

A Near-Infrared Absorptive and Emissive Poly(*p*-phenylene vinylene) Derivative Containing Azobenzene–Boron Complexes

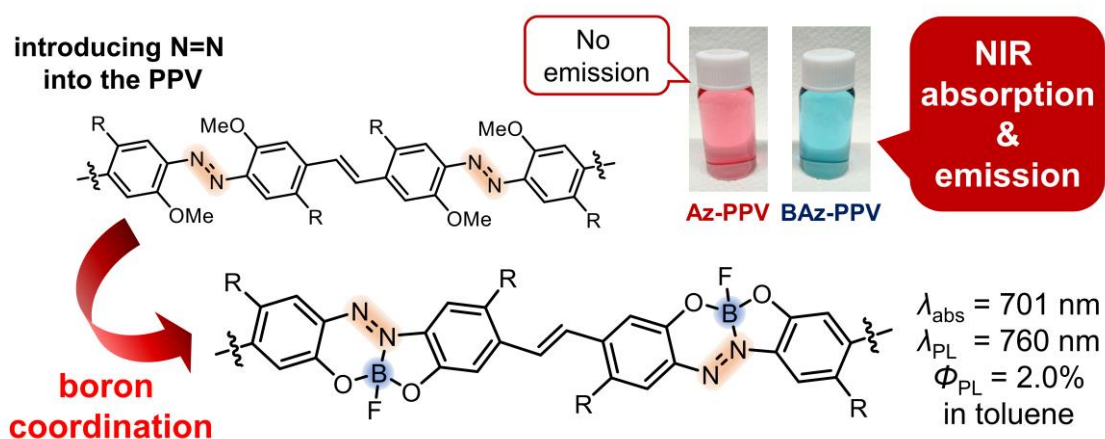
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Key words: near-infrared absorption; near-infrared emission; poly(*p*-phenylene vinylene); azobenzene; boron

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Abstract

Poly(*p*-phenylene vinylene) (PPV) is known to be a typical π -conjugated polymer and used as a commodity platform for constructing optoelectronic organic devices because of superior optical and material properties. PPV derivatives generally show large degree of light absorption and intense emission in the visible region, meanwhile very few examples have been reported to offer near-infrared (NIR)-absorptive and emissive PPV derivatives. In this study, we designed and synthesized a novel PPV derivative, named **BAz-PPV**, containing boron-fused N=N double bond units in the main chain. **BAz-PPV** showed intense NIR absorption and emission ($\lambda_{\text{abs}} = 702 \text{ nm}$, $\lambda_{\text{PL}} = 760 \text{ nm}$ and $\Phi_{\text{PL}} = 2.0\%$ in diluted toluene). This polymer had a narrow energy band gap because of not only extension of main chain π -conjugation over 50 monomer units but also stabilization of energy level of the lowest unoccupied molecular orbital (LUMO). Moreover, the polymer shows high stability toward photo-degradation and sufficient carrier-transport ability for the applications to organic semiconducting devices. Advantages of the introduction of the N=N double bond to main-chain conjugation followed by the boron coordination for the development of NIR materials is demonstrated in this manuscript.

Introduction

Owing to the development of various synthetic approaches and the improvement of accuracy of quantum calculations, π -conjugated polymers have increasingly attracted attention as a promising platform for fabricating advanced optoelectronic materials.¹ π -Conjugated polymers show luminescent properties and high carrier-transport ability originating from their extended π -conjugated systems through polymer main chains and flexibility, lightness, solubility and processability similarly to typical polymers. Therefore, π -conjugated polymers have been applied as a key component in a variety of organic devices, such as photovoltaic cells², organic light emitting diodes (OLEDs)³ and organic field-effect transistors.⁴ Among various types of π -conjugated polymers, poly(*p*-phenylene vinylene) (PPV) is one of representative skeletons.⁵ Comparing to the structures consisting of direct connection between aromatic rings, planar structures are obtained in the PPV structure because of smaller steric hindrances. In addition, rotations around the polymer chain, which are generally observed in the ethynyl-inserted structure, are suppressed in the PPV structure. Therefore, it can be said that the PPV structure is favorable for building robust π -conjugated systems through polymer main chains. On the basis of these structural advantages, to control optical properties, such as absorption and luminescent color, several PPV derivatives have been designed and indeed applied for polymer-based OLEDs.⁶ Carrier mobility is also tuned with the PPV-based materials. Pei, J *et al.* reported the rigid coplanar PPV derivatives with electron-withdrawing groups and hydrogen bonds displayed high electron mobility.^{7,8} Much effort has been still directed to develop advanced optoelectronic polymers based on the PPV derivatives.

