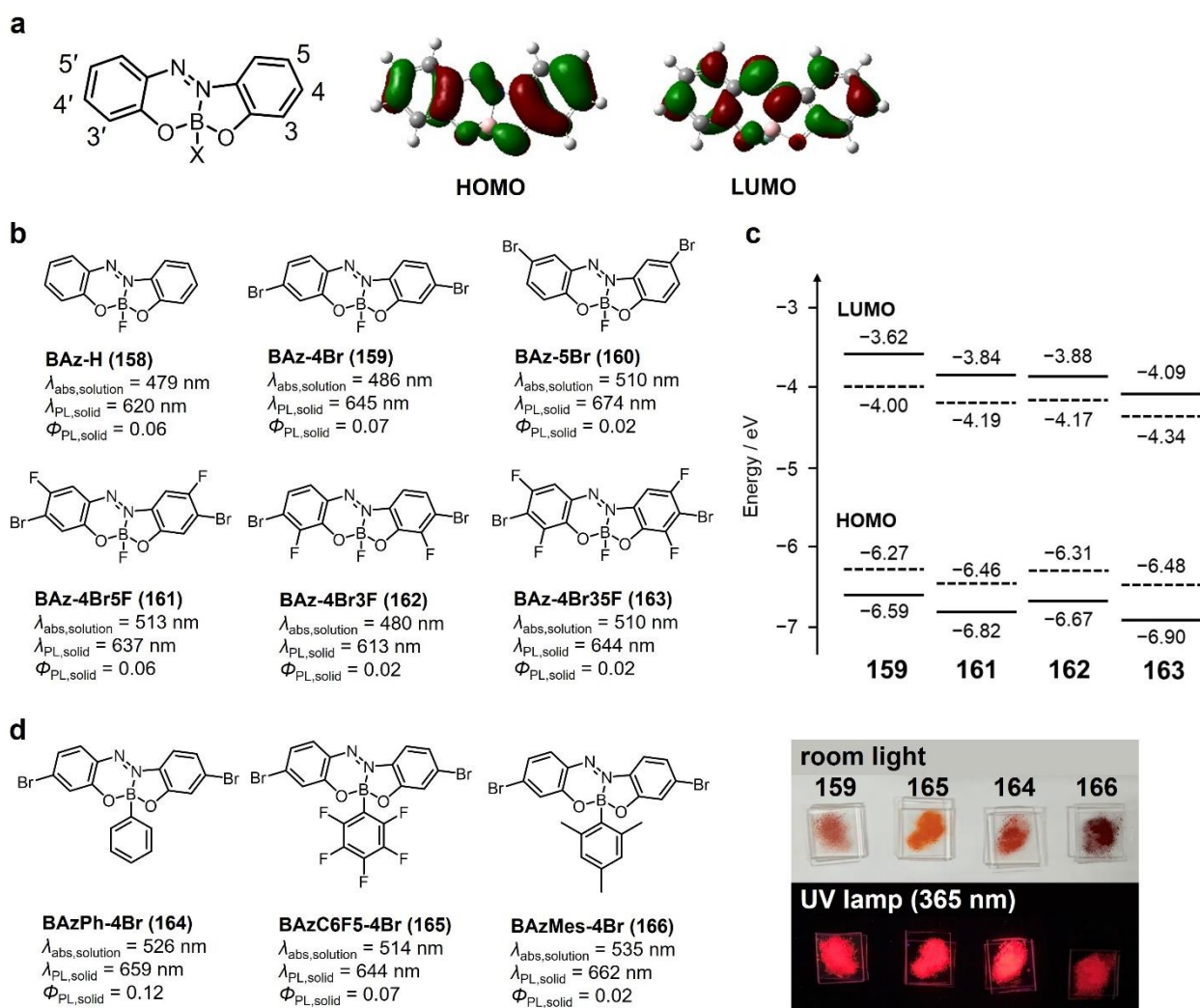
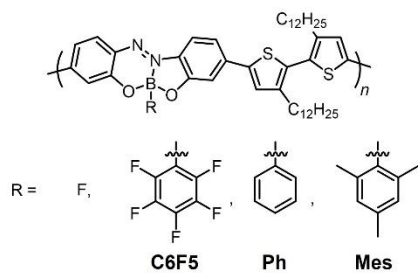


Figure 19. (a) Conventional name of substituent positions and HOMO and LUMO of **BAz-H** with DFT calculation. (b) Substituent effect and optical properties of BAZ derivatives. (c) Energy diagrams of BAZ derivatives (solid line: from DFT calculation, dotted line: from cyclic voltammetry and UV-vis absorption spectra) (d) Substituent effect, optical properties and the photograph of BAZ derivatives under room light (upper) and 365 nm UV lamp (lower). Reprinted with permission from ref 149. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted with permission from ref 150. Copyright 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted with permission from ref 160. Copyright 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



■ Solution

P-BAz	P-BAzPh	P-BAzC6F5	P-BAzMes
R = F	R = Ph	R = C6F5	R = Mes
$\lambda_{\text{abs}} = 632 \text{ nm}$	$\lambda_{\text{abs}} = 646 \text{ nm}$	$\lambda_{\text{abs}} = 651 \text{ nm}$	$\lambda_{\text{abs}} = 653 \text{ nm}$
$\lambda_{\text{PL}} = 751 \text{ nm}$	$\lambda_{\text{PL}} = 742 \text{ nm}$	$\lambda_{\text{PL}} = 767 \text{ nm}$	$\lambda_{\text{PL}} = 736 \text{ nm}$
$\Phi_{\text{PL}} = 0.25$	$\Phi_{\text{PL}} = 0.15$	$\Phi_{\text{PL}} = 0.14$	$\Phi_{\text{PL}} = 0.04$

