**Aggregation-Induced Emission as a Promising Solution for Overcoming Aggregation Caused Quenching**

Emissive organic materials are versatile for the application to advanced organic devices such as paper displays, flexible photovoltaic cells, and printing electronic circuits. In particular, organoboron complexes including polymers have gathered much attention as a key building block for the next-generation of opto-electronic devices because of their opto-electronic functions.1 Most of organoboron molecules are composed of four-coordinated boron and can show a variety of optical properties. Indeed, so far, various types of luminescent materials involving the four-coordinate boron have been prepared. As one of typical examples, boron dipyrromethene (BODIPY) derivatives, which possess superior optical properties such as large light absorption and emission ability, sharp spectra, and high photo-stability, are used for a wide variety of applications in material science as well as biotechnology. Thus, optically-functional materials such as solid-state emitters, light absorbers, light-harvesting antennae and white-light emitting materials can be produced with BODIPY derivatives. Furthermore, we recently reported the BODIPY derivative-containing conjugated polymers can work not only as efficient emitters in deep-red and near infrared regions but also as an efficient electron-carrier materials. It should be mentioned that higher electron-carrier ability from the film samples composed of the BODIPY derivative-containing conjugated polymers was obtained than those of Alq3 crystal which is commonly used as an electron-carrier material in the conventional optical devices. This result means that these polymers should be promised to be the key materials in modern organic opto-electronic devices with printing methods. When organoboron luminescent dyes are actually utilized in the devices, we often have one critical problem to be overcome. In general, bright emission can be observed from the diluted solution state. On the other hand, most of emission properties are spoiled in the condensed state such as in the film and powder. These behaviors are called as concentration quenching or aggregation-caused quenching (ACQ). To receive the highly-efficient emission from the devices, ACQ should be avoided. On the contrary, it has been reported that some of organic compounds presented stronger emission only in the aggregation states. Tang et al. firstly showed unique behaviors with tetraphenyl-substituted silole compounds in 2001.2 Only when the compounds were aggregated in the poor solvent, the bright emission can be obtained. This phenomenon is called aggregation-induced emission (AIE). In order to overcome ACQ and to receive bright emission from the solid samples, the mechanism of AIE behaviors and AIE-active materials have been significantly focused. Therefore, many researchers devoted their effort to explore new AIE-active units for obtaining highly-efficient materials.

**“Element-Block Polymers”, New Strategy for Material Design**

We have recently proposed a new concept of “element-block” consisting of nanobuilding units or clusters of heteroatoms for the material design.3 In this review, we describe recent advances on the development of AIE-inducible organoboron “element-blocks”. Simply by introducing “element-blocks” composed of organoboron complexes in the conjugated system and connecting with other functional units, the series of functional emissive materials can be readily obtained. Additionally, by the combination with stimuli-responsivity of the materials, emissive chemical sensors can be constructed. Initially, the transformation of commodity fluorescent organoboron dyes to the AIE-active molecules is presented. Based on this result, the conjugated polymers with AIE properties were obtained. The optical properties of conjugated polymers involving boron element are illustrated. Moreover, the applications of these AIE-active polymers for the film-type sensors are mentioned. Next, as another instance of the AIE-inducible “element-block” composed of organoboron molecules, the AIE behaviors observed in the solid state are mentioned. The material design and unique solid-state emission of the carborane materials are demonstrated.

**Transformation of Conventional Fluorescent Dyes to AIE-Active Molecules**

Boron diketonates are one of simple and stable organoboron complexes, and so far, various optical materials have been developed based on boron diketonates.4 Therefore, boron diketonates are regarded as versatile “element-blocks” for constructing functional emissive materials. However, emission efficiencies were often crucially lowered in the solid state because of ACQ. Particularly, organoboron conjugated polymers suffered from ACQ when these materials have been used as an emissive unit in the optical devices. In order to overcome ACQ and to realize AIE-active materials, we designed and synthesized the new ligands based on boron diketone.5 It was presumed that by replacing oxygen to nitrogen, the flexibility of the complex should be enhanced. As a result, excitation energy can be consumed in the solution state, resulting in annihilation. In the solid state, molecular tumbling should be restricted. Moreover, the distortion around nitrogen could contribute to disturbing undesired intermolecular interaction. Therefore, we expected strong emission can be observed from the solid sample. To confirm the validity of this idea, boron ketoiminates and diminates were synthesized, and their optical properties were examined. In summary, significant AIE behaviors were observed from these complexes. For instance, in THF, emission was hardly observed from boron ketoiminate. In contrast, bright emission was observed from the samples in the mixed solvent system of THF / H2O (1/9 v/v), Φagg = 0.30–0.76. Furthermore, in the crystalline state of boron diiminate, further enhancement to emission intensity was observed by the phase transition from amorphous to crystalline states. These data meant that new boron complexes have crystallization-induced emission enhancement (CIEE) as well as AIE properties.6 Based on these solid-state emission properties, various types of luminescent chromism were observed such as vapochromism6 and mechanofluorochromism7.