One of potential approaches for developing π -conjugated polymers having unique properties is to replace C=C double bonds with heteroatom–heteroatom ones into main-chain conjugation. Although there are still challenges to obtain the polymers including the heteroatom–heteroatom double bond in main chains due to synthetic difficulty and instability of these kinds of bonds, owing to the recent developments in synthetic chemistry, several examples were accomplished and intriguing functions have been discovered. Protasiewicz *et al.* reported the optical properties of the PPV derivatives including P=P double bonds stabilized by the bulky substituents.⁹ It was revealed that the P=P double bonds play a critical role in emission annihilation of the PPV moiety. Tamao *et al.* presented that the π -conjugated oligomers containing Si=Si double bonds and found bathochromic shifts of absorption and luminescence bands in the optical spectra in comparison to the structural analogues replaced with the C=C double bond.¹⁰ This means that electronic interaction could occur through polymer main chains. The azobenzene unit, which includes an N=N double bond and is well known to exhibit *cis-trans* photoisomerization,¹¹ is also inserted into polymer main chains. Masuda *et al.* reported PPV derivatives containing azobenzene in the main chain and their stimuli-responsiveness.^{12–14} As is commonly known that azobenzene is non-emissive moiety because of photoisomerization in the excited state,^{11,15,16} the π -conjugated polymer showed slight emission and their electronic properties, such as carrier mobility, are still veiled.

Four-coordinate organoboron compounds with the rigid ligand often show good photoluminescence quantum yields and high hole and/or electron mobility.^{17–34} The boron coordination can improve molecular rigidity and planarity which lead to

functional luminescent materials. The coordination potentially lowers the energy level of the lowest unoccupied molecular orbital (LUMO) because of the interaction between a lone pair of a nitrogen atom and a vacant p-orbital of a boron atom.^{35,36} Kawashima *et al.* reported that by forming a N–B coordination with azobenzene, the resulting complexes showed intense fluorescence.^{37–40} It is clarified that fluorescence can be induced by intramolecular N–B interaction which inhibits photoisomerization at the azobenzene scaffold and allowed the electronic transition related to the emission.

Recently, we proposed the concept for a new material design with a “element-block” which is a minimum functional unit containing heteroatoms.^{41,42} By the connection, combination and assembly of element-blocks, we expect to create highly-functional polymeric materials with the properties originating from incorporated heteroatoms. By focusing on boron atoms, we have obtained various optical and/or electronic materials such as narrow band gap polymers,^{43,44} electron-carrier polymers,⁴⁵ dual emission molecules,^{46–48} stimuli-responsive materials.^{49,50} More recently, we reported highly-emissive donor–acceptor (D–A) type π -conjugated polymers containing azo (--N=N--)^{51,52} or azomethine (--C=N--) linkages.⁵³ By the coordination of boron to the ONO-type azobenzene tridentate ligand, photoisomerization can be efficiently restricted in the resulting boron-fused azobenzene complex. Consequently, near-infrared (NIR) emission can be induced from the strong D–A interaction derived from the largely-stabilized LUMO level of the boron-fused azobenzene complex. However, the absorption wavelength was still in the visible region due to the limited conjugation system. Additionally, electronic data, such as carrier transport ability, regarding non D–A type N=N double bond-based polymers were completely concealed. Thus, construction of robust π -conjugation involving N=N bonds and fundamental

understanding on their electronic properties are of great significance not only for clarifying another role of heteroatoms but also for producing NIR materials based on a new strategy.

In this study, we designed an NIR absorptive and emissive polymer with the PPV structure by employing an N=N double bond. Two key ideas are involved in the molecular design to fulfill NIR absorption and emission. First, by replacing C=C double bonds with N=N ones in the PPV structure, the significant effect to narrow energy band gaps is presumable according to quantum calculation.⁵⁴ Second, by using the N=N double bond as a coordination point with boron in the polymer main chain, further narrowing is expected. It is suggested that skeletal planarity and rigidity can be greatly enhanced by boron coordination. These structural features are advantageous for reinforcing electronic interaction, followed by bathochromic shifts of absorption and emission bands. In order to prove validity of this idea, we synthesized polymers and evaluated their optical properties.

