



Synthesis, properties and structure of borafluorene-based conjugated polymers with kinetically and thermodynamically stabilized tetracoordinated boron atoms

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Abstract

Herein, borafluorene-conjugated polymers with a dibromoborafluorene monomer and various boronic acid ester comonomers are reported. By employing the Suzuki–Miyaura cross-coupling reaction, a series of copolymers was prepared with the boron atoms in tetracoordinated states. Based on comparison to the optical properties of gallafluorene copolymers, higher luminescence quantum yields were obtained from the synthesized borafluorene copolymers due to the weak spin-orbit interaction of boron compared to that of gallium. Additionally, the results from the electrochemical measurements indicated that the electron-withdrawing property of the boron atoms led to stabilization of the lowest unoccupied molecular orbitals (LUMOs) of the borafluorene copolymers. In the X-ray diffraction profiles, significant peaks originating from π – π stacking and assembly of the side chains were observed. The borafluorene copolymers were more crystalline than the gallafluorene polymers.

Introduction

By introducing “element-blocks”, which are defined as minimum functional units composed of heteroatoms, into conjugated systems, unique characteristics are often obtained due to the electronic states of the heteroatoms [1, 2]. Therefore, “element-blocks” with group 13 elements are typical candidates for constructing luminescent materials [3–17]. For example, the boron atoms in the main chain of conjugated polymer systems have various properties, such as electronic-defective [18, 19], a strong electron acceptor in the donor–acceptor system [20–22] and affinity for fluoride anions [23–25]. Based on these properties,

boron-containing conjugated polymers are expected to be a platform for developing advanced optical materials [26–31]. Furthermore, a series of gallium-containing stable “element-blocks” were obtained by developing sophisticated synthetic protocols and chemical tactics for improving molecular stability [32–38]. Similar or occasionally distinctly different luminescent properties have been observed for boron [32, 33].

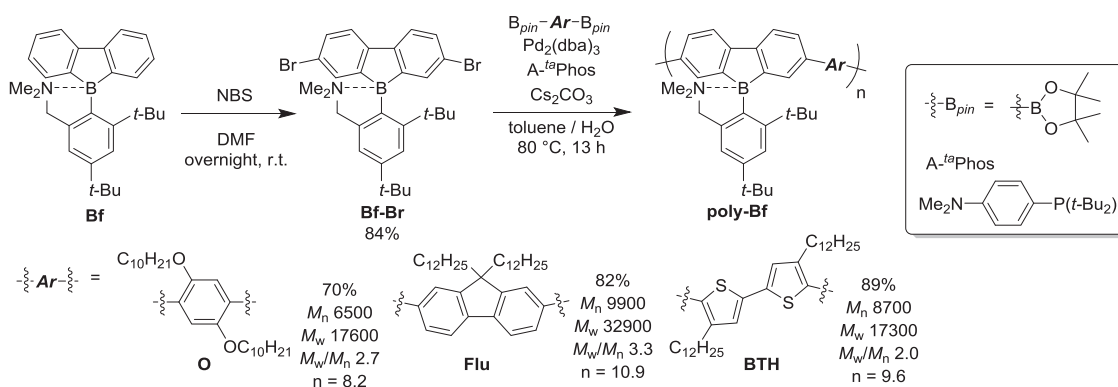
To establish the material-design strategy using “element-blocks”, as well as heteroatoms, a deep understanding of the influence of heteroatoms on the electronic properties is required. Heterofluorene is a versatile structure for incorporation of heteroatoms into aromatic conjugation [39–43]. By modulating the type of bridging atom, electronic structures can be greatly varied. To obtain systematic information, the effect of boron on the electronic properties of the conjugated polymers has been investigated with a series of borafluorenes [20, 23, 25, 44–46]. Although significant characteristics have been clarified from comparisons with group 13 element-containing heterofluorene molecules [44], the number of studies with conjugated polymers remains limited. To gain insight into the contribution of the heteroatom to the electronic properties, construction of conjugated polymers and comparison of their electronic structures are essential.