■ Film

P-BAz	P-BAzPh	P-BAzC6F5	P-BAzMes
R = F	R = Ph	R = C6F5	R = Mes
$\lambda_{\text{abs}} = 661 \text{ nm}$	$\lambda_{\text{abs}} = 662 \text{ nm}$	$\lambda_{\text{abs}} = 665 \text{ nm}$	$\lambda_{\text{abs}} = 668 \text{ nm}$
$\lambda_{\text{PL}} = 818 \text{ nm}$	$\lambda_{\text{PL}} = 793 \text{ nm}$	$\lambda_{\text{PL}} = 814 \text{ nm}$	$\lambda_{\text{PL}} = 787 \text{ nm}$
$\Phi_{\text{PL}} = 0.04$	$\Phi_{\text{PL}} = 0.09$	$\Phi_{\text{PL}} = 0.06$	$\Phi_{\text{PL}} = 0.05$

Figure 20. Chemical structures and optical properties of BAz polymers in solution (1.0×10^{-5} M per repeating unit in toluene) and film states. ref 149.

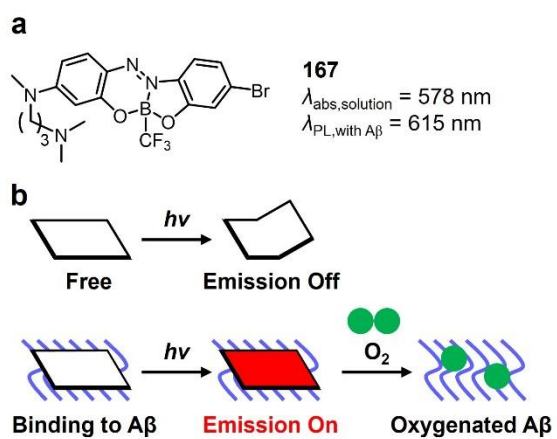
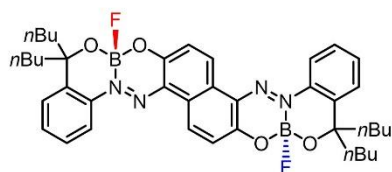


Figure 21. (a) Chemical structure and optical properties of photocatalyst. (b) Strategy of a photooxygenation catalyst. ref 161.



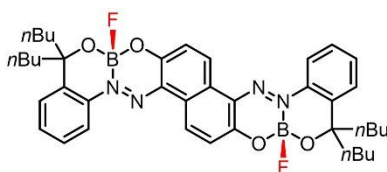
monoBAzM (168)

$\lambda_{\text{abs, solution}} = 500, 530 \text{ nm}$
 $\lambda_{\text{PL, aggregation}} = 641 \text{ nm}, \lambda_{\text{PL, crystal}} = 655 \text{ nm}$
 $\Phi_{\text{PL, solution}} < 0.01, \Phi_{\text{PL, aggregation}} < 0.01, \Phi_{\text{PL, crystal}} < 0.01$
 $\Phi_{\text{PL, solution, 77K}} = 0.77, \Phi_{\text{PL, solution, viscous}} = 0.01$



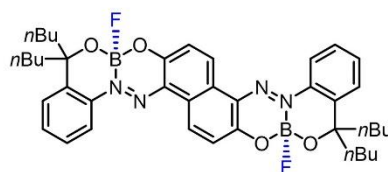
anti-bisBAzM-n (anti-169)

$\lambda_{\text{abs, solution}} = 532, 570 \text{ nm}$
 $\lambda_{\text{PL, aggregation}} = 651 \text{ nm}, \lambda_{\text{PL, crystal}} = 643 \text{ nm}$
 $\Phi_{\text{PL, solution}} = 0.05, \Phi_{\text{PL, aggregation}} = 0.03, \Phi_{\text{PL, crystal}} = 0.06$



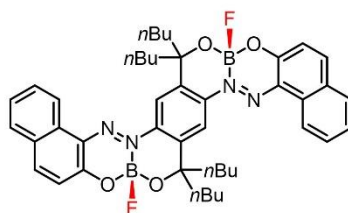
syn-bisBAzM-n (syn-169)

$\lambda_{\text{abs, solution}} = 532, 570 \text{ nm}$
 $\lambda_{\text{PL, aggregation}} = 649 \text{ nm}, \lambda_{\text{PL, crystal}} = 669 \text{ nm}$
 $\Phi_{\text{PL, solution}} = 0.05, \Phi_{\text{PL, aggregation}} = 0.02, \Phi_{\text{PL, crystal}} = 0.03$



anti-bisBAzM-b (anti-170)

$\lambda_{\text{abs, solution}} = 600, 642 \text{ nm}$
 $\lambda_{\text{PL, aggregation}} = 756 \text{ nm}, \lambda_{\text{PL, crystal}} = 783 \text{ nm}$
 $\Phi_{\text{PL, solution}} = 0.03, \Phi_{\text{PL, aggregation}} = 0.02, \Phi_{\text{PL, crystal}} = 0.09$



syn-bisBAzM-b (syn-170)

$\lambda_{\text{abs, solution}} = 600, 642 \text{ nm}$
 $\lambda_{\text{PL, aggregation}} = 755 \text{ nm}, \lambda_{\text{PL, crystal}} = 767 \text{ nm}$
 $\Phi_{\text{PL, solution}} = 0.03, \Phi_{\text{PL, aggregation}} = 0.02, \Phi_{\text{PL, crystal}} = 0.02$

Figure 22. Chemical structure and optical properties of monoBAzM and bisBAzM derivatives. ref 162.