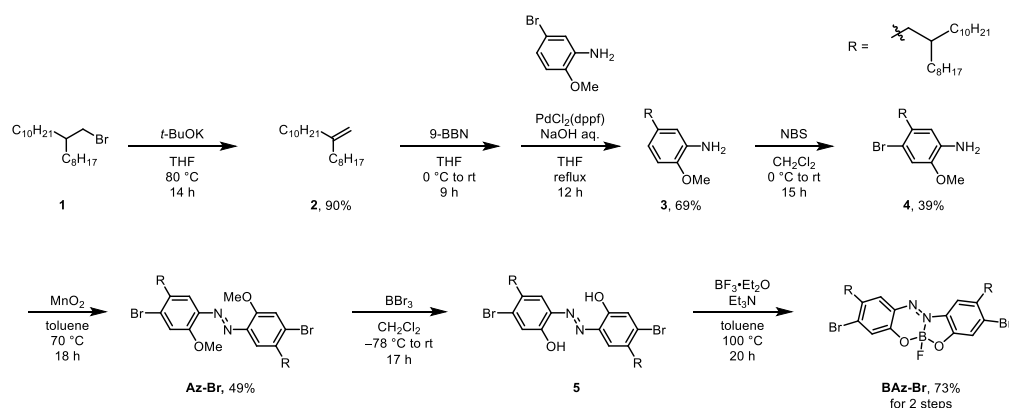
Results and Discussion

Synthesis

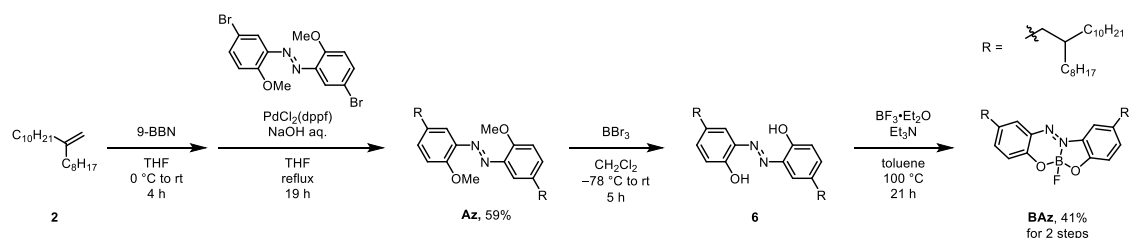
Scheme 1 shows the synthesis of monomers. At first, we introduced branched alkyl chains for improving solubility in common organic solvents, such as toluene, chloroform and dichloromethane. We synthesized 9-methylenenonadecane (**2**) from 9-(bromomethyl)nonadecane (**1**) by E2 reaction. Compound **2** was subject to a hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN) to obtain a solution of B-alkyl-9-BBN, and subsequently alkylated aniline **3** was obtained in the Suzuki–Miyaura cross-coupling reaction with 5-bromo-2-methoxyaniline in 69% isolated yield.⁵⁵ Compound **3** was brominated by *N*-bromosuccinimide to obtain **4** in 39% isolated yield. An oxidative coupling reaction of **4** with manganese(IV) oxide (MnO₂) was carried out to afford azobenzene derivative **Az-Br** in 49% isolated yield. Methoxy groups of **Az-Br** were converted to hydroxyl groups (**5**) with boron tribromide (BBr₃) and the compound **5** was readily reacted with BF₃·Et₂O to afford **BAz-Br** as a deep red oil in 73% isolated yield in 2 steps. Model compounds were synthesized according to Scheme 2. **BAz** without Br atoms was prepared from 1,2-bis(5-bromo-2-methoxyphenyl)diazene.⁵² **Az** was obtained through the Suzuki–Miyaura cross-coupling reaction with the same procedure with **3** in 59% isolated yield. **BAz** was also obtained by the transformation from methoxy groups of **Az** to hydroxyl ones (**6**), followed by the boron coordination with BF₃·Et₂O (41% in 2 steps).

As shown in Scheme 3 and Table 1, polymerization of **BAz-Br** was carried out with *trans*-1,2-bis(tributylstannyl)ethylene (**7**) in the catalytic system of Pd₂(dba)₃ using 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) as a phosphine ligand. The polymeric product **BAz-PPV** was obtained in 68% isolated yield, and polymer

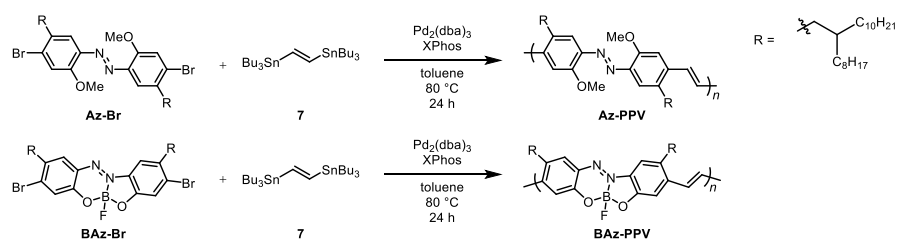
properties ($M_n = 46,700$, $M_w/M_n = 3.2$) were determined by gel permeation chromatography (GPC) with polystyrene standards by using chloroform as an eluent (Figure S1). A non-fused polymer **Az-PPV** was also prepared in 75% isolated yield ($M_n = 35,500$, $M_w/M_n = 2.9$) with the same coupling reaction condition as **BAz-PPV** by using **Az-Br** as a monomer. The structures of all new compounds in this study were confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{11}B NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. These data and detailed synthetic procedures are shown in Supporting Information.



Scheme 1. Synthesis of **Az-Br** and **BAz-Br**.



Scheme 2. Synthesis of **Az** and **BAz**.



Scheme 3. Synthesis of **Az-PPV** and **BAz-PPV**.