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**Fig. 1** Chemical structures of AIE-inducible organoboron “element-blocks”.

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Film-Type Sensors Based on Oxidation-Induced Emission Properties

To extend the application of the stimuli-responsive AIE-active materials to the film-type chemical sensors, conjugated polymers composed of boron diiminate were designed. The thin films with the AIE-active copolymers composed of fluorene comonomers and the sulfide-substituted boron diiminate were synthesized, and the changes in the optical properties by the oxidation were monitored. Slight emission was observed from the film sample before the oxidation by H$_2$O$_2$, which can transform sulfide to sulfoxide. By soaking the film sample of the polymer in the solution containing H$_2$O$_2$, the increase of the yellow color emission of the film was detected. From the quantitative analyses for quantum yields, the emission intensity was finally enhanced from the charge transfer state through the polymer main-chain. In other words, oxidation-induced AIE can be realized with the sulfide-modified organoboron polymers. It can be expected that the AIE-active polymeric materials should be a versatile platform as a biosensor for longitudinal monitoring of the bio-related reactions. Especially, H$_2$O$_2$ is known to be one of reactive oxygen species and is endogenously produced in energy metabolism. Therefore, our materials could be valid for sensing generation of reactive oxygen species and oxidative stresses caused by these reactive molecules.

Stimuli-Responsive AIE Regulation with o-Carborane Materials

The modulation of emissive properties of the o-carborane-containing polymeric materials by environmental alteration was accomplished based on hydrogel matrices. The cross-linking reagent composed of o-carborane was synthesized (Fig. 4a). By using this cross-linker, the translucent hydrogels consisting of poly-$\gamma$-glutamic acid) were prepared. By the gel-shrinkage from the change of ionic strength, it was found that the luminescence intensity from the modified hydrogels was drastically changed. Weak emission was obtained in the swollen state. The bright emission was observed by drying the hydrogel. Moreover, these changes in the emission intensity were reversibly repeated many times between the swollen and dried states. According to the AIE mechanism of the o-carborane-containing unit, these behaviors can be explained by the fact that the molecular motion at the o-carborane cross-linkers should be suppressed in the dried state. Then, the significant emission can be observed from the material. In the swollen state, the molecular motion should be recovered, leading to the annihilation of the emission. We also prepared the o-carborane derivative and found multi-chromism behaviors (Fig. 4b).

o-Carborane-Based AIE-Inducible “Element-Blocks” and Extremely-Efficient Solid-State Emissive Materials

As the next example of the AIE-inducible “element-block”, unique optical properties of organoboron clusters called as o-carboranes are introduced. o-Carboranes are icosahedral clusters consisting of 10 boron and 2 carbon atoms with three-center two-electron bonds. Since the three-dimensional electron delocalization in the carborane cage contributes to improving thermal and chemical stabilities, o-carborane derivatives have been used for heat-resistant materials. In addition, owing to the intrinsic reactivity of boron under radiation irradiation, o-carborane derivatives have been applied as the positron sources in positron electron tomography treatments. In 2009, we firstly found that o-carborane can work as a key unit for presenting AIE. The alternating polymers were prepared with o-carborane and p-phenyleneethynylene sequences, and their optical characteristics were examined. In summary, the typical AIE behaviors were observed from the o-carborane-containing main chain-type polymers. Significant emission was hardly observed from the THF solution of the polymers having electron-donating $\pi$-conjugated linkers. On the other hand, by adding the water content in the solution for the formation of aggregation, emission intensity was enhanced. Finally, similarly to the previous example having AIE properties, in the mixed solvent of THF/H$_2$O = 1/99, bright emission was obtained. From these experiments, it was proposed that the o-carborane polymers can work as an AIE-active material.

To comprehend the AIE mechanism in the o-carborane-containing polymers, the series of mechanistic studies with o-carboranes were performed. Accordingly, it was clarified that the intramolecular charge transfer should occur by the photo-irradiation because of strong electron-accepting properties of o-carborane and electron-rich linkers. In the excited state, the electrons should be delocalized involving the C–C bond in the o-carborane unit. By the structural vibration at the o-carborane moiety, excitation energy was consumed, leading to the quenching of the emission. In the solid state, most of molecular motions should be suppressed, resulting in the strong emissions. Thus, AIE behaviors should be obtained from the polymers. Based on this mechanism, we aimed to modulate AIE properties by altering environmental factors.
In this mini review, the recent progress for the development of the AIE-inducible organoboron complexes and the resulting AIE-active molecules including polymers are introduced. AIE-active materials can be readily prepared by introducing AIE-inducible organoboron “element-blocks” in the conjugation systems including polymers. As a result, various types of solid-state emissive materials with unique optical properties were observed. Finally, based on these emissive materials, the series of AIE-active conjugated polymers, film-type chemical sensors, and bright solid-state emissive materials can be obtained. The design strategies for the functional materials based on “element-blocks” are promised to be a versatile concept not only for improving the efficiencies of the conventional devices but also for generating novel organic devices.

References