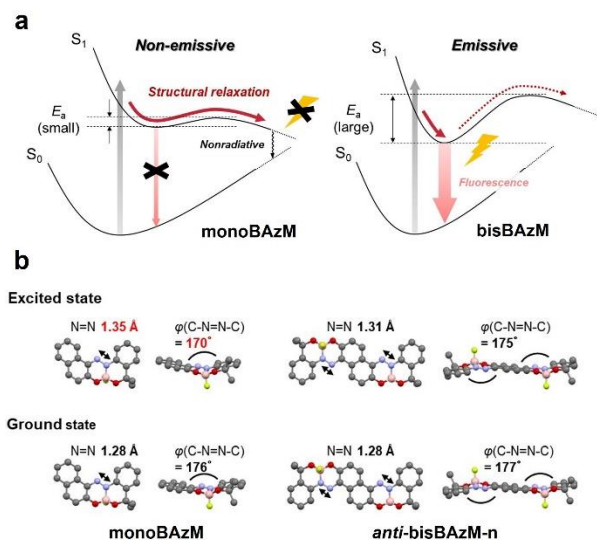


Figure 23. (a) Schematic illustrations for S_0 and S_1 energy diagrams of monoBAzM and bisBAzM. (b) Optimized geometries in the ground and excited states of **BAzM (168)** and *anti*-bisBAzM-n (*anti*-169) obtained with DFT and TD-DFT calculations, respectively. Reprinted with permission from ref 162. Copyright 2021 The Royal Society of Chemistry.