Table 1. Polymerization results

	yield/%	M_n	M_w	M_w/M_n	n
Az-PPV	68	35,500	101,900	2.9	43
BAz-PPV	75	46,700	148,500	3.2	56

Photostability

To evaluate photostability, UV-vis absorption spectra of polymers and model compounds were monitored before and after UV light irradiation by a transilluminator (365 nm, $6500 \mu\text{W cm}^{-2}$) in diluted solutions (1.0×10^{-5} M in chloroform) (Figures 1 and S2). The model compound **Az** showed typical *cis-trans* photoisomerization (Figure S2a). The spectrum started to change after several seconds from UV light irradiation, and the spectrum alteration reached a plateau within three minutes. This spectrum returned to the initial state for 30 minutes under room light irradiation (Figure S2b). **BAz** showed the spectrum variation not resulting from *cis-trans* isomerization but irreversible dissociation of the boron atom (Figure S2c).⁵¹ In contrast, both **Az-PPV** and **BAz-PPV** hardly showed spectral changes under UV light irradiation over 1 h (Figures 1a and 1b). The result of **Az-PPV** is similar to the Masuda's report.^{12,14} It is suggested that expansion of π -conjugation not only restrained the *cis-trans* photoisomerization but also stabilized boron coordination. From these results, it is concluded that the polymer containing azobenzene moieties has high stability toward light irradiation.

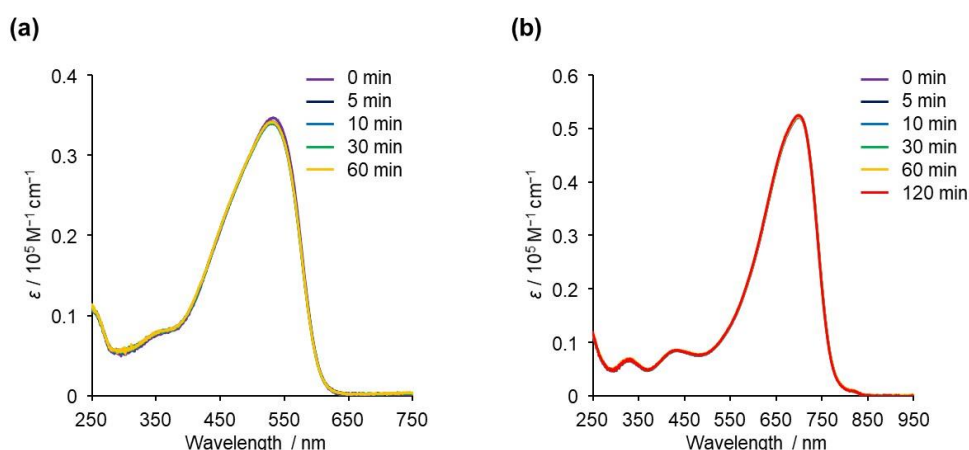


Figure 1. Photostability tests of (a) **Az-PPV** and (b) **BAz-PPV** in CHCl_3 (1.0×10^{-5} M per repeating unit) irradiated by transilluminator (365 nm) at room temperature.

NIR absorption and emission

Figure 2a shows UV-vis-NIR absorption spectra of model compounds and polymers (1.0×10^{-5} M for **Az** and **BAz** in toluene, and 1.0×10^{-5} M per repeating unit for **BAz-PPV** and **Az-PPV** in toluene). The spectroscopic data were summarized in Table 2. The **Az** showed typical azobenzene absorption bands which consist of weak and large absorption bands in longer and shorter wavelength regions assigned to $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively.¹¹ Meanwhile, **BAz** exhibited a large absorption band in the longer wavelength region assigned to $\pi-\pi^*$ transition, meaning that boron coordination induced drastic changes in electronic structures, similarly to the previous reports.^{37,51,52} The absorption band of the boron coordinated polymer **BAz-PPV** was detected in the longer wavelength region than that of **Az-PPV**. The peak of absorption maximum and the onset wavelength were 702 nm and 773 nm, respectively. The band gap is calculated as 1.60 eV, clearly indicating that **BAz-PPV** is the NIR absorption material.

To obtain deep insight on influence of the boron coordination on electronic structures in the ground state, we compared the spectra between polymers and model compounds. As shown in Figure 2a, the absorption bands of **Az-PPV** and **BAz-PPV** were obtained in longer wavelength regions compared with each corresponding model compound. It is suggested that π -conjugation should be efficiently elongated through polymer main chains. Furthermore, we assessed effective conjugation length with absorption spectra of **BAz-PPV**. The samples were prepared by the fractionation with a preparative HPLC (Figure S3). As the number average molecular weight (M_n) increased, the maximum absorption wavelength of the polymer showed bathochromic shift. From the degree of shifting, the effective conjugation length was estimated to be $n > 50$, indicating that **BAz-PPV** had a very long effective conjugate length. The comparison of

the absorption spectra of **BAz-PPV** in solution and film states is shown in Figure S4. In the film state, the absorption bands were observed in longer wavelength regions. It is likely that intermolecular π - π stacking should occur and conformation should be fixed in condensed state,⁵⁶ which is common situation for most PPV derivatives.⁵⁷ It is also suggested that the polymer hardly form aggregation in solution.

