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# A Highly-Efficient Near-Infrared-Emissive Copolymer with N=N Double-Bond π-Conjugated System Based on a Fused Azobenzene–Boron Complex

Masayuki Gon, Kazuo Tanaka* and Yoshiki Chujo*

**Abstract:** The fused azobenzene–boron complexes (BAzs) were prepared, and highly-efficient near-infrared (NIR) emission was observed from the nitrogen–nitrogen double bond (N=N) containing π-conjugated copolymer. From the optical measurements, it was found that BAz worked as a strong electron-acceptor originating from intrinsic electron-deficiency of the N=N double bond and the boron–nitrogen (B–N) coordination which dramatically lowered the energy level of the lowest unoccupied molecular orbital (LUMO) of the azobenzene ligand. The simple donor–acceptor (D–A) type copolymer with bithiophene (BT) and BAz exhibited intense photoluminescence (PL) in the NIR region both in the dilute solution ($\lambda_{PL}$ = 751 nm, $\Phi_{PL}$ = 0.25) and in the film ($\lambda_{PL}$ = 821 nm, $\Phi_{PL}$ = 0.038). Moreover, BAz monomer showed slight PL in the diluted solution, meanwhile aggregation-induced emission (AIE) was detected. We proposed that N=N double bonds should be attractive and functional building blocks for designing π-conjugated materials.

In designing π-conjugated polymers, electronic functions of the monomer unit are a striking factor in device property.[1] Thus, introduction of unique π-conjugated units into polymer main chains and comprehension of their electronic properties are essential for realizing superior properties from the products. From this stand point, the concept of "element-blocks", which are structural functional units consisting of various groups of element, is valid for creating functional polymers.[2]

By the combination of carbon–carbon double bonds (C=C) and construction of conjugated system, polymeric materials having efficient PL properties can be obtained such as poly(*para*-phenylenevinylene) (PPV) which was used for firstly fabricating an organic light-emitting diode (OLED).[3,4] On the other hand, in comparison to conventional π-conjugated system with C=C double bonds, the number of π-conjugated polymers including heteroatom–heteroatom double bonds (X=X) is limited.[5,6] Due to their intrinsically high reactivity and difficulty in handling, it is still challenging to obtain robust materials.[7] A N=N double bond shows relatively higher stability among the other X=X double bonds. As a representative example, azobenzene has been widely used as a key component in stimuli-responsive materials based on the *cis*–*trans* photoisomerization derived from the N=N double bond.[8] So far, several π-conjugated polymers containing N=N double bonds in the main chain have been reported, and their photoisomerization, electrochemical and photovoltaic properties were investigated,[9] while there were, to the best of our knowledge, no report about photoluminescent properties. It is well recognized that excited deactivation of azobenzene would rapidly proceed via the non-radiative photoisomerization processes.[10] Therefore, the azobenzene is considered to be not suitable for the application to light-emitting materials.[11] On the other hand, Kawashima and coworkers proposed that azobenzene was a potential building block as a highly-efficient emitter if the photoisomerization was restricted and the electronic structures were varied, for example, by formation of the B–N coordination.[12] Additionally, it was proposed that the energy level of the LUMO of the π-conjugated molecule involving the N=N double bond was lower than that of the C=C analog.[13] Furthermore, the B–N coordination in the π-conjugated system effectively lowered the LUMO level of the π-conjugated unit.[14] That is, the N=N double bond has a potential to work as a strong electron-acceptor in the π-conjugated system as well as an emitter. Thus, it can be expected that the N=N double bond could be a new element-block for realizing narrow band-gap π-conjugated polymers.

Herein, we report multi functions of the azobenzene complex with the fused structure by boron coordination. Although the synthesis of BAz analogs was already achieved by Hohaus in 1980s,[15] the optical properties were still vailed. This is the first example, to the best of our knowledge, to offer unique optical performances of the N=N double bond in the expanded π-conjugated system.

Scheme 1 shows the synthesis of the BAzs and the pristine azobenzene compounds. **BAz-H** was easily synthesized by boron complexation with the commercially-available compound, 2,2'-dihydroxyazobenzene (**1**). The dibrominated monomer **BAz-Br** was prepared from 4-bromo-2-methoxyaniline (**2**). The ligand **3** was obtained via the oxidative coupling reaction with manganese(IV) oxide ($MnO_2$) and followed by the conversion from the methoxy groups to hydroxyl one with boron tribromide ($BBr_3$). After boron complexation, **BAz-Br** was obtained. The pristine azobenzene **Az-H** was also synthesized by the oxidative coupling reaction of *o*-anisidine (**4**) with $MnO_2$.

