Modulation of Solid-state Luminescent Properties of Conjugated Polymers by Changing Connecting Points at Flexible Boron Element-Blocks

Kazuo Tanaka* and Yoshiki Chujo

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University

Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp

Tel: +81-75-383-2604

Fax: +81-75-383-2605

RUNNING HEAD

Emissive polymers with variable connecting points

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ABSTRACT

A flexible molecule is known to be unfavorable for designing a luminescent dye because its excitation state would be rapidly decayed through molecular motions. Meanwhile, we recently found that some of flexible boron complexes, which potentially show larger degree of structural relaxation in the excited state, and their polymers exhibit unique optical properties with high environmental sensitivity by adding structural restriction, such as aggregation-induced emission (AIE) and luminochromism triggered by external stimuli. Moreover, it was shown that these optical properties were drastically changed by modulating the connecting points in polymers. In this review, recent progresses in the developments of luminescent polymer films with stimuli-responsiveness are illustrated. In particular, influence of the alteration of connecting points on luminescent behaviors is explained. It is demonstrated that polymerization is a versatile strategy not only for transforming a class of non-emissive molecules to luminescent dyes but also for precisely regulating optical properties of film materials which are promised to be applied as a scaffold for advanced chemical sensors.

INTRODUCTION

We have recently proposed a new concept for material design based on an "element-block" which is a minimum functional unit containing heteroatoms.[1,2] Creation of a wide variety of materials with unique functions originating from heteroatoms can be expected by the connection and assembly even with the single type of element-blocks and resulting element-block polymers are promised to show not only superior properties to those of conventional organic materials but also diverse functions originating from the combination with element-blocks. Because of positive effects of boron complexation as mentioned above, we have also explored luminescent boron element-blocks and found unique optical and electronic properties from conjugated polymers consisting of boron element-blocks.[3]

To obtain intense emission from organic materials including polymers, the improvement of molecular rigidity at the chromophore unit is essential for suppressing energy-consumable molecular motions in the excited state (Scheme 1). Actually, flexible molecules generally show poor luminescence in the absence of solid matrices. By the boron complexation, molecular rigidity and planarity at the local site can be greatly improved.[4] These structural features are favorable for extending robust conjugation systems. Therefore, various types of luminescent dyes have been developed based on boron complexes.[5] In addition, useful electronic properties, such as carrier-transporting ability, are often observed from these rigid and planar structures. In particular, since these luminescent and electronic properties are feasible for fabricating highly-efficient organic light-emitting diodes (OLEDs), boron complexes with π-conjugated ligands are known to be a promising platform for constructing advanced

optoelectronic devices.

Scheme 1

For example, boron dipyrromethene (BODIPY) is widely known as a representative luminescent boron complex. By extending π-conjugation, deep-red or near-infrared emission can be obtained.[6,7] Owing to intense emission properties derived from the rigid and planar dipyrromethene ligand reinforced by the boron complexation, a series of light-absorption and luminescent polymers can be obtained.[8–11] To avoid aggregation-caused quenching (ACQ), which is a critical annihilation process and is commonly observed in the condensed state of organic luminescent dyes, BODIPY-containing polymers were loaded in organic–inorganic hybrid matrices.[12] Consequently, highly-stable films possessing preserved emission properties were obtained.[13] As another instance, by expanding π-conjugated systems of the dipyrromethene ligand through polymer main-chains, longer-wavelength emission was observed (Figure 1a).[14–16] Moreover, it was shown that these polymers exhibited superior electron-carrier ability in amorphous to the aluminum complex conventionally utilized in OLEDs (Figure 1b).[17] Thus, boron element-blocks are regarded as a potential unit for constructing advanced functional polymers.

Figure 1

As next generation of OLEDs, many researches have devoted their efforts to develop film-type optical sensors. If optical properties can be changed by external stimuli, these

films would be directly used for constructing sensing materials. Owing to various advantages of organic devices, such as lightness, flexibility and thinness, these film sensors could be applicable for developing advanced sensing tools, such as wearable devices and ultra-tiny sensors. To realize these future sensing technologies, development of stimuli-responsive luminescent films are needed. For example, we manufactured elastic hybrid materials consisting of polyhedral oligomeric silsesquioxane (POSS)-capped polyurethane and polyfluorene.[18] Thermally-stable hybrid films showed a dual-emission property containing intrinsic fluorescence from polyfluorene and excimer emission. Interestingly, emission color changes were detected by stretching the film samples attributable to alteration of the intensity ratio between fluorescence and excimer emission. By replacing polyfluorene to the doped poly(3-hexylthiophene), it was shown that conductivity was varied by stretching.[19] Interchain interaction and polymer morphology followed by electronic properties of main-chain conjugation should be drastically changed by stretching sample films. Thereby, these responses are observed by applying mechanical forces. These materials are promised to be the paint-type sensors for detecting applied forces as well as distortions of product surfaces. We also found that dye-loaded POSS networks with water-dispersibility can exhibit luminescent color changes in the presence of plastic particles.[20] Environmental changes around dyes should be induced when adsorbed onto particle surfaces. Furthermore, the size of plastic particles was able to be discriminated by the degree of luminescent property changes. This system could be applicable for evaluating water contamination by plastic particles through the simple protocols. In these examples, luminescent materials are loaded onto physically-flexible matrices. In contrast, we herein explain stimuli-responsive luminescent films based on “flexible”

boron complexes,[21–26] which potentially show large degree of structural relaxation in the excited state (Scheme 1and Figure 2). As easily predicted, flexible boron complexes generally show extremely-poor luminescence, meanwhile we recently found that their flexibility can be utilized as the origin for expressing unique stimuli-responsiveness especially in solid toward slight environmental changes and tiny eternal stimuli. Consequently, a series of film-type sensors were obtained based on the polymers containing flexible boron complexes. Therefore, we regard a class of flexible boron complexes as a stimuli-responsive element-block with luminescent properties to fabricate advanced sensors.

Figure 2

We have designed luminescent films with stimuli-responsiveness based on main-chain-type conjugated polymers involving flexible boron complexes. In particular, we discovered that various environment-sensitive optical properties, such as aggregation-induced emission (AIE), can be induced by changing connecting points in polymer main-chains (Scheme 1). Mainly from these studies, we will explain the results and basic chemistry in these materials.

