



Control of solution and solid-state emission with conjugated polymers based on the boron pyridinoiminate structure by ring fusion

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ABSTRACT

The two types of conjugated polymers were synthesized with boron pyridinoiminate with or without the fused structure in the ligand moiety. From optical measurements, it was shown that the polymer involving the fused complex had intense luminescent property only in the solution state. In contrast, another polymer presented similar emission intensities both in the solution and film states. By introducing the simple ring fuse structure, solution and solid-state luminescent properties of conjugated polymer can be tuned. Finally, the aggregation-caused quenching-resistant luminescent polymer can be produced.

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1. Introduction

One of great advantages of conjugated polymers as a platform for constructing advanced optically-functional materials is applicability of molecular designs at the monomer level for receiving desired functions from the final polymeric products. The one of potential strategies is to employ functional molecules containing heteroatoms and introduce them into main-chain conjugation. For example, these polymers are expected to be a key material for developing superior optoelectronic materials such as photovoltaic cells^{1,2} and luminescent devices^{3,4}. As a promising candidate for obtaining versatile functions, we have paid attention to “element-blocks”, which are defined as a minimum functional unit composed of heteroatoms.^{5,6} For instance, various types of solid-state luminescent boron difluoride complexes such with near-infrared emission^{7–9} and mechanochromism^{10–12} have been recently reported. By employing similar boron complexes as an element-block and combining with π -conjugated organic units, various types of materials having unique luminescent properties have been discovered from polymeric materials.^{13,14} Thus, introduction of functional units into polymer chains and evaluation of the resulting

properties are essential information for building advanced polymeric materials having superior properties.

Most of conjugated polymers can show intense emission in the diluted solution, while luminescence is usually spoiled in the condensed state due to aggregation-caused quenching (ACQ). Oppositely, the class of organic dyes presenting aggregation-induced emission (AIE) have been reported.^{15–18} In the diluted solution, these AIE-active molecules showed slight emission through emission quenching via molecular tumbling, meanwhile emission intensity is drastically enhanced in the aggregation by suppressing energy-consumable molecular motions.^{15–18} Because of large versatility, many researchers have dedicated much effort to explore new AIE-active molecules^{19–25} and to comprehend mechanism for applications of AIE-active molecules to optically-functional materials^{26–30}. Recently, we have demonstrated transformation from ACQ molecules to AIE-active ones by employing boron complexes.^{31,32} Simply by replacing the coordinated molecules with boron in the ligand and introduction of the connecting bond at the single site, the opposite behaviors were obtained. Based on the polymers having these AIE-inducible structures, the series of luminescent materials were developed, such as AIE-active polymers,³³ and the sensors for protein,³⁴ acid³⁵ or hydrogen peroxide.³⁶ It was proposed that degree of structural relaxation in the excited state which was regulated by the fused structure should be responsible for expressing AIE from boron complexes according to theoretical investigations.³⁷ Next our goal is to realize transformation with conjugated polymers for obtaining solid-state

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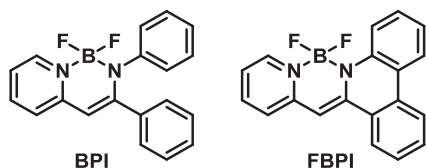
luminescent materials.

Herein, regulation between the ACQ and continuous emission behaviors is described based on the boron-containing conjugated polymer including the pyridinoiminate (Scheme 1)³² structure. According to our previous work, it was shown that boron pyridinoiminate was an AIE-active molecule.³² Moreover, it was demonstrated that molecular motions were suppressed by fusing the ligand moiety, followed by recovering bright emission even in the solution state. In addition, due to enhanced planarity, ACQ occurred in the solid state. As a result, the opposite responses were obtained from boron pyridinoiminate and the fused one. In this study, based on this mechanism, we designed the conjugated polymers containing the pyridinoiminate structure and detected the different luminescent behaviors in the solution and solid states before and after fusion at the molecular skeleton.

2. Results and discussion

The ligands for **BPI** and **FBPI** were prepared through the imine formation and the coupling reaction with imidoyl chloride and lithiated methylpyridine, respectively (Scheme S1).³² By treating these ligands with $\text{BF}_3 \cdot \text{OEt}_2$, the boron complex monomers were obtained. Polymerization was performed via the palladium-catalyzed Suzuki–Miyaura coupling with [9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid and the monomer in the toluene/water solvent mixture in the presence of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) and tris(dibenzylideneacetone) dipalladium ($\text{Pd}_2(\text{dba})_3$) (Scheme 2). The products were characterized with ^1H and ^{11}B NMR spectroscopies by comparing the spectra to those of the monomers (Charts S1–S9). From these data, it was confirmed that the products had the designed structures. The size exclusion chromatography (SEC) in CHCl_3 with the polystyrene standards revealed the number-average molecular mass (M_n) and the molecular mass distribution (M_w/M_n) of 8000 and 2.4 for **P-BPI**, 5200 and 1.7 for **P-FBPI**, respectively (Table S1). The thermal properties of the synthesized polymers were investigated with thermogravimetric analyses (Figure S1 and Table S1). The decomposition temperatures with 5 wt % weight losses (T_{d5}) of boron pyridinoiminate polymers were observed at 409 °C for **P-BPI** and 411 °C for **P-FBPI**. In the previous report, it was already known that **BPI** and **FBPI** showed lower thermal stabilities ($T_{d5} = 256\text{--}312$ °C).³² It was clearly indicated that polymerization of boron pyridinoiminate improved thermal stability.