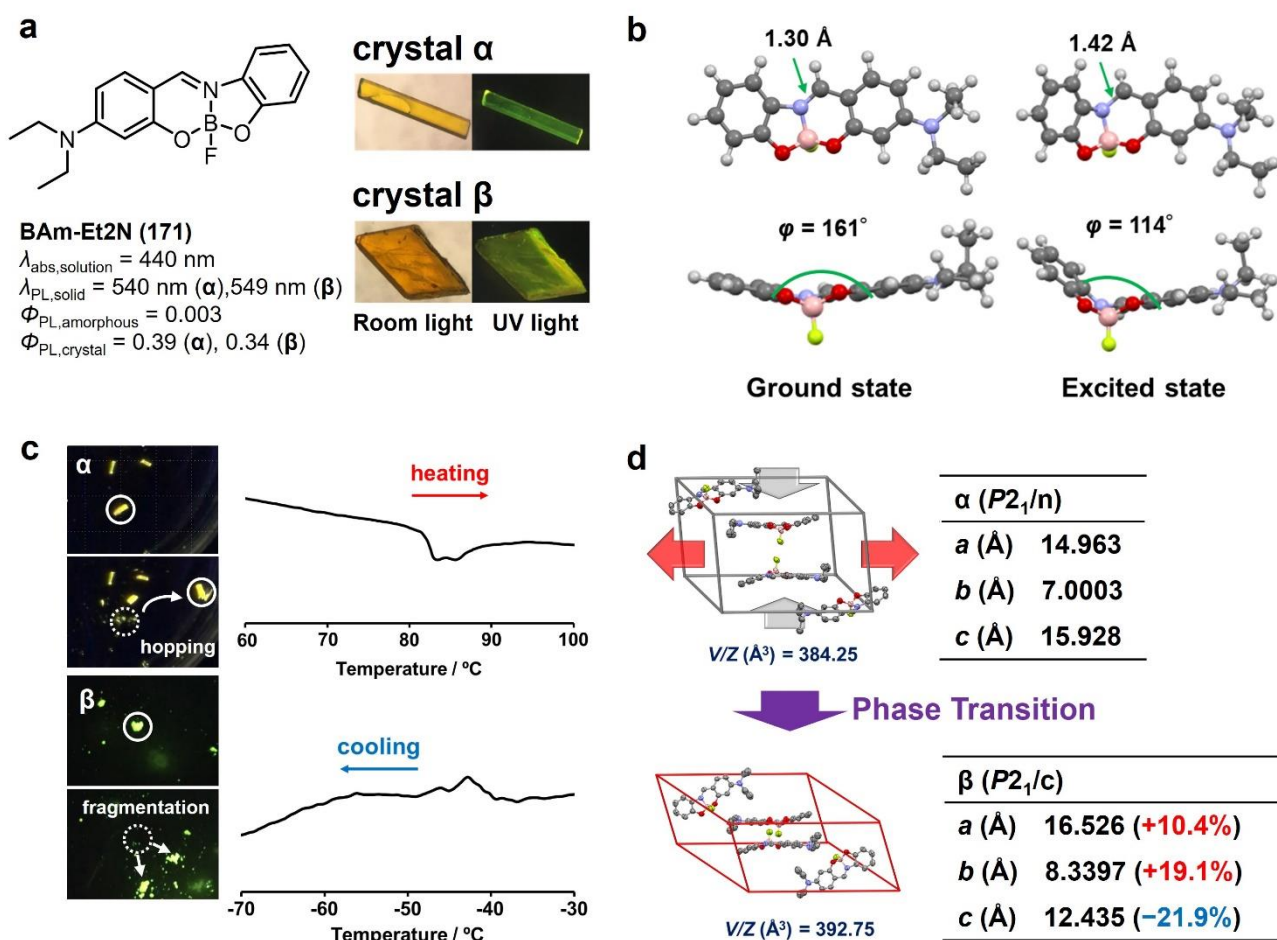


Figure 24. (a) Chemical structure, optical properties and crystal polymorphs of **BAm-Et₂N (171)**. (b) Optimized structures in the ground and excited states of **BAm-Et₂N** with DFT and TD-DFT calculations, respectively. (c) Snapshots of thermosensitive behaviors and differential scanning calorimetry (DSC) curves of crystal α and β . (d) Anisotropic deformation of unit cells of α and β during $\alpha \rightarrow \beta$ crystal-crystal transition. Reprinted with permission from ref 166. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

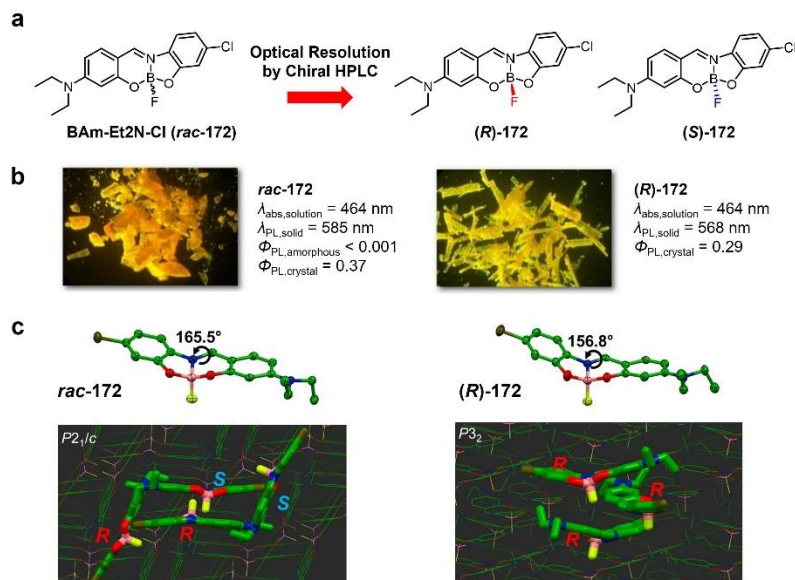
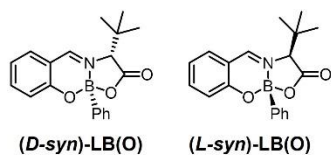


Figure 25. (a) Chemical structures of **BAm-Et₂N-Cl (172)** and separation of enantiomers. (b) Crystal behaviors irradiated by UV lamp (365 nm) and optical properties of *rac*-172 and (*R*)-172. (c) Thermal ellipsoid (probability level 50%) and packing structures of *rac*-172 and (*R*)-172. Reprinted with permission from ref 171. Copyright 2020 The Royal Society of Chemistry.

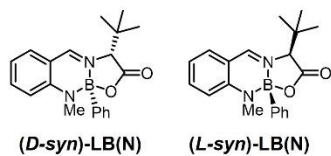


LB(O) (173)

$\lambda_{\text{abs, solution}} = 390 \text{ nm}$

$\lambda_{\text{PL, solution}} = 510 \text{ nm}$

$\Phi_{\text{PL, solution}} = 0.009$



LB(N) (174)

$\lambda_{\text{abs, solution}} = 490 \text{ nm}$

$\lambda_{\text{PL, solution}} = 610 \text{ nm}, \lambda_{\text{PL, solid}} = 600 \text{ nm},$

$\Phi_{\text{PL, solution}} = 0.017, \Phi_{\text{PL, solid}} = 0.19 \pm 0.04$

Figure 26. Chemical structures and optical properties of **LB(O) (173)** and **LB(N) (174)**. ref 174.

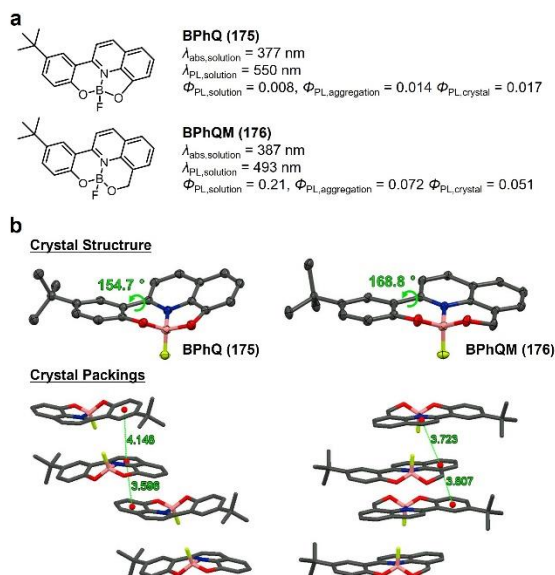


Figure 27. (a) Chemical structures and optical properties of **BPhQ (175)** and **BPhQM (176)**. (b) ORTEP drawings and crystal packing structures of **175** and **176**. Reprinted with permission from ref 176. Copyright 2020 MDPI (Basel, Switzerland).