Initially, we explain the discovery of AIE-active boron ketoiminate, which is the first example as a flexible boron complex in our research (Figure 2). Commodity boron complexes show intense emission only in solution, while some of boron ketoiminates exhibited enhanced emission by aggregation. Based on these molecules, we constructed polymers, and it was demonstrated that optical properties were changed between ACQ

and AIE by changing connecting points. This is the typical example to demonstrate tuning of material properties just by altering the connecting motif with the single type of element-blocks. To preserve solid-state luminescent properties for improving emission efficiency in film, we designed the fused ketoiminate ligand, and the polymers showed relatively-high efficiency. In particular, we also found that environment-dependency was enhanced by introduction of the fused structure into boron ketoiminate. The resulting polymers having the linear and zigzag structures showed thermochromic and mechanochromic luminescence, respectively. Furthermore, based on the idea for improving flexibility, we designed boron diiminate in which weaker bonds were introduced into the boron complex moiety. AIE properties of the polymers consisting of boron diiminate were clearly changed by altering the connecting points. Finally, we explain the establishment of molecular designs for switching optical properties from scratch in polymer films. We theoretically explored flexible boron complexes and designed polymers with variable connecting points. By suppressing or releasing molecular motions which were predicted by quantum chemical calculations, optical properties between ACQ and multi-state emission can be controlled. The mechanisms in these materials are illustrated.

1. Boron ketoiminate

Boron diketonate is one of typical boron complexes having luminescent properties.[3] By modulating π-conjugation, luminescent properties can be tuned.[27] For instance, Fraser *et al.* synthesized the monoiodo complex and observed dual-emission property involving intrinsic fluorescence and phosphorescence caused by the heavy-atom effect of iodine.[28] Only phosphorescence quenching followed by alteration of intensity ratios

toward oxygen-resistant fluorescence can be induced under aerobic condition. As a result, oxygen levels in tumor regions were able to be assessed by intensity ratio changes. Moreover, other types of boron ketoiminates show mechanochromic luminescent behaviors.[29–33] By applying mechanical forces to crystal samples, molecular distribution is drastically altered by morphology changes from crystal to amorphous. Correspondingly, luminescent chromism was induced.

As introduced above, although some of complexes are able to show emission in solid, most of complexes commonly suffer from ACQ. We prepared the main-chain-type ligand polymer involving the diketone structure and investigated influence of boron complexation through polymer reactions on optical properties (Figure 3).[34] Accordingly, it was clearly shown that boron complexation contributes to enhancing emission intensity by forming robust main-chain conjugation. In the solution state, intense emission bands with higher quantum yields were obtained in the longer wavelength region after boron complexation. However, critical ACQ was observed from the film samples.

Figure 3

To construct robust conjugation involving boron, the ketoiminate polymers were designed and synthesized (Figure 4).[35] From the ligand polymer, intense green emission was observed only in the diluted solution, and ACQ was observed in film. Meanwhile, red emission was induced by boron complexation, indicating that conjugation system should be elongated through the polymer main-chain. Interestingly, the

boron-containing polymer showed higher emission efficiency in film than that in solution. This is the typical AIE behavior.

Figure 4

The idea of AIE was firstly reported by Tang *et al.* in 2001 with the modified silole compounds, and tetraphenylethene was also found as an AIE-active molecules.[36,37] Owing to versatile properties such as environment-switchable luminescent properties, AIE-active materials have been applied in material science as well as biotechnology.[38–43] In these AIE-active dyes, it is suggested that molecular motions in the excited state should be responsible for emission annihilation in the solution state. To understand the mechanism of an AIE property of boron ketoiminate polymers, we prepared boron complexes and examined optical properties (Figure 5).[44] ACQ and AIE were observed from boron diketonate and ketoiminates, respectively. Moreover, under high viscosity and frozen conditions where molecular motions are critically restricted, significant emission enhancements were observed in both states, indicating that molecular motions in the excited state play an important role in emission annihilation similarly to the previous AIE dyes. From a series of mechanistic studies including quantum calculations, the plausible mechanism can be proposed. By replacing one of oxygen atoms to nitrogen, molecular rigidity should be lowered because of weaker bond strength of B–N than that of B–O.[45] Therefore, emission annihilation is able to be induced in solution due to molecular motions. In the solid state, non-radiation paths caused by these molecular motions would be suppressed owing to structural restriction. Furthermore, according to quantum calculation, localization of highest occupied molecular orbitals at

the oxygen side was proposed in boron ketoiminate, implying that intermolecular interaction could be disturbed even in the condensed state. As a result, luminescence could be able to be preserved in solid. In conclusion, AIE properties are obtained by the combination with emission annihilation in solution and solid-state luminescence.

Figure 5

The different types of the polymers containing boron ketoiminate were prepared by changing connecting points (Figure 6).[46] According to optical measurements, it was revealed that solid-state luminescence was observed although ACQ was also detected. These data suggest that molecular motions in the phenyl groups at the base of ketone should play a critical role in AIE properties of boron ketoiminates. The switching between AIE and ACQ was demonstrated by changing the connecting points in polymer main-chains.

Figure 6

To avoid ACQ, one of conventional strategies is the modification with bulky substituents.[47–58] Since intermolecular interaction is disturbed in condensed state, intrinsic emission can be preserved. Another strategy is to employ transparent matrices. By loading luminescent dyes onto polymers or organic–inorganic hybrids, chromophores are located under similar environment to the solution state.[12] As a result, solid-state emission can be maintained. However, these strategies are unfavorable for obtaining stimuli-responsive materials. As is often the case with the above materials,

environmental sensitivity is spoiled. Basically in these strategies, chromophores tend to be isolated from any interactions, followed by insensitivity in environmental changes and external stimuli. Hence, it is still challenging to simultaneously realize solid-state emission and environmental responsiveness. In contrast, it was found that solid-state luminescent properties of flexible boron complexes had environmental sensitivity.[21] Therefore, luminochromic behaviors were observed by changing molecular morphology in aggregation as well as solid.

For instance, boron ketoiminate was introduced into a hydrogel matrix, and optical properties were monitored by swilling and shrinking (Figure 7).[59] As we expected, AIE was observed from the modified gel. Interestingly, we found that the AIE color was varied by soaking the hydrogels into organic solvents for shrinking the hydrogels. It was proposed that aggregation-induced blue shift emission should be induced in relatively-polar organic solvents by forming tight aggregation. Based on this color changes in the shrinking, the protein sensing was demonstrated. In the presence of proteins, blue-shifted emission was obtained through adsorption followed by aggregation. Unique sensing materials can be obtained owing to environmental sensitivity of boron ketoiminate.