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Scheme 1 Synthesis of borafluorene-based conjugated polymers

Herein, the syntheses and optical properties of a series of alternating copolymers composed of borafluorene and various types of comonomers are reported. Polymerization was performed via the Suzuki–Miyaura cross-coupling reaction to yield the desired copolymers. Based on comparison to the optical properties of gallafluorene copolymers with the same structures, the borafluorene copolymers exhibited higher luminescent quantum yields. Moreover, lower LUMO levels were observed in the borafluorene copolymers than in the gallafluorene ones. Therefore, the stronger electron-withdrawing ability of boron may play a role in lowering of the LUMO energy level. The morphology differences in the polymer films are also discussed.

Results and discussion

The dibromoborafluorene monomer was synthesized according to a previously reported protocol [46]. The peak that originated from boron was observed at 5.57 p.p.m. in the ^{11}B NMR spectrum. This result indicates that the boron atom formed a tetracoordinated structure in the monomer. The polymerization progressed via a Suzuki–Miyaura coupling reaction in the presence of tris(dibenzylideneacetone)dipalladium ($\text{Pd}_2(\text{dba})_3$) and A^{ta}Phos with various comonomers, such as dialkoxybenzene (O), fluorene (Flu), and bithiophene (BTH), which are shown in Scheme 1. The number average molecular weights of the products were estimated using size-exclusion column chromatography (Table 1). The corresponding NMR spectra were obtained of the monomer units in the ^1H NMR spectra. In particular, as shown in their ^{11}B NMR spectra, the signal peaks were observed at ~ 3.00 p.p.m. These values indicate that the boron atoms exhibited a tetracoordinated structure even in the polymers [46]. The synthesized polymers had good solubility in common organic solvents, such as chloroform, dichloromethane, and tetrahydrofuran. Moreover, critical decomposition was barely detected during analyzes under ambient atmosphere. Therefore, the products possess the

Table 1 Reaction yields, molecular weights, and decomposition temperatures of the products

	Yield ^a (%)	M_n^b	M_w^b	M_w/M_n^b	DPn ^c
poly-BfO	70	6500	18,000	2.7	8.2
poly-BfFlu	82	9900	33,000	3.3	10.9
poly-BfBTH	89	8700	17,000	2.0	9.6

^aIsolated yield

^bEstimated by size-exclusion chromatography (SEC) based on polystyrene standards in chloroform

^cAverage number of repeating units estimated from M_n and molecular weights of the repeating units

desired structures with sufficient stability for optical measurements.

To compare the electronic structures of borafluorene and gallafluorene polymers, the optical properties of the synthesized borafluorene polymers were investigated (Fig. 1, Table 2). The data from the gallafluorene polymers are summarized in Supplementary Tables S2, S3 in the Supporting Information [47]. Initially, the absorption and photoluminescence spectra were measured in the solution state. The shapes of the spectra were varied by changing the comonomer units. Additionally, absorption and emission bands were observed at similar positions for both the borafluorene and gallafluorene polymers with the same comonomers. This result indicates that electronic delocalization should occur through the polymer backbone. Moreover, the effect of replacing boron with gallium on electronic structures should be small due to conjugation in the main chain. In the solution state, the emission quantum yields of the borafluorene polymers were higher compared to those of the gallafluorene polymers. Boron is a low period element and possesses weak spin-orbit interaction. Intersystem crossing from singlet states to triplet states can be excluded in borafluorene polymers. Therefore, suppression of vibrational quenching in the triplet excited states can be obtained, resulting in a higher emission efficiency. In the film state, bathochromic luminescence bands or shoulders in the