To examine electronic properties in the excited state and prove the validity of our concept for obtaining NIR-emissive polymers, the emission spectra of **BAz** and **BAz-PPV** were measured (1.0×10^{-5} M **BAz** in toluene, and 1.0×10^{-5} M per repeating unit for **BAz-PPV** in toluene, Figure 2b). No emissions from **Az** and **Az-PPV** were detected, and **BAz** showed very weak photoluminescence (absolute photoluminescence quantum yield: $\Phi_{\text{PL}} < 1.0\%$). Surprisingly, **BAz-PPV** showed significant NIR emission at the peak top of 760 nm ($\Phi_{\text{PL}} = 2.0\%$), suggesting that both polymerization and boron coordination should be necessary for inducing luminescence. In addition, since there is almost no solvent dependency (Figure S5), it should be emphasized that emission of **BAz-PPV** is not from a charge-transfer excited state but from a locally-excited state. In other words, the emission band of **BAz-PPV** in the NIR region is originated from robust conjugation in the polymer main chain. The vinylene linker should be responsible for effective electronic interaction via the connection of π -conjugated monomers owing to less steric hindrance. To investigate emission characters in the frozen state, we also acquired emission spectra and Φ_{PLS} at 77 K in 2-methyltetrahydrofuran (Figure 2c, Table 3). Accordingly, **Az** and **Az-PPV** exhibited no emission even at 77 K as well as room temperature, whereas, **BAz** and **BAz-PPV** showed larger Φ_{PLS} at 77 K in comparison to room temperature. This fact means that molecular motion plays a critical role in emission annihilation, meaning that polymerization contributes to enhancement

of emission efficiency by disturbing molecular motions. The Φ_{PL} of **BAz-PPV** was still lower than that of **BAz** even at 77 K due to the energy gap law.^{58–60}

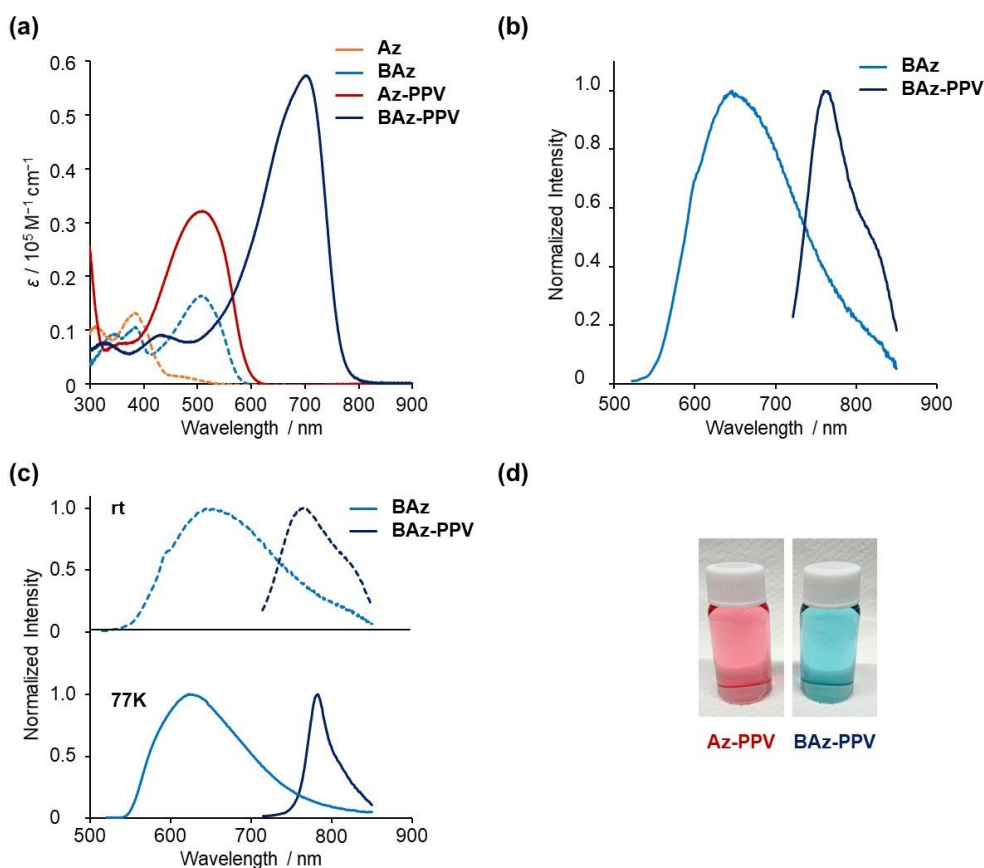


Figure 2. (a) UV–vis absorption spectra of **Az**, **BAz**, **Az-PPV** and **BAz-PPV** in toluene (1.0×10^{-5} M for **Az** and **BAz**, 1.0×10^{-5} M per repeating unit for **Az-PPV** and **BAz-PPV**). (b) Photoluminescence spectra of **BAz** and **BAz-PPV** in toluene (1.0×10^{-5} M for **BAz**, 1.0×10^{-5} M per repeating unit for **BAz-PPV**). (c) Normalized emission spectra of **BAz** and **BAz-PPV** in 2-methyltetrahydrofuran/ CHCl_3 = 99/1 at room temperature (above) and at 77 K (bottom). (d) Photos of **Az-PPV** and **BAz-PPV** in toluene (1.0×10^{-5} M per repeating unit).