Following Scheme 2, the copolymers with BT were synthesized. The Migita–Kosugi–Stille coupling polymerization[16] of **BAz-Br** was carried out with 5,5'-bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene (**5**) in the catalytic system of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) using 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) as a phosphine ligand to obtain **P-BAz** as a deep red purple solid in 85% isolated yield ($M_n$ = 21,400, $M_w$ = 55,600, $M_w/M_n$ = 2.59). The pristine azobenzene copolymer

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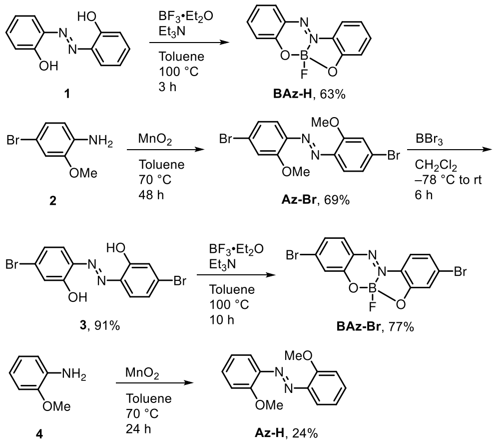
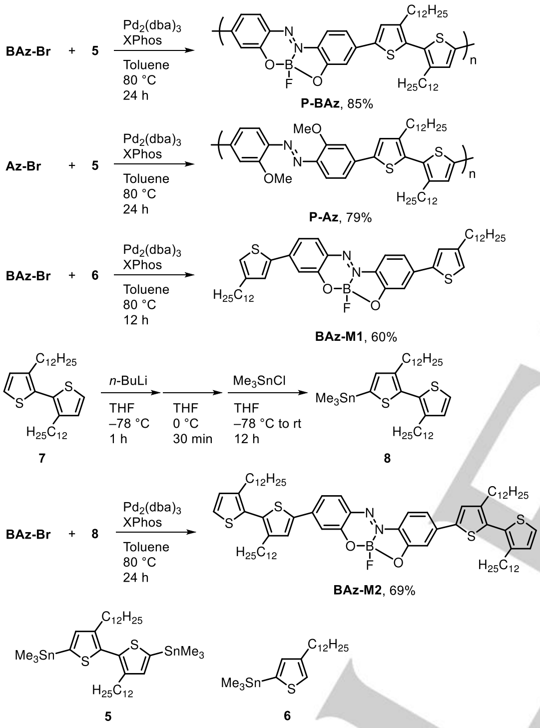


**Scheme 1.** Synthesis of azobenzene and BAz derivatives



**Scheme 2.** Synthesis of copolymers and model compounds

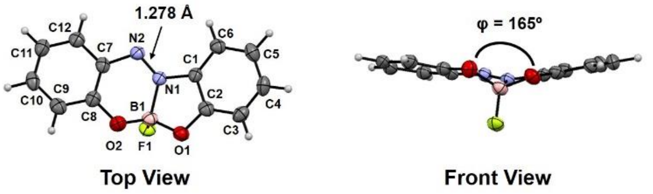


**Figure 1.** ORTEP drawings of **BAz-H** (50% probability for thermal ellipsoids). A minor conformation of **BAz-H** is omitted to clarify. All crystallographic data are shown in Supporting Information.

**Table 1.** Spectroscopic data of pristine and fused azobenzenes

| | $\lambda_{abs}$[a] /nm | $\lambda_{PL}$[a] /nm | $\Phi_{PL}$[a,b] | $\tau$[a,c] /ns | $k_r$[d] /s$^{-1}$ | $k_{nr}$[d] /s$^{-1}$ |
|---|---|---|---|---|---|---|
| **Az-H** | 372 | – | – | – | – | – |
| **P-Az** | 458 | – | – | – | – | – |
| **BAz-H** | 479 | 617 | <0.001 | <0.10 | – | – |
| **(Aggregation)[e]** | | (603) | (0.023) | (1.09) | (2.1×10$^{7}$) | (9.0×10$^{8}$) |
| **BAz-M1** | 558 | 643 | 0.005 | <0.10 | >5.0×10$^{7}$ | >9.9×10$^{9}$ |
| **BAz-M2** | 601 | 690 | 0.038 | 0.17 | 2.3×10$^{8}$ | 5.8×10$^{9}$ |
| **P-BAz** | 632 | 751 | 0.25 | 0.68 | 3.7×10$^{8}$ | 1.1×10$^{9}$ |
| **(Film)[f]** | (661) | (821) | (0.038) | | | |