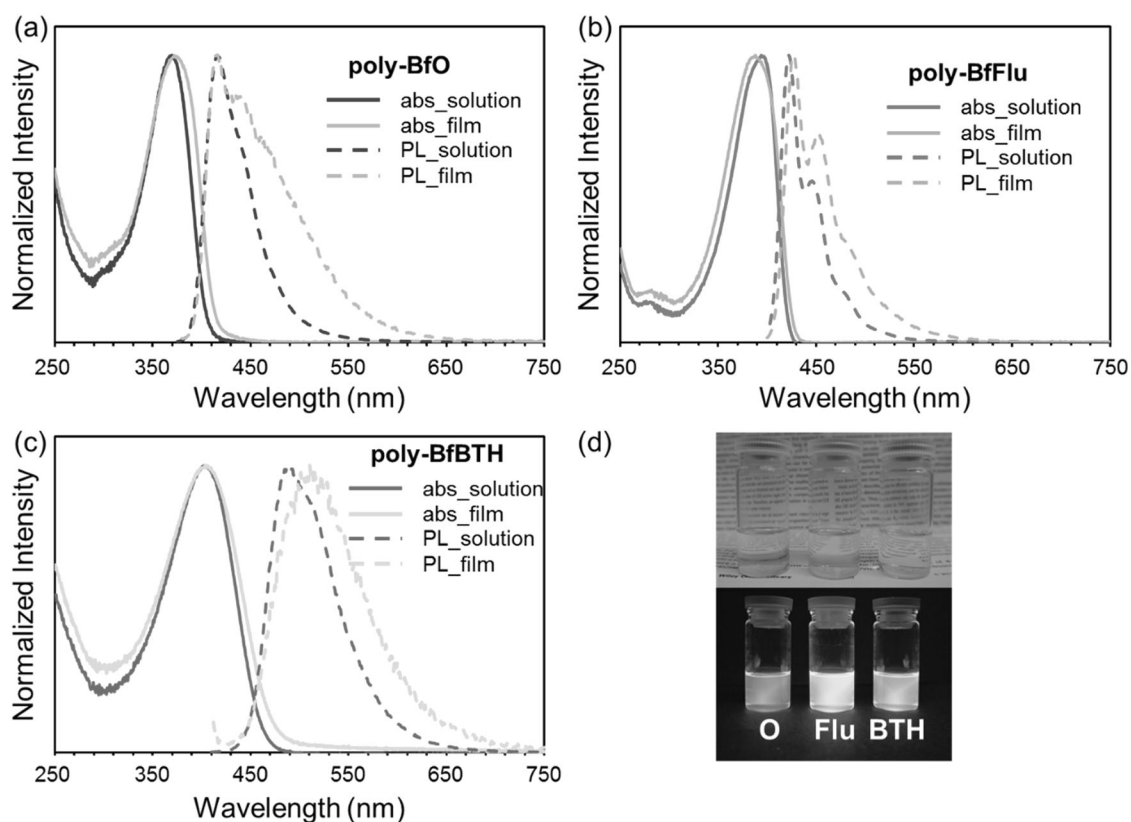


Fig. 1 UV–Vis absorption (solid lines) and photoluminescence (excited at $\lambda_{\text{abs, max}}$, dashed lines) of a 1.0×10^{-5} M CHCl_3 solution and films of **a** poly-BfO, **b** poly-BfFlu, and **c** poly-BfBTH.

d Photographs of the polymers in chloroform under visible (top) and UV light ($\lambda = 365$ nm, bottom) irradiation (Color figure online)

Table 2 UV–Vis absorption and photoluminescence data for the borafluorene polymers

	$\lambda_{\text{max,abs}}$ (nm) ^{a,b}	ϵ ($\text{cm}^{-1} \text{M}^{-1}$) ^{a,c}	$\lambda_{\text{max,abs}}$ (nm) ^d	$\lambda_{\text{max,FL}}$ (nm) ^{a,e}	$\Phi_{\text{F}}^{\text{f}}$	$\lambda_{\text{max,FL}}$ (nm) ^{d,e}	$\Phi_{\text{F}}^{\text{d,f}}$
O	370	3.82×10^4	372	416	0.52	416	0.06
Flu	395	7.01×10^4	388	422	0.80	428	0.09
BTH	403	3.64×10^4	405	491	0.29	510	0.02

^aDetermined in chloroform (1.0×10^{-5} M)

^bAbsorption maxima

^cMolar extinction coefficients at the absorption maxima

^dDetermined with the film samples

^eFluorescence maxima with the excitation at $\lambda_{\text{max,abs}}$

^fAbsolute quantum yield

redshifted region were observed in the photoluminescence spectra of the borafluorene polymers compared to those in the solution state. Intermolecular interactions, such as π – π stacking, should be induced, and slight peak shifts were observed.