Figure 7

2. Fused boron ketoiminate

Flexible boron complexes with luminochromic properties showed very low emission efficiency. For example, most of emission quantum yields of the mechanochromic

luminescent molecules involving the boron ketoiminate structure were within several percentages before and after the mechanical treatment.[60–62] Next, to enhance environmental responsiveness as well as emission efficiency to boron ketoiminate, the complex having the fused ligand was designed (Figure 8).[63] By expanding π-conjugated system and anchoring the boron complex moiety, it was expected that solid-state emission in the AIE behavior can be preserved in any state without critical loss of environmental responsiveness. A series of the fused boron ketoiminates were synthesized, and their optical properties were monitored in many phases. Accordingly, constant emission efficiencies were observed in solution, crystal and amorphous from each complex. In addition, peak shifts of emission bands were observed after applying mechanical forces to the crystal powders, indicating that mechanochromic luminescent properties can be realized with good emission efficiencies.

Figure 8

By utilizing the fused complexes as a monomer, polymers were obtained (Figure 9).[64] The obtained polymers exhibited intense emission in both solution and film states. Interestingly, we found that one of the linear polymers presented thermochromic luminescence in solution. In the emission spectra, the polymer solution in chloroform showed two emission bands around 530 nm and 580 nm below 30 °C, while by heating the polymer solution, the emission band around 580 nm drastically decreased and almost disappeared at 50 °C. Only the emission band around 530 nm was detected after heating. Because of these optical changes, thermochromic luminescence was obtained from the solution sample containing the linear-shaped polymer. From the series of

mechanistic analyses, it was shown that chain assembly should be responsible for luminescent color changes.

Figure 9

A mechanochromic luminescent property was observed from the zigzag-type polymer in the solid state (Figure 9).[64] The pristine powder sample exhibited orange luminescent color, while yellow emission was induced by grinding. From differential scanning calorimetry, the melting temperature of the pristine sample disappeared after grinding. It is implied that polymer chain assembly could be collapsed by applying mechanical forces. These morphology changes should provide environmental alteration followed by different luminescent color. These data involving thermochromic luminescent behaviors indicate that expansion ofπ-conjugated system should contribute to enhancing not only emission efficiency but also environment sensitivity. As a result, luminochromism originating from morphology changes can be induced.

3. Boron diiminate

By introducing a B–N bond, flexibility was improved, and subsequently, AIE and stimuli-responsive luminochromism can be induced. Therefore, it can be expected that higher environmental sensitivity, followed by stimuli-responsiveness would be obtained if molecular flexibility is enhanced. Based on this idea, boron diiminates, in which another oxygen atom was also replaced to nitrogen in boron ketoiminate, were designed and synthesized (Figure 10).[65,66] It was found that boron diiminates with various

substituent groups exhibit CIE as well as AIE with variable luminescent color in crystal. It is likely that more structural restriction should be necessary for suppressing emission annihilation by molecular motions. Similarly to boron ketoiminates, main-chain-type polymers were synthesized, and it was observed that emission intensity and color can be tuned by the substituent effects (Figure 11a).[67] By utilizing the property-tunability with the substituent at the side-chains, film-type sensors were developed. For instance, when the film of the dimethylamine-substituted polymer was fumed to acid vapor, red-color emission was turned to yellow. Subsequently, by fuming basic vapor, emission color was recovered to red. It is because electronic conjugation would be drastically changed by acidification at the side chains of dimethylamine. Then, such vapochromic luminescent behaviors can be detected. As another instance, the methyl sulfide-substituted polymer was synthesized and cast films were prepared (Figure 11b).[68] The pristine sample showed slight yellow emission, whereas emission intensity increased by soaking the film into the aqueous solution containing hydrogen peroxide which is one of reactive oxygen species and plays a crucial role in oxidative damages in cell. By the oxidation at the methyl sulfide group, methyl sulfoxide was generated according to the results from ^{1}H NMR analyses. The electronic property of the substituent was changed from electron donating to accepting by the oxidation. Finally, emission intensity was able to be enhanced. The film-type sensor for the bio-significant molecule can be readily constructed based on the substituent effects.

Figures 10 and 11

Further enhancement of molecular flexibility was also accomplished by replacing

boron to heavier element. For example, we prepared the diamine complexes with aluminum and gallium which belong to the same group as boron in the periodic table.[69,70] Both complexes show CIE, and gallium diiminate exhibits vapochromic luminescent properties. It should be mentioned that the degree of luminescent chromism was critically depended not on the chemical components of the captured volatile organic compounds but on their radius of gyration. It is proposed that crystal–crystal transitions could readily occur owing lower packing density of gallium diiminate than that of boron one. Gallium diiminate-containing polymers were also prepared, and AIE was observed.[71] These results also support that enhancement of molecular flexibility by introducing a heavier element should be also valid for improving environmental sensitivity.

To examine influence of the alteration of connecting points in details, a series of alternating copolymers composed of boron diiminate were prepared (Figure 12).[72] All polymers had AIE properties, and various colors from green to orange depended on the type of comonomers, such as fluorene and bithiophene, and the connecting points were observed in film. To clarify the mechanism on such clear color changes, several optical measurements were performed. Accordingly, it was shown that the charge transfer character between boron diiminate and comonomer units was critically changed by changing the connecting points. Theoretical investigation suggested that boron diiminate should be a strong electron-acceptor when the comonomer was connected to one or both of the phenyl groups on the nitrogen atoms. On the other hand, a weak electron-donating property was expressed in the polymers where the comonomers were connected at the phenyl groups on the carbon atoms in the boron-containing

six-membered ring. It was demonstrated that luminescent properties can be tuned simply by changing the connection motif with the flexible boron complex.