[a] In toluene (1.0×10$^{-5}$ M); excited at $\lambda_{abs}$ for PL. [b] Absolute PL quantum efficiency excited at $\lambda_{abs}$. [c] Emission lifetime at $\lambda_{PL}$. [d] $k_r = \Phi_{PL}/\tau$, $k_{nr} = (1 - \Phi_{PL})/\tau$. [e] In 1,4-dioxane/$H_2O$ = 1/99 (1.0×10$^{-4}$ M). [f] Spin-coated film on the quartz substrate (1 cm×5 cm) prepared from chloroform solution (0.10 mL, 1000 rpm, concentration: 1.0 mg / 0.30 mL).

**P-Az** was prepared as a red solid in 79% isolated yield ($M_n$ = 20,900, $M_w$ = 52,100, $M_w/M_n$ = 2.50) with the same reaction condition for **P-BAz**. Model compounds **BAz-M1** and **BAz-M2** were also prepared with the same protocol for preparing the copolymers using 5-trimethylstannyl-3-dodecylthiophene (**6**) and 3,3'-didodecyl-5-trimethylstannyl-2,2'-bithiophene (**8**), respectively. The structures of all new compounds were confirmed by $^{1}$H, $^{13}$C and $^{11}$B NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analyses. The film samples were prepared via the spin-coating on the quartz substrate with the chloroform solutions.

The structure of **BAz-H** was clarified by a single crystal X-ray analysis. Figure 1 shows ORTEP drawings of **BAz-H**. The 2,2'-dihydroxyazobenzene scaffold worked as a tridentate ligand and was fixed by the four-coordinated boron atom with the formation of the fused five and six membered ring system. The structure has in common with the double bond-included tridentate ligands such as 2,2'-dihydroxyazomethine.[17,18] The azobenzene scaffold of **BAz-H** was slightly bent due to the tetrahedral structure of the boron atom. The torsion angle (*φ*) of the C(1)–N(1)–N(2)–C(7) was 165°. The bond length of the N=N double bond was 1.278 Å, and the fluorine atom projected from the azobenzene surface. Because of the asymmetric structure, the boron atom became chirality center. Indeed, **BAz-H** formed racemic crystal (Figure S32). The enantiomers were able to be separated with chiral liquid chromatography. Although the details of the chiroptical properties were still under investigation, the conditions of the optical resolution, circularly dichroism (CD) spectra and simulated CD spectra are shown in Figure S33.

To examine electronic structures in the ground state, the absorption properties of the compounds were evaluated (Table 1). Figures 2 and 3 show the UV–vis absorption spectra in toluene (1.0×10$^{-5}$ M and 1.0×10$^{-5}$ M per repeating unit for the copolymers). **Az-H** presented the typical spectra composed of the strong absorption bands assigned to the permitted π–π* transition in the shorter wavelength region (ca. 350−400 nm) and the weak absorption bands originating from the forbidden n–π* transition in the longer wavelength region (ca. 400−500 nm). Meanwhile, it should be noted that **BAz-H** exhibited the strong absorption band attributed to the π–π* transition in the longer wavelength region (479 nm). This indicates that the B–N coordination transformed the $S_0$–$S_1$ transition from the forbidden n–π* transition to the permitted π–π* one. This drastic change would play a positive role in inducing intense photoluminescence (PL) property from azobenzene.[12]

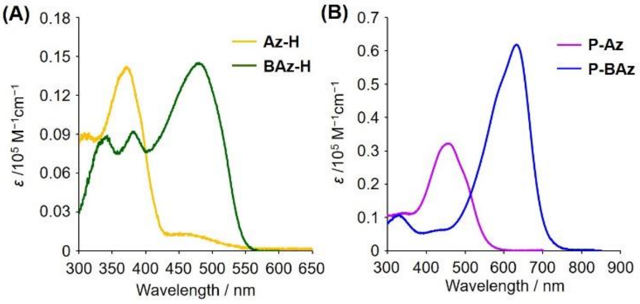


**Figure 2.** UV–vis absorption spectra of (A) **Az-H** and **BAz-H** in toluene ($1.0\times10^{-5}$ M); (B) **P-Az** and **P-BAz** in toluene ($1.0\times10^{-5}$ M per repeating units).