Optical properties of **P-BPI** and **P-FBPI** in the ground state were investigated (Table 1). In UV–vis absorption spectra in CHCl_3 (1.0×10^{-5} M), large absorption bands attributable to $\pi\text{--}\pi^*$ transition were observed from both polymers (Figure 1). Compared to **BPI** and **FBPI**, longer wavelength shifts of absorption bands were observed (**P-BPI**: +43 nm, **P-FBPI**: +45 nm), indicating extension of conjugated system through polymer chains.³² **P-FBPI** showed the larger absorption band in the longer wavelength region than **P-BPI**. This result means that **P-FBPI** had smaller band gap energy than **P-BPI**. Because of higher planarity of the fused structure in **P-FBPI**, π -conjugation should be developed through the polymer chain.



Scheme 1. Chemical structures of boron pyridinoiminates.

To determine energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both complexes, cyclic voltammetry (CV) was carried out with the solution samples (Figure S2 and Table S2). From the onset values of the first reduction waves, LUMO levels were determined. Their HOMO energy levels were calculated from LUMO energy levels and energy band gap E_g which was obtained from the onset wavelength in the UV–vis absorption spectra. These electrochemical data also indicated that the narrower band gap of **P-FBPI** appeared than that of **P-BPI**. Quantum chemical calculations with the density functional theory (DFT) method at the B3LYP/6-31G (d) level were performed (Figure S3).³⁷ Corresponding to the experimental data, **P-FBPI** presented the narrower band gap originated from higher HOMO and lower LUMO levels. It is likely that the higher planar fused structure in **P-FBPI** should contribute to extension of π -conjugated system. Then, the narrower band gap was obtained.

To examine electronic structures in the excited state, photoluminescence (PL) spectra were measured with the solution samples (1.0×10^{-5} M in CHCl_3) containing the polymers (Figure 1 and Table 1). **P-BPI** presented the emission band with the excitation light at the peak wavelength of the absorption band (449 nm), meanwhile, due to small degree of the Stokes shift in **P-FBPI** originated from the rigid structure, the excitation light at 350 nm was irradiated to the solution of **P-FBPI**. Compared to **BPI** and **FBPI**, longer wavelength shifts of emission bands were observed (**P-BPI**: +74 nm, **P-FBPI**: +75 nm).³² Extension of π -conjugation should be responsible for these shifts. Distinctly differences in luminescent efficiencies were observed with the solutions. The luminescence quantum yield of **P-BPI** was very small ($\Phi_{\text{PL}} = 0.07$), while **FBPI** showed efficient emission ($\Phi_{\text{PL}} = 0.42$). Compared to **BPI** and **FBPI** ($\Phi_{\text{PL}} = 0.01$), **P-BPI** showed stronger emission. It was proposed that emission quenching of the boron pyridinoiminate moiety in solution state should proceed during large structural relaxation in excited state.³² Indeed, from the calculation of the rates of radiative (k_r) and non-radiative (k_{nr}) processes, the larger k_{nr} value was obtained from **P-BPI** than that from **P-FBPI** (Table 1). It is likely that structural restriction by connecting to the comonomers can inhibit molecular motions in solution state.

PL spectra were measured in 2-methyltetrahydrofuran (2-MeTHF) at 77 K (1.0×10^{-5} M, Figure S4 and Table 1) to investigate influence of suppression of molecular motion and structural relaxation on optical properties. Under frozen condition, both complexes showed larger emission bands in the shorter wavelength regions than those under room-temperature condition. It should be emphasized that **P-BPI** presented bright emission, indicating that intramolecular motion should be responsible for excitation decay peculiarly in **P-BPI**. By cooling, the emission bands in the longer wavelength region appeared. According to the previous work, these emission bands are attributable to phosphorescence.³²

Finally, optical properties of **P-BPI** and **P-FBPI** in the film state were investigated (Figure 2 and Table 1). Compared to the solution states, PL spectra showed longer wavelength shift. Because of intermolecular interaction such as stacking, bathochromic shifts should be induced. The luminescence quantum yield of **P-BPI** in the film state was similar ($\Phi = 0.07$) to that in the solution, while critical reduction of emission efficiency of **P-FBPI** ($\Phi = 0.01$) was detected in the film. These data indicate that **P-BPI** is the ACQ-resistant luminescent polymer, whereas **P-FBPI** shows ACQ similarly to conventional conjugated polymers. By fusing the ligand moiety in the boron complex, molecular planarity should be drastically improved. As a consequence, the conventional luminescent behavior with bright emission in the solution state and ACQ in the film was obtained from **P-FBPI**. Meanwhile, in the case of **P-BPI**, several factors should be responsible for luminescent properties.

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