Figure 12

4. Theoretical prediction

The final topic is concerning the establishment of material designs for stimuli-responsive luminescent polymers composed of flexible boron complexes from scratch. As mentioned above, flexibility in this manuscript means degree of structural transformation caused by relaxation in the excited molecule.[45] We presumed that degree of structural relaxation can be estimated by comparing the optimized structures in the ground and excited states. Thus, flexible boron complexes are able to be designed with the theoretical approach. Based on this idea, the pyridinoiminate complex **BPI** was obtained (Figure 13).[73,74] A large difference between optimized structures in the ground and excited states, which can be obtained by the calculations with density functional theory (DFT) and time-dependent DFT methods, respectively, was proposed.[73] Therefore, it was expected that boron pyridinoiminate can work as an AIE behavior. The fused molecule **FBPI**, which hardly shows structural transformation because of the anchoring effect by the fused structure, was also prepared as a comparison. In summary, as we expected, **BPI** showed AIE, while **FBPI** exhibited ACQ.[73] Moreover, in the optical spectra, larger degree of Stokes shift was observed only from **BPI**, suggesting that structural relaxation occurred. These data indicate that a flexible boron complex is predictable from scratch through the quantum chemical approach. This result involves another significant issue. According to the comparison data, the movable points in the

excited state are able to be estimated. Therefore, we assumed that sensitivity toward environmental factors could be controllable by connecting at the movable or immovable points. Similarly to the results from the polymers with the fused boron ketoiminate structure, it was presumed that the polymer composed of the **BPI** unit might show a multi-state emission property.

Figure 13

To evaluate validity of this idea, the polymers were prepared with **BPI** or **FBPI** (Figure 14).[75] From optical measurements, it was observed that the **FBPI** polymer had intense luminescent property only in the solution state and showed ACQ. In contrast, the **BPI** polymer exhibited multi-state emission. Similar emission intensities were obtained both in the solution and film states. By connecting at a potential movable point in the excited state predicted by quantum calculations, optical properties can be switched between ACQ and multi-state luminescence. This strategy is a valid strategy for designing the aggregation-caused quenching-resistant luminescent polymers.

Figure 14

CONCLUSION

Emission intensity and color of small-molecular dyes with solid-state luminescent properties are occasionally depended on molecular distribution in solid. In these cases, luminochromism can be correspondingly induced by morphology changes. On the other hand, when these stimuli-responsive luminescent molecules are polymerized, such

environmental responsiveness is often spoiled especially in film. Due to ACQ, emission intensity in film tends to be critically lowered. Furthermore, since polymer films generally form amorphous, only monotonous optical properties are able to be obtained. Even though crystallization can be partially induced, significant influence would be hardly obtained on optical properties. Meanwhile, mobility of flexible boron complexes in the excited state is restricted by the incorporation into polymer main-chains. This kind of “a frustrated state” is the origin for expressing environmental sensitivity, followed by stimuli-responsiveness in luminochromism. From a conventional stand point for obtaining luminescent dyes, a class of flexible complexes is out of potential targets. In contrast, it is demonstrated in this manuscript that material designs based on flexible element-blocks includes large possibility to present highly-sensitive stimuli-responsive polymer films. Hence, it can be said that not only exploration of new flexible element-blocks but also clarification of structural relaxation in the excited state could be a key study for making a breakthrough in the development of a new series of advanced luminescent devices and sensors.

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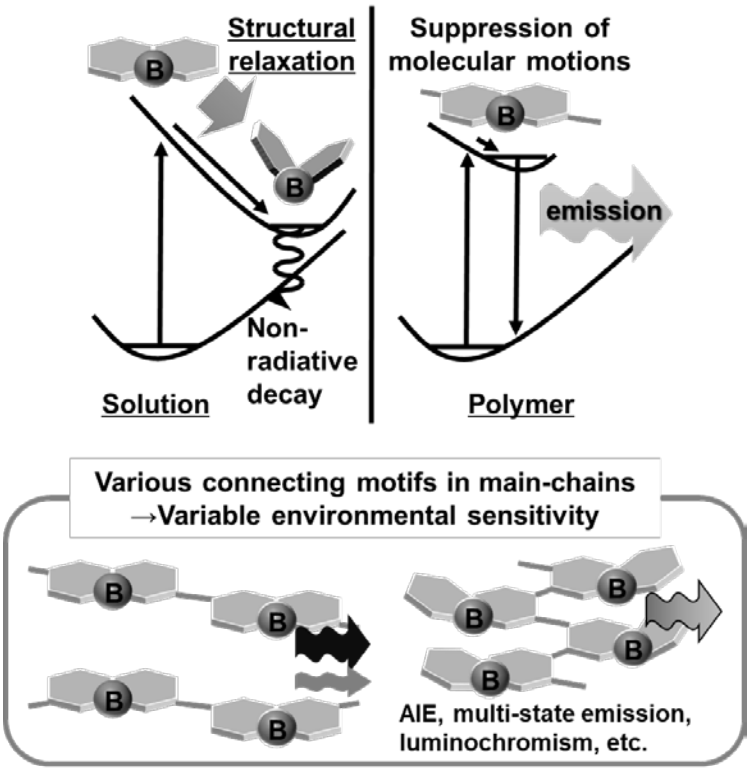
FIGURES



Scheme 1. Concept for obtaining stimuli-responsive luminescent polymers based on flexible boron complexes and tuning of stimuli-responsiveness by altering connecting points.

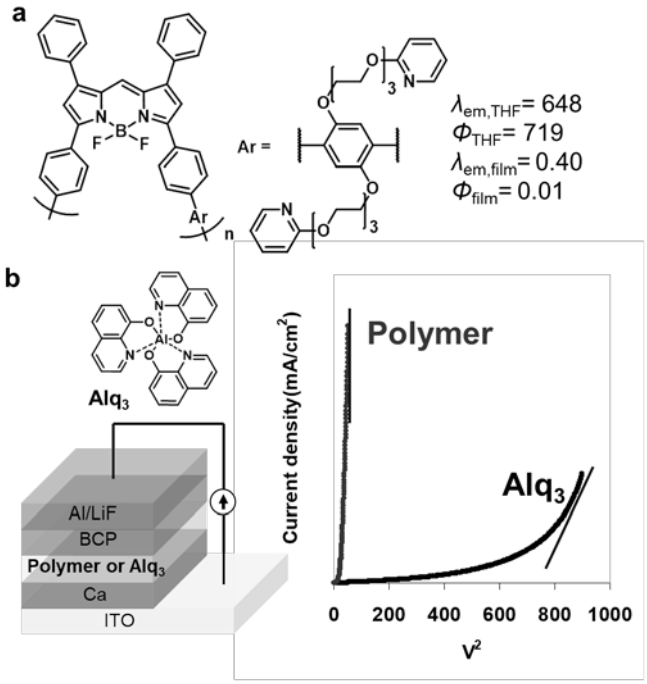


Figure 1. (a) Near-infrared emission and (b) superior electron-carrier ability of the BODIPY-containing polymer. Adapted with permission from ref. 17. Copyright 2014 American Chemical Society.