Table 2. Spectroscopic data of polymers and model compounds.

	$\lambda_{\text{abs, max}}^a$	$\lambda_{\text{abs, edge}}^a$	E_g^b	λ_{PL}^a	$\Phi_{\text{PL}}^{a,c}$
	/nm	/nm	/eV	/nm	/%
Az	384	451	2.75	—	—
BAz	507	574	2.16	646	0.5
Az-PPV	510	600	2.07	—	—
BAz-PPV	702	773	1.60	760	2.0
BAz-PPV_Film ^d	718	—	—	789	0.7

^a In toluene (1.0×10^{-5} M for **Az** and **BAz**, 1.0×10^{-5} M per repeating unit for **Az-PPV** and **BAz-PPV**); excited at absorption maxima for PL.

^b $E_g = 1240/\lambda_{\text{abs, edge}}$

^c Absolute PL quantum yields excited at absorption maxima.

^d Spin-coated film on the quartz substrate (1 cm×5 cm) prepared from CHCl₃ solution (0.10 mL, 1000 rpm, concentration: 1.0 mg/0.30 mL).

Table 3. Spectroscopic data of polymers and model compounds at room temperature and 77 K

	$\lambda_{\text{abs}}/\text{nm}^a$	$\lambda_{\text{PL-rt}}^a/\text{nm}$	$\lambda_{\text{PL-77K}}^a/\text{nm}$	$\Phi_{\text{rt}}^b/\%$	$\Phi_{77\text{K}}^b/\%$
Az	385	—	—	—	—
BAz	505	647	623	0.4	11
Az-PPV	495	—	—	—	—
BAz-PPV	699	765	783	2.0	6.0

^a In 2-methyltetrahydrofuran/CHCl₃ = 99/1 (1.0×10^{-5} M for **Az** and **BAz**, 1.0×10^{-5} M per repeating unit for **Az-PPV** and **BAz-PPV**); excited at absorption maxima for PL.

^b Absolute PL quantum yields excited at absorption maxima.

Cyclic Voltammetry

To understand the origin of peak positions in absorbance, we estimated energy levels of the highest occupied molecular orbital (HOMO) and LUMO of the polymers and model compounds by cyclic voltammetry. LUMO energy levels were estimated from the onset reduction potentials of the first negative cycles and then, HOMO energy levels were calculated from the optical band gaps. The results of electrochemical properties are summarized in Table 4 and Figure 3. The cyclic voltammograms are shown in Figure S6. Comparing the energy levels of HOMOs and LUMOs between polymers and model compounds, higher HOMO and lower LUMO energy levels were obtained than those of model compounds. It clearly represents that π -conjugation is effectively expanded through the polymer main chain. Both **Az-PPV** and **BAz-PPV** had lower HOMO and LUMO energy levels than a representative PPV composed of C=C double bonds (HOMO: -5.2 eV, LUMO: -2.7 eV).^{61–63} Moreover, **BAz-PPV** had much lower HOMO and LUMO levels than **Az-PPV**. It is suggested that the HOMO and LUMO of **BAz-PPV** are greatly stabilized by the boron coordination. It is noteworthy that the LUMO energy level of **BAz-PPV** is equal to that of several ambient-stable n-type polymers,⁶⁴ such as NDI-based polymers.⁶⁵ This means that **BAz-PPV** worked as a strong electron acceptor because of both N=N double bonds and boron coordinations.³⁵

Table 4. Electrochemical data of polymers and model compounds

	E_g^a/eV	$E_{\text{onset}}^{\text{red}}/\text{eV}$	$E_{\text{LUMO}}^c/\text{eV}$	$E_{\text{HOMO}}^d/\text{eV}$
Az	2.75	-1.86	-2.94	-5.69
Az-PPV	2.07	-1.57	-3.23	-5.30
BAz	2.16	-1.00	-3.80	-5.96
BAz-PPV	1.60	-0.82	-3.98	-5.58

^a $E_g = 1240/\lambda_{\text{abs,edge}}$.

^b In CH_2Cl_2 (1.0×10^{-3} M for **Az** and **BAz**, 1.0×10^{-3} M per repeating unit for **Az-PPV** and **BAz-PPV**) containing $n\text{Bu}_4\text{NPF}_6$ (0.10 M) using a glassy carbon (GC) working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode, and a Fc/Fc^+ external standard at room temperature with a scan rate of 0.1 V s^{-1} .

^c $E_{\text{LUMO}} = -4.8 - E_{\text{onset}}^{\text{red}}$.^{62,63} ^d $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$.