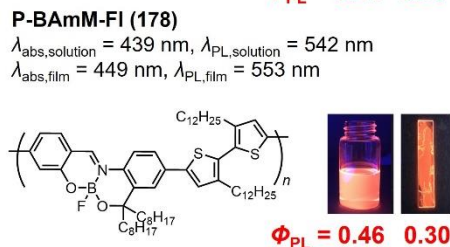
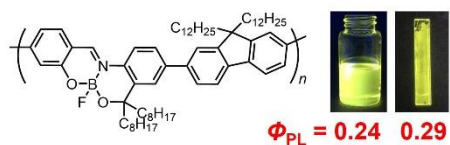
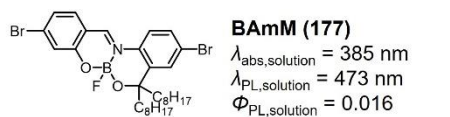
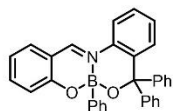


Figure 28. (a) Chemical structures and optical properties of BAm monomers and polymers with photos in solution and film states irradiated by UV lamp (365 nm). Reprinted with permission from ref 177. Copyright 2020 American Chemical Society.

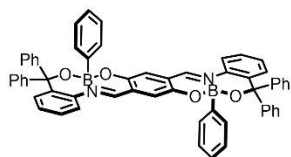


monoBAmM (180)

$\lambda_{\text{abs, solution}} = 419 \text{ nm}$

$\lambda_{\text{PL, solution}} = 522 \text{ nm}$, $\lambda_{\text{PL, solid}} = 551 \text{ nm}$

$\Phi_{\text{PL, solution}} = 0.003$, $\Phi_{\text{PL, solid}} = 0.007$

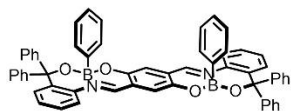


anti-bisBAmM (anti-181)

$\lambda_{\text{abs, solution}} = 595 \text{ nm}$

$\lambda_{\text{PL, solution}} = 729 \text{ nm}$, $\lambda_{\text{PL, solid}} = 745 \text{ nm}$

$\Phi_{\text{PL, solution}} = 0.038$, $\Phi_{\text{PL, solid}} = 0.052$



syn-bisBAmM (syn-181)

$\lambda_{\text{abs, solution}} = 559 \text{ nm}$

$\lambda_{\text{PL, solution}} = 731 \text{ nm}$, $\lambda_{\text{PL, solid}} = 757 \text{ nm}$

$\Phi_{\text{PL, solution}} = 0.035$, $\Phi_{\text{PL, solid}} = 0.035$

Figure 29. Chemical structures and optical properties of **monoBAmM (180)** and **bisBAmM (181)**. ref 179.

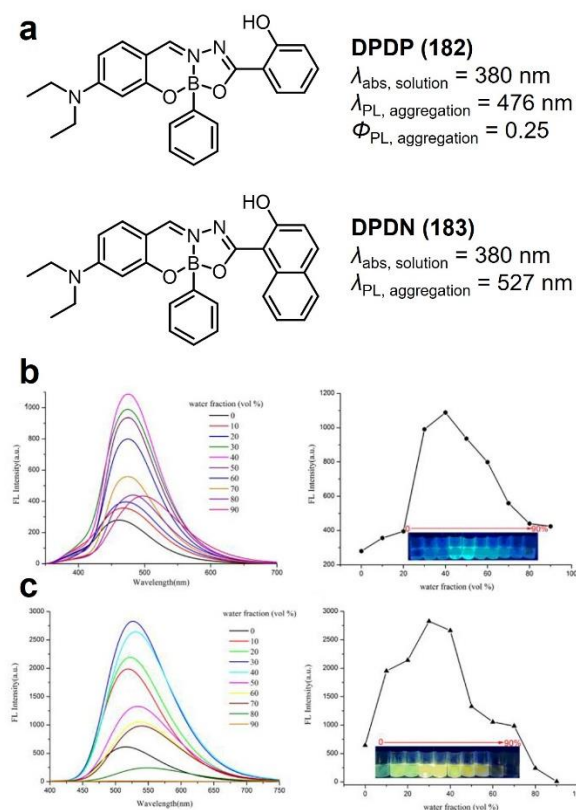


Figure 30. (a) Chemical structures and optical properties of **DPDP (182)** and **DPDN (183)**. (b) PL spectra and plot of relative PL intensity at peak position of **182** in DMF-water mixed solvent with different water fractions (f_w). Inset: Photos of **182** under 365 nm UV lamp at 0% and 90% f_w . (c) PL spectra and plot of relative PL intensity at peak position of **183** in DMF-water mixed solvent with different water fractions (f_w). Inset: Photos of **183** under 365 nm UV lamp at 0% and 90% f_w . Reprinted with permission from ref 180. Copyright 2021 Elsevier.