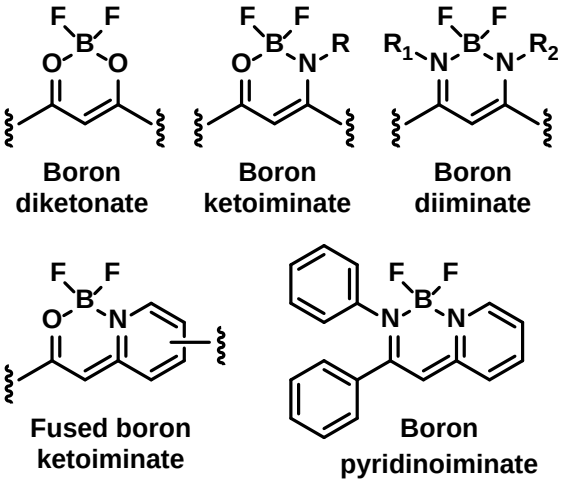


Figure 2. Chemical structures of boron complexes introduced in this review.

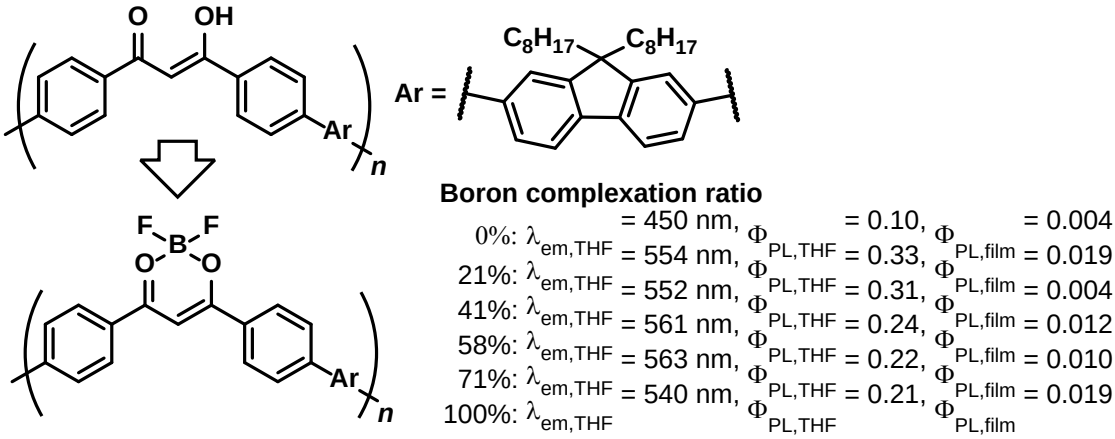


Figure 3. Enhancement of luminescent properties by boron complexation in the boron diketonate polymer.

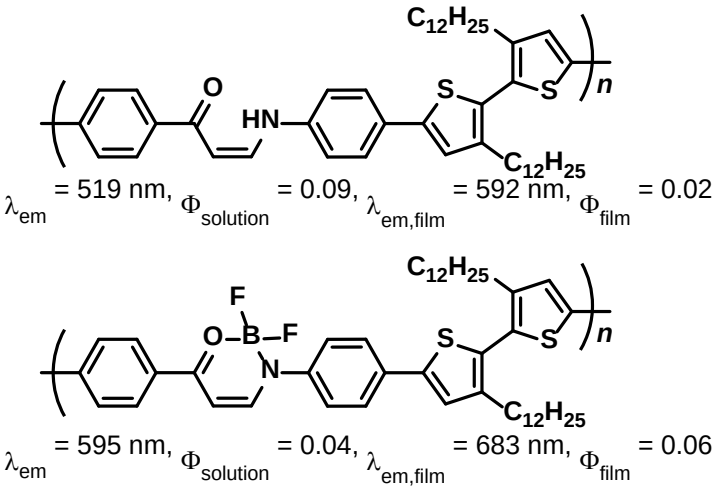


Figure 4. Chemical structures and optical properties of ketoiminate polymers with or without boron complexation.

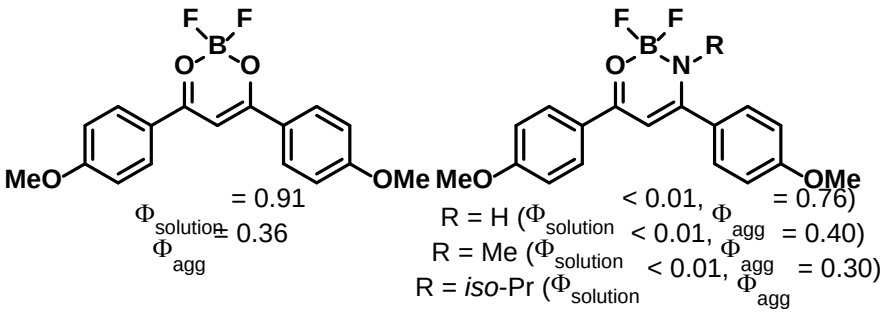
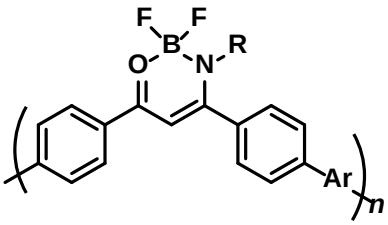
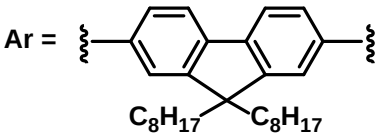
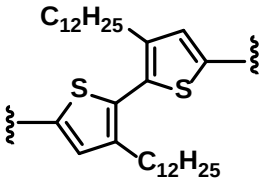


Figure 5. Chemical structures of boron ketoiminate derivatives and their optical properties.