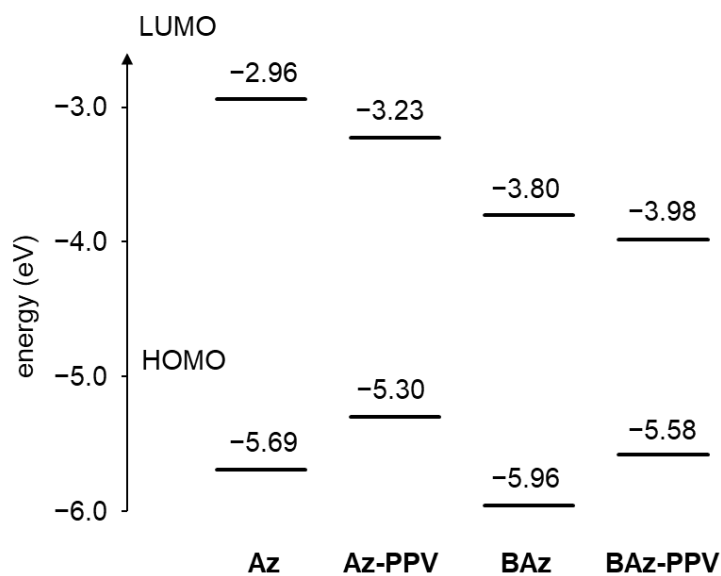


Figure 3. Energy levels of HOMOs and LUMOs estimated from cyclic voltammetry. The onset potentials were converted to electronvolt units according to the following formula: $E_{\text{HOMO}} (\text{eV}) = E_{\text{LUMO}} - E_g$, $E_{\text{LUMO}} (\text{eV}) = -4.80 - E_{\text{red,onset}}$.^{62,63}

Theoretical calculation

Computational analyses using density functional theory (DFT) and time-dependent DFT (TD-DFT) of the **BAz-PPV'** having two BAz moieties revealed that both of the HOMOs and the LUMOs are uniformly delocalized along the entire polymer backbone, similarly to that of conventional PPV (Figures 4, S7 and S8). It is shown that the boron coordination can support π -conjugation through polymer main chains. Moreover, by the boron coordination, the LUMO energy level is stabilized with efficiently-expanded π -conjugated system. As a result, **BAz-PPV** has the narrow energy band gap followed by the NIR absorption. Figure S9 and Tables S2 and S3 show that oscillator strength (f) of selected transition bands of **Az-PPV'** having two Az moieties and **BAz-PPV'**. **Az-PPV'** has a small oscillator strength at the S_0 – S_1 and S_0 – S_2 transitions and a large oscillator strength at the S_0 – S_3 transition, whereas **BAz-PPV'** has a large oscillator strength at the S_0 – S_1 transition attributable to HOMO–LUMO transition. The larger oscillator strength of **BAz-PPV'** than that of **Az-PPV'** is consistent with the result of the increased molar extinction coefficient (ϵ) in the absorption spectra (Figure 2a). Further, since the S_0 – S_1 transition is the forbidden n – π^* transition in common azobenzene derivatives, no emission is basically expected. In our experiment, **Az-PPV** hardly showed photoluminescence even at 77 K, while **BAz-PPV** exhibited high emission efficiency. The orbital symmetry of the S_0 – S_1 transition should be perturbed by the boron coordination, resulting in enhancement of emission efficiency.^{37,51,52,66}

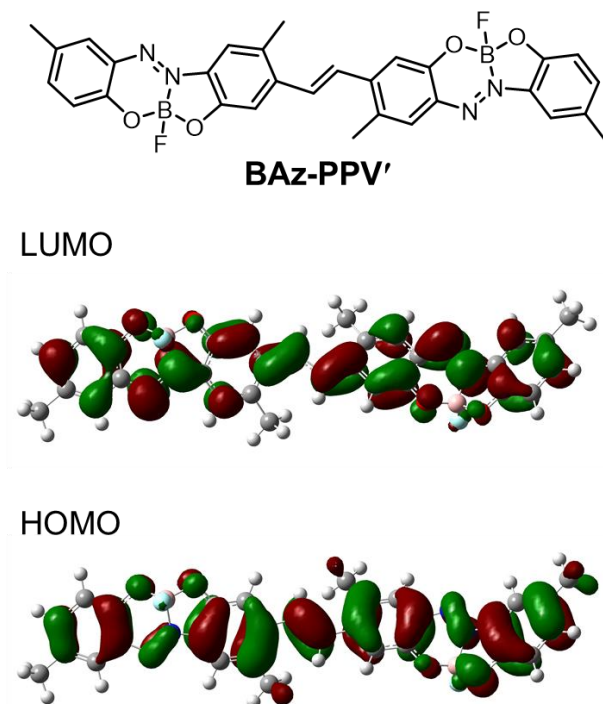


Figure 4. Selected MOs of **BAz-PPV'** obtained by DFT at the B3LYP/6-311G(d,p) level (isovalue = 0.02).