To evaluate the energy levels of the frontier orbitals, cyclic voltammetry was employed using the borafluorene polymers in the film state (Table 3, Supplementary Fig. S12). The energy levels of their highest occupied molecular orbitals (HOMO) and lowest unoccupied MO

(LUMO) were calculated from the onset of the oxidation and reduction waves using the following equations [48]:

$$E_{\text{HOMO}} = -4.8 - E_{\text{ox}},$$

$$E_{\text{LUMO}} = -4.8 - E_{\text{red}}.$$

The energy levels of the frontier orbitals for all borafluorene polymers decreased relative to those of the gallafluorene polymers. In particular, the LUMOs of the borafluorene polymers were substantially lower. Boron

Table 3 Electrochemical properties of the borafluorene polymers^a

	E_{ox} (V) ^b	E_{red} (V) ^c	E_{HOMO} (eV) ^d	E_{LUMO} (eV) ^e	E_{g} (eV) ^f
poly-BfO	0.61	-1.98	-5.41	-2.82	2.59
poly-BfFlu	0.68	-2.20	-5.48	-2.60	2.89
poly-BfBTH	0.49	-1.99	-5.29	-2.81	2.48

^aMeasured by cyclic voltammetry of polymer films cast on ITO substrates. The measurement was carried out in an acetonitrile solution containing LiClO₄ (0.10 M) as a supporting electrolyte with a Pt wire electrode, a Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature using a scan rate of 0.01 V/s under Ar

^bEstimated from the onset of the first oxidation wave (vs Fc/Fc⁺)

^cEstimated from the onset of the first reduction wave (vs Fc/Fc⁺)

^d $E_{\text{HOMO}} = -4.8 - E_{\text{ox}}$

^e $E_{\text{LUMO}} = -4.8 - E_{\text{red}}$

^f $E_{\text{g}} = E_{\text{LUMO}} - E_{\text{HOMO}}$

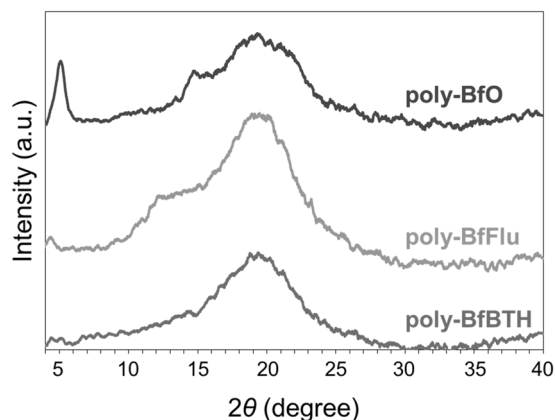


Fig. 2 X-ray diffraction of poly-BfO, poly-BfFlu, and poly-BfBTH in their film states on a slide glass after 2 h of annealing at 120 °C (Color figure online)

has a larger electronegativity than gallium. Therefore, these stabilization effects may result from the weaker electron-donating property of boron compared to that of gallium [49, 50].

The morphology of the polymers in the film states was evaluated from the X-ray diffraction analyzes. The profiles are shown in Fig. 2. The peaks corresponding to alignment of the polymer backbones were observed at $\sim 2\theta = 20^\circ$ for all borafluorene polymer films. A significant peak was only observed at $2\theta = 5.1^\circ$ in the poly-BfO film. The sharp diffraction peak may originate from the regular structures of the aligned side chains in poly-BfO. For gallafluorene polymers, broad, and weak peaks were observed at $\sim 19^\circ$ compared to those for the borafluorene-based polymers (Supplementary Fig. S13). These data suggest that the borafluorene polymers may have higher crystallinity than the gallafluorene polymers. Electrostatic intermolecular interactions may have been formed due to the strong

electron-withdrawing properties of the boron atoms. Therefore, the boron atoms may contribute to improving the crystallinity.

Conclusion

A series of alternating copolymers with borafluorene were synthesized using palladium-catalyzed Suzuki–Miyaura cross-coupling reactions. The tetracoordinated states of the boron atoms were maintained after polymerization. Based on the optical measurements, the electronic properties of the conjugated polymers were evaluated and compared to those of gallafluorene polymers with the same skeleton. Extension of the π -conjugated system along the polymer backbone was observed, and higher quantum emission efficiencies were obtained from the borafluorene polymers than from the gallafluorene polymers. The electron-withdrawing property of the boron atom led to deeper LUMO levels relative to those in the gallafluorene polymers. Moreover, based on morphology analyzes of the film states, poly-BfO can partially form a crystalline state. In summary, this study demonstrates that electronic and structural alterations can be induced in conjugated polymers by replacing the type of heteroatom in the same element group.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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