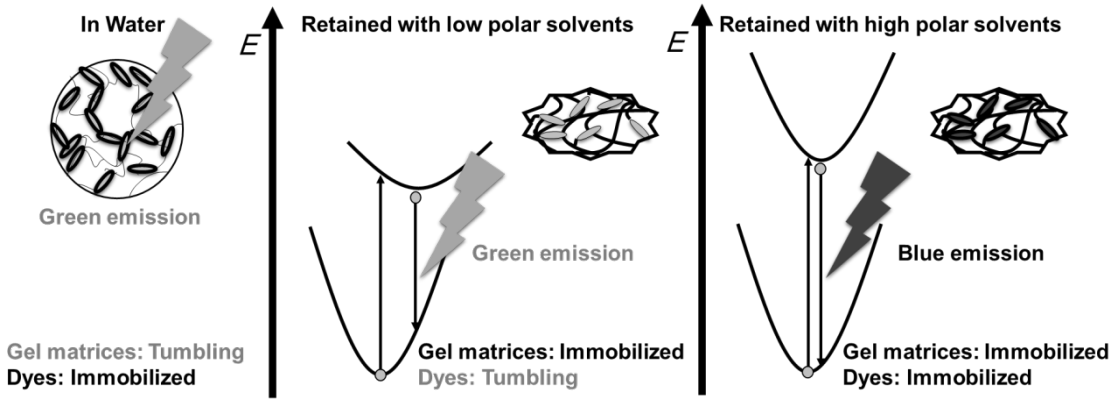
flu



bithio

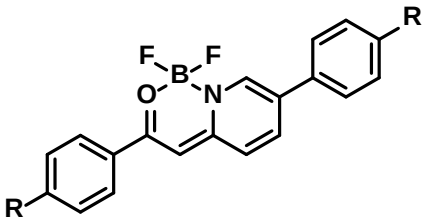
R = H; Ar = flu (λ_{em} = 514 nm, $\Phi_{solution}$ = 0.80, Φ_{film} = 0.38)
R = Me; Ar = flu (λ_{em} = 486 nm, $\Phi_{solution}$ = 0.46, Φ_{film} = 0.16)
R = H; Ar = bithio (λ_{em} = 604 nm, $\Phi_{solution}$ = 0.49, Φ_{film} = 0.13)
R = Me; Ar = bithio (λ_{em} = 556 nm, $\Phi_{solution}$ = 0.47, Φ_{film} = 0.22)

Figure 6. Chemical structures and optical properties of boron ketoiminate polymers with different connecting points.



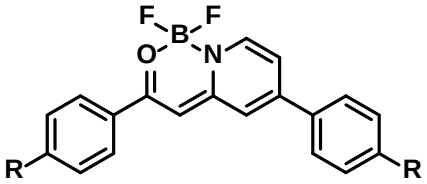
	Water	DMSO	DMF	MeCN	MeOH	Acetone	IPA	THF	Dioxane
λ_{em} (nm)	517	449	450	465	463	465	506	507	505
Φ_{PL}	0.083	0.059	0.055	0.054	0.098	0.048	0.11	0.029	0.058

Figure 7. Schematic illustration on aggregation-induced blue shift emission of boron ketoiminate-modified hydrogel. Reprinted with permission from ref 57. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.



R = H: $\lambda_{em,solution}$ = 450, $\Phi_{solution}$ = 0.17, $\lambda_{em,crystal}$ = 497, $\Phi_{crystal}$ = 0.25, $\lambda_{em,ground}$ = 466, Φ_{ground} = 0.20

R = OMe: $\lambda_{em,solution}$ = 468, $\Phi_{solution}$ = 0.58, $\lambda_{em,crystal}$ = 488, $\Phi_{crystal}$ = 0.68, $\lambda_{em,ground}$ = 479, Φ_{ground} = 0.64



R = H: $\lambda_{em,solution}$ = 460, $\Phi_{solution}$ = 0.35, $\lambda_{em,crystal}$ = 543, $\Phi_{crystal}$ = 0.38, $\lambda_{em,ground}$ = 507, Φ_{ground} = 0.24

R = OMe: $\lambda_{em,solution}$ = 463, $\Phi_{solution}$ = 0.80, $\lambda_{em,crystal}$ = 500, $\Phi_{crystal}$ = 0.81, $\lambda_{em,ground}$ = 496, Φ_{ground} = 0.97

Figure 8. Chemical structures and optical properties of fused boron ketoiminates.

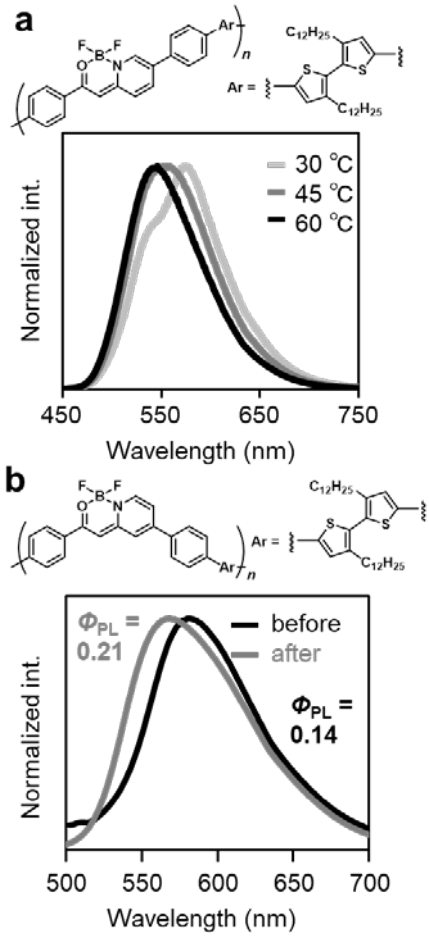
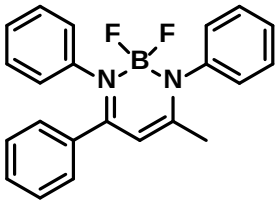
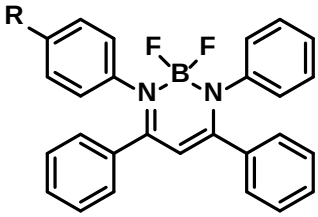


Figure 9. Chemical structures and (a) thermochromic luminescence in solution and (b) mechanochromic luminescence of the fused boron ketoiminate polymers. Reproduced from Ref. 62 with permission from The Royal Society of Chemistry.



λ_{em} = 448 nm, Φ_{agg} = 0.02, Φ_{cr} = 0.11



R = H (λ_{em} = 473 nm, Φ_{agg} = 0.02, Φ_{cr} = 0.23)
R = OMe (λ_{em} = 470 nm, Φ_{agg} = 0.04, Φ_{cr} = 0.59)
R = NO_2 (λ_{em} = 509 nm, Φ_{agg} = 0.01, Φ_{cr} = 0.04)
R = NMe_2 (λ_{em} = 602 nm, Φ_{agg} = 0.01, Φ_{cr} = 0.08)

Figure 10. Chemical structures and optical properties of boron diiminates.