Table 10. Modified *o*-carboranes with AIE properties

compd.	$\lambda_{\text{em, solution}}$ [nm]	$\Phi_{\text{PL, solution}}$	$\lambda_{\text{em, AIE}}$ [nm]	$\Phi_{\text{PL, AIE}}$	ref.
184	-	-	565	0.68	[187]
185	-	-	563	0.62	[188]
186	-	-	528	0.99	[189]
187	-	-	533	0.90	[189]
188	-	-	597	0.91	[190]
189	-	-	678	0.59	[190]
190	-	-	599	0.44	[191]
191	-	-	494	0.14	[191]
192	-	-	587	0.47	[191]
193	384	n.d.	518	0.11	[192]
194	387	n.d.	537	0.29	[192]
195	396	n.d.	605	0.15	[192]
196	441	n.d.	608	0.039	[192]
197	-	-	475 ^[a]	-	[201]
198	-	-	450 ^[a]	-	[193]
199	404	0.01	477	0.71	[194]
200	372	<0.01	500	0.04	[194]
201	483	0.05	534	0.53	[195]
202	534	0.0008	523	0.28	[195]
203	-	0.008	600 ^[a]	0.128	[196]
204	590 ^[a]	-	520 ^[a]	0.565	[197]
205	367	-	601	0.167	[198]
206	369	-	693	0.218	[198]
207	371	-	631	0.209	[198]
208	587	<0.01	538	0.999	[199]
209	587	<0.01	579	0.855	[199]
210	633	<0.01	591	0.606	[199]
211	615	0.03	548	0.51	[200]
212	640	<0.01	640	0.38	[200]

^[a] estimated from the spectra.

Table 11. Stimuli-responsive *o*-carboranes with AIE properties

compd.	$\lambda_{\text{em, solution}}$ [nm]	$\Phi_{\text{PL, solution}}$	$\lambda_{\text{em, AIE}}$ [nm]	$\Phi_{\text{PL, AIE}}$	ref.
213	645	0.18	660	0.26	[202]
214	n.d.	n.d.	570 ^[a]	-	[204]
215	620	0.007	573	0.338	[205]
216	615	0.021	567	0.524	[205]
217	612	0.032	563	0.687	[205]
218	404/658	0.05	434/604	0.18	[206]
219	628	0.11	557	0.26	[206]
220	381	<0.01	410	0.02	[207]
221	377/580	0.02	519	0.87	[207]
222	321/584	0.01	343/584	0.04	[207]
223	324/550	0.01	457	0.02	[207]
224	435/622	0.33	608	0.69	[208]
225^[a]	651	-	573 634	0.2630 0.0547	[209]
226	442	<0.01	592	0.01	[210]
227^[a]	477	0.03	525 575	0.04 0.12	[210]
228^[a]	426	<0.01	575 561	0.02 0.03	[210]
229	484	<0.01	484	0.071	[211]
230	550 ^[b]	< 0.01	520 ^[b]	>0.99	[212]

^[a] two polymorphs. ^[b] estimated from the spectra.

Table 12. Modified *o*-carboranes showing mechanistic insights

compd.	$\lambda_{\text{em, solution}}$ [nm]	$\Phi_{\text{PL, solution}}$	$\lambda_{\text{em, AIE}}$ [nm]	$\Phi_{\text{PL, AIE}}$	ref.
231	628	0.16	600 ^[a]	-	[213]
232	407, 645	< 0.01	600 ^[a]	-	[213]
233	408, 656	0.02	600 ^[a]	-	[213]
234	388	<0.01	625 ^[a]	0.05	[214]
235	391, 461	0.06	630 ^[a]	0.19	[214]
236	n.d.	<0.01	503	0.26	[215]
237	n.d.	<0.01	515	0.19	[215]
238	577	0.05	536	0.36	[215]
239	n.d.	-	522	-	[216]
240	n.d.	-	503	-	[216]
241	367, 382	<0.01	-	-	[217]
242	387	n.d.	596	-	[217]
243	n.d.	n.d.	580	-	[217]
244	n.d.	n.d.	578	-	[217]
245	n.d.	-	592	-	[218]
246	n.d.	-	578	-	[218]
247	n.d.	-	559	-	[218]
248	n.d.	-	591	-	[218]
249	368	-	596	-	[219]
250	n.d.	-	601	-	[219]
251	384, 503	0.02	475 ^[a]	0.19	[220]
252	381	<0.01	475 ^[a]	0.03	[220]
253	635	0.11	624	-	[221]
254	639	0.02	622	-	[221]
255	n.d.	<0.01	625	-	[221]
256	n.d.	<0.01	624	-	[221]
257	n.d.	n.d.	552	0.10	[222]
258	n.d.	n.d.	557	0.20	[222]
259	n.d.	n.d.	559	0.35	[222]
260	n.d.	n.d.	556	0.47	[222]
261	-	-	560	0.263	[223]
262	-	-	567	0.634	[223]
263	-	-	571	0.482	[223]
264	-	-	608	0.90	[224]
265	-	-	585	0.99	[224]
266	-	-	602	0.41	[224]
267	-	-	589	0.96	[224]

268	-	-	606	0.99	[224]
269	-	-	616	0.99	[224]
270	-	-	608	0.99	[224]
271	609	<0.01	545	0.04	[225]
272	571	<0.01	543	0.08	[225]
273	382, 684	-	468	0.24	[226]

^[a] estimated from the spectra.