Time-of-flight (TOF) measurement

Finally, we investigated carrier mobility to evaluate bulk electronic properties using a time-of-flight (TOF) technique.⁶⁷ The device structure of the TOF technique was ITO (50 nm)/**Az-PPV** (8 μm) or **BAz-PPV** (11 μm)/Al ($\approx$ 50 nm). The results are summarized in Figures 5 and S10. The carrier mobilities of **Az-PPV** and **BAz-PPV** were almost same values at 10^{-2} – 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ order, and both hole and electron flew to the same degree. It is presumable that the boron coordination and protruding fluorine might inhibit consecutive intermolecular π – π interactions and subsequently reduce the carrier transport ability. On the other hand, our data mean that the bulk career

mobility should be conserved by introducing boron atoms. The values were higher than those of the reported PPV derivatives^{68–70} and the other conventional π -conjugated polymers.^{71–74} Introduction of the N=N double bonds might be effective in increasing carrier mobility of π -conjugated polymer. By the simple strategy for the boron coordination to the nitrogen atoms based on the PPV backbone, we received positive effects not only on emission efficiency but also on carrier transport ability.

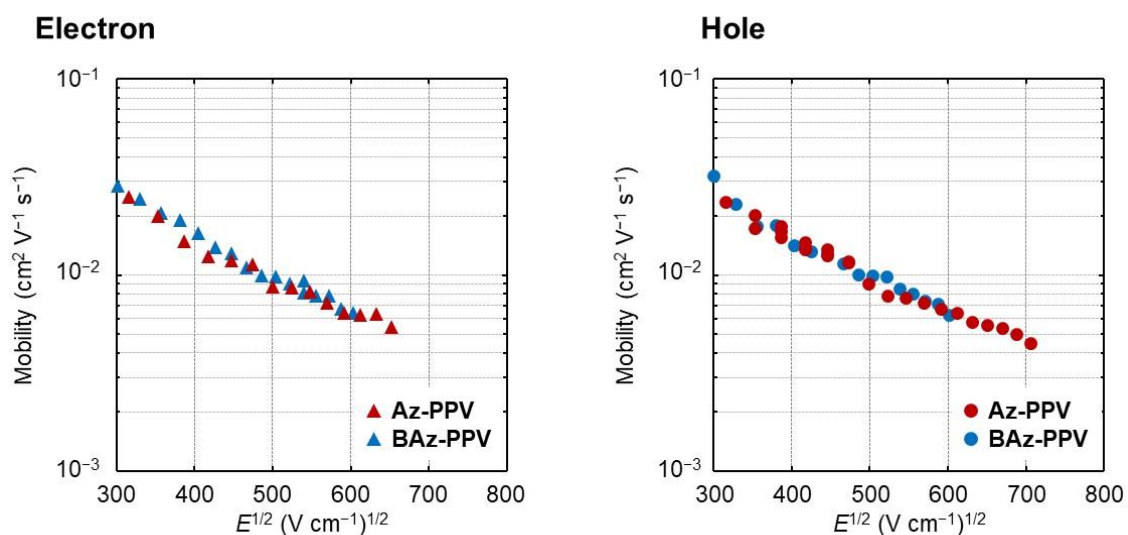


Figure 5. Electron and hole mobilities of **Az-PPV** and **BAz-PPV** measured by a time-of flight technique with the device composed of ITO (50 nm)/**Az-PPV** (8 μ m) or **BAz-PPV** (11 μ m)/Al ($\approx$ 50 nm).

Conclusion

We designed the PPV derivative containing the boron-coordinated N=N double bond in the main chain. The introduction of the N=N double bond into the PPV backbone is able to provide promising coordination points with boron and lower the LUMO level of main-chain conjugation. The boron coordination at the N=N units contributes to extension of robust main-chain conjugation owing to enhanced planarity and rigidity. As a result, the NIR absorptive and emissive polymer can be obtained. Since only **BAz-PPV** showed emission at room temperature, it is shown that both polymerization and coordination of boron atoms are responsible luminescence. Furthermore, it was demonstrated that **BAz-PPV** showed similar degree of carrier mobility to the ligand polymer **Az-PPV** and the other conventional π -conjugated polymers. In summary, based on the simple strategy for coordinating boron atoms to the nitrogen atoms in the PPV backbone, we accomplished changing the energy levels and photo properties. We assume that this strategy using the coordination structure might be applicable to obtain advanced organic semiconducting devices.

Acknowledgement

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Supporting Information.

General method, Materials, Synthetic procedures and characterization, ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B NMR spectra, GPC chromatograms (Figure S1), Photostability tests (Figure S2), Molecular weight dependence (Figure S3 and Table S1), Absorption and emission spectra in film state (Figure S4), Lippert–Mataga plots (Figure S5), Cyclic voltammograms (Figure S6), Computational details (Figures S7–S9, Tables S2 and S3), Time-of-flight measurement (Figure S10)

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