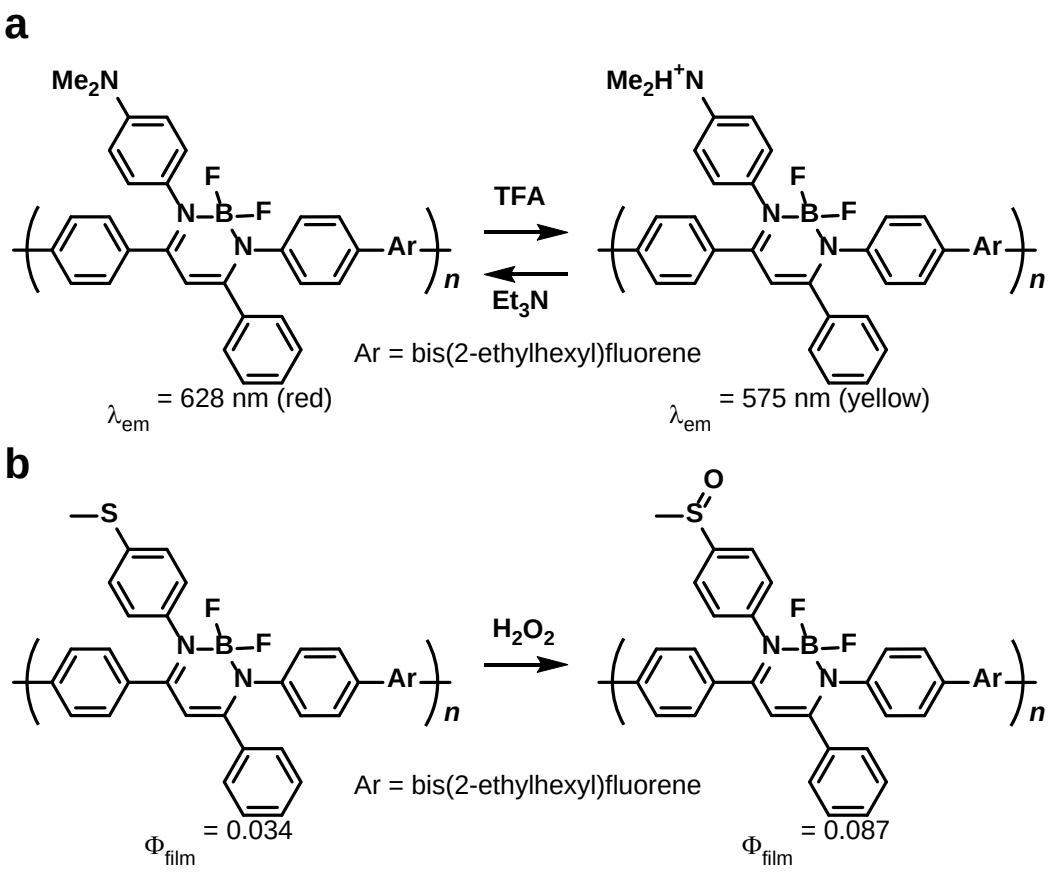


Figure 11. Chemical structures and plausible reaction schemes of film-type sensors for (a) acid vapor and (b) hydrogen peroxide.

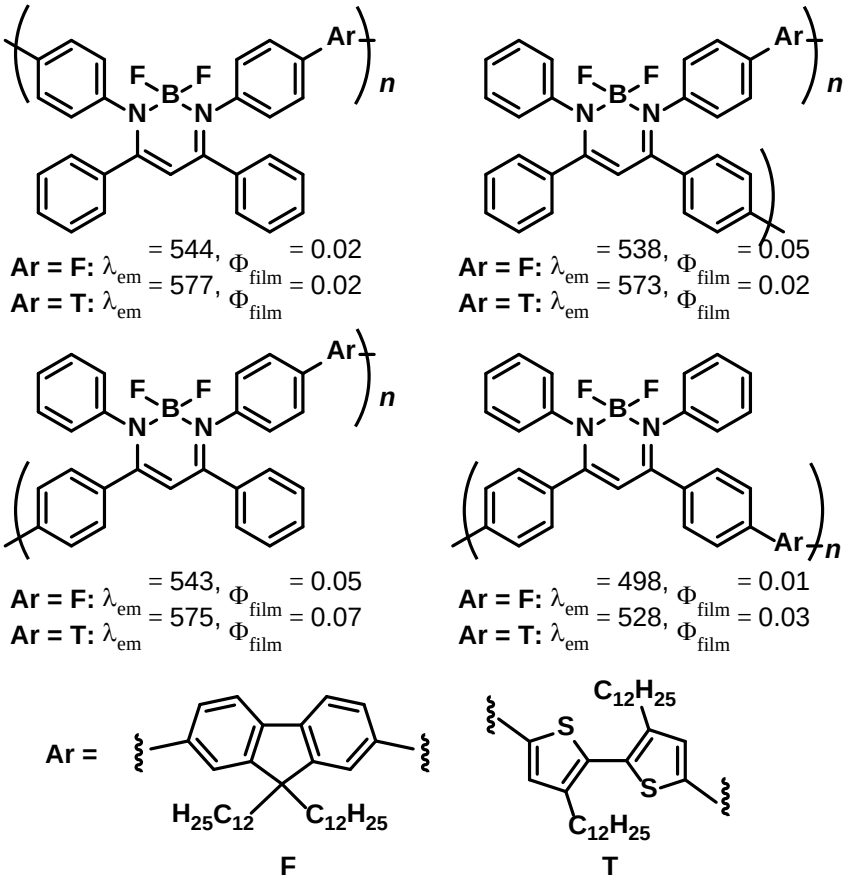


Figure 12. Chemical structures and optical properties of boron diiminate polymers with variable connecting points.