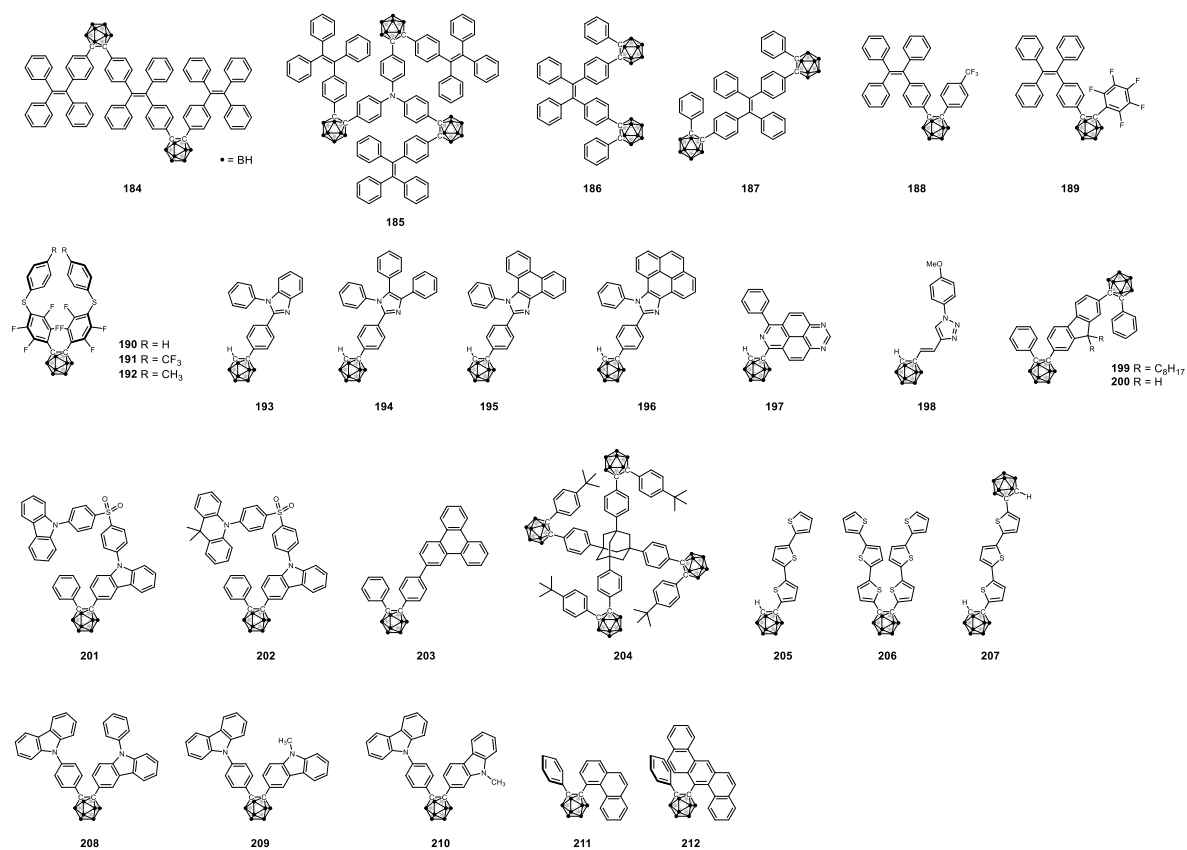


Figure 31. Chemical structures of AIE-active *o*-carboranes.

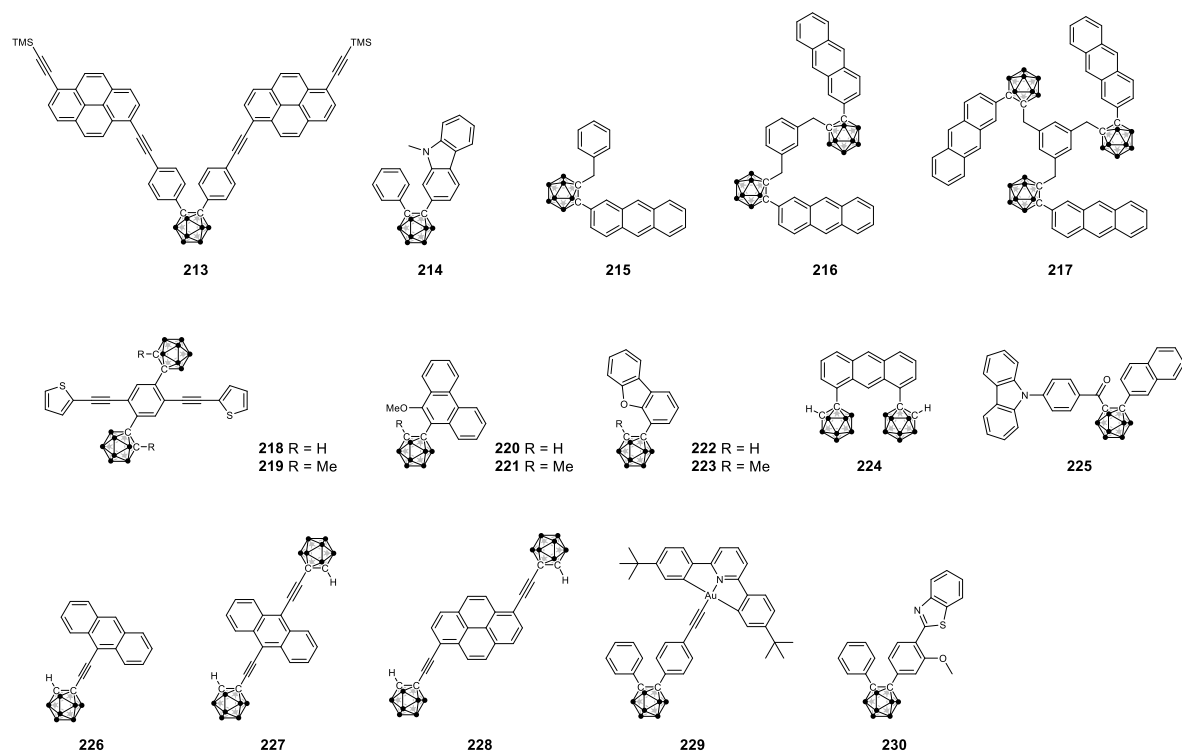


Figure 32. Chemical structures of stimuli-responsive AIE-active *o*-carboranes.

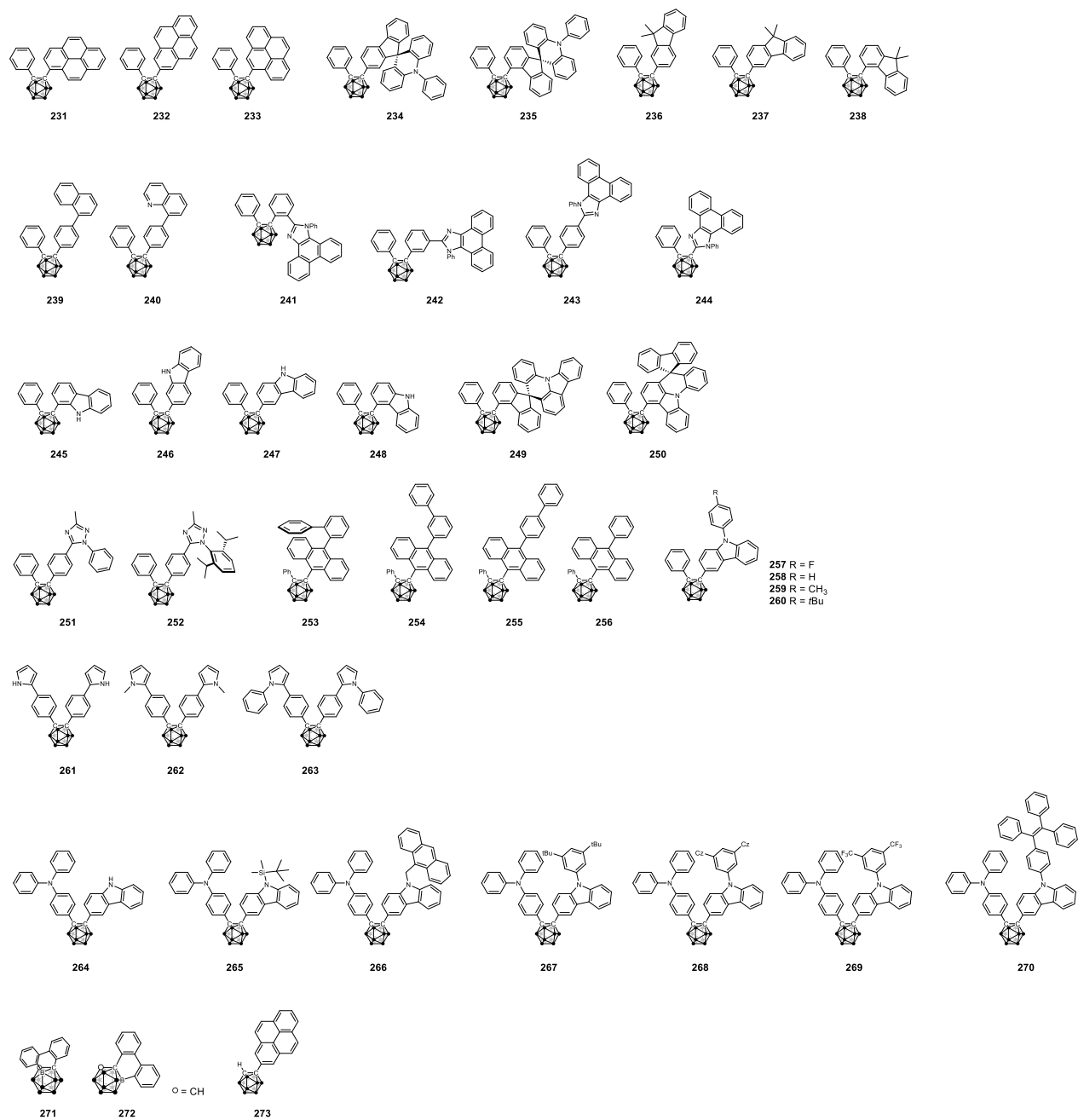
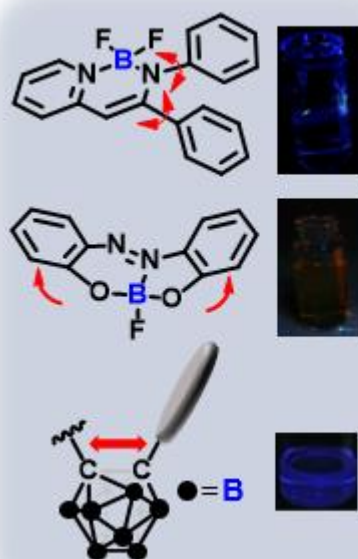


Figure 33. Chemical structures of AIE-active *o*-carboranes showing mechanistic insights.

Molecular Motion



AIE Active