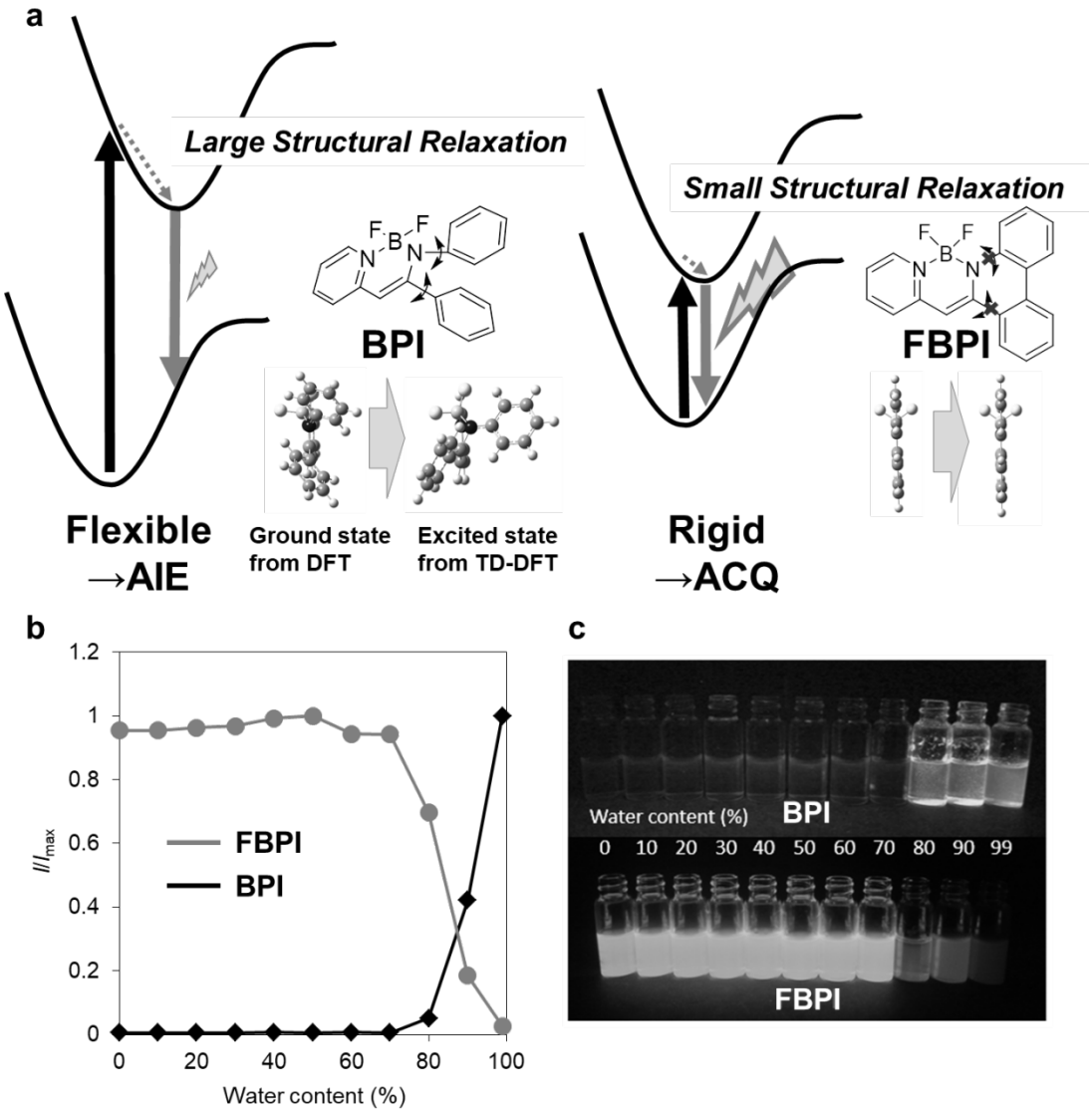


Figure 13. (a) Chemical structures of **BPI** and **FBPI** and plausible models of the difference in the degree of structural relaxation in the excited states. (b) Changes in intensity ratios by the aggregation formation in the THF solutions with variable water concentrations and (c) their appearances under UV irradiation (365 nm). Reproduced from Ref. 71 with permission from The Royal Society of Chemistry.

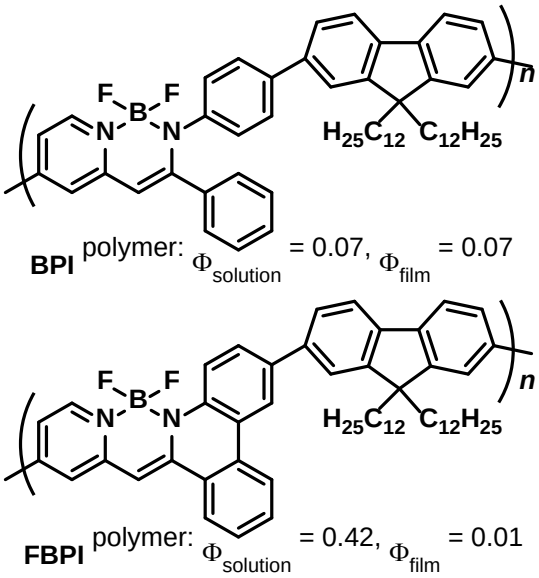


Figure 14. Chemical structures and optical properties of boron pyridinoiminate polymers.

GRAPHICAL ABSTRACT

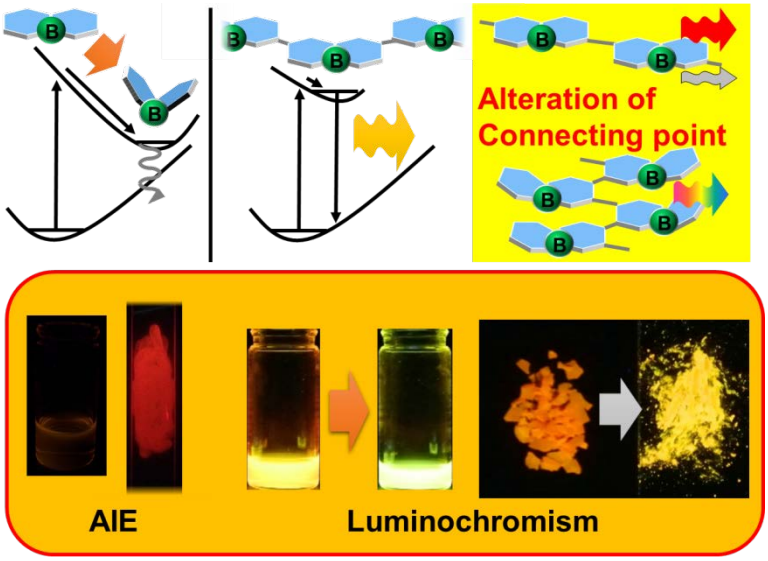


FIGURE LEGENDS

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