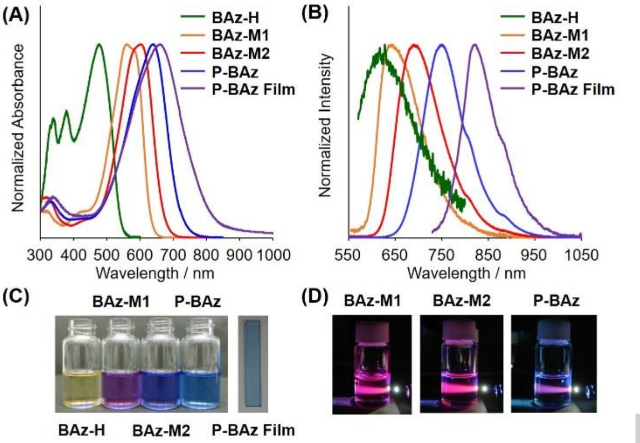


**Figure 3.** (A) Normalized UV–vis absorption spectra and (B) PL spectra of **BAz-H**, **BAz-M1**, **BAz-M2** and **P-BAz** in toluene ($1.0\times10^{-5}$ M, per repeating units for **P-BAz**) and the film of **P-BAz** prepared on the quartz substrate. (C,D) Photos of **BAz-H**, **BAz-M1**, **BAz-M2**, **P-BAz** and film of **P-BAz** under room light and excited by white LED.

In both copolymers **P-BAz** and **P-Az**, the wavelengths of the peak tops were significantly red-shifted compared with those of the monomers. This means that electron delocalization through the main chain including the N=N double bonds should be extended. In the case of the pristine azobenzene-containing polymers, it was reported that the absorption bands attributable to n–π* and π–π* transitions were observed in the similar region.[9j] Correspondingly, the absorption band of **P-Az** with the peak at 458 nm was detected in the similar area of that originating from n–π* transition of the monomeric unit **Az-H**. Meanwhile, the significant absorption band with the peak at 632 nm appeared from **P-BAz** in distinctly different wavelength region from those of the π–π* transition of **BAz-H**. These data strongly support extension of electronic delocalization through the polymer main chains in **P-BAz**. In UV–vis absorption spectra of the model compounds **BAz-M1** and **BAz-M2**, which were mono and bithiophene-substituted BAzs, respectively, the red-shifted absorption bands were also observed, indicating that robust electronic interaction should exist between BAz and thiophene units. **P-BAz** showed good film-formability, and the homogeneous film was able to be obtained. As shown in Figure 3A, the peak-top wavelength of the film sample was slightly red-shifted (661 nm) in comparison with that in the diluted solution in toluene (632 nm) and those of the model compounds (558 nm for **BAz-M1**, 601 nm for **BAz-M2**).

Figures 3B and S34 show the PL spectra in toluene ($1.0\times10^{-5}$ M). Emission band of **Az-H** was not observed and that was in common with conventional azobenzene derivatives which hardly showed emission due to the fast non-radiative deactivation process. From **BAz-H**, weak PL was detected (Tables 1 and S2, $\lambda_{PL}$ = 617 nm, $\Phi_{PL} < 0.001$). Those data were different from the Kawashima and coworkers' reports on the 2-borylazobenzene derivatives having intense emission in the diluted solution.[12] In contrast, it should be noted that the emission intensity was enhanced by forming aggregates or suppressing the molecular motion in the polymer matrix. (Tables 1 and S2, Figure S35), indicating that the **BAz-H** has AIE property.[19] This fact involves two significant issues. First, as we presumed according to the Kawashima's report, the fused azobenzene has PL properties. However, emission annihilation occurred even in the solution state. Second, the AIE behavior of **BAz-H** is unusual according to the photochemical mechanism (restriction of intramolecular rotation, RIR) in conventional AIE-active molecules.[20] It is suggested that emission annihilation should be generally induced by molecular motions and vibration at the substituents in the solution state.[21] However, **BAz-H** has rigid structure fixed by boron complexation. Additionally, the wavelengths of PL peak tops were blue-shifted after aggregation formation. These results suggest that the AIE property was originated not from conventional RIR mechanism but from suppression of structural relaxation of the π-conjugated complex in the excited state. We have recently reported that the fused boron–azomethine complex also showed the AIE property in the absence of movable substituents.[17]

Next, emission properties of the polymers were examined. Surprisingly, the intense emission band was obtained from **P-BAz** in the NIR region ($\lambda_{PL}$ = 751 nm, $\Phi_{PL}$ = 0.25 in toluene) although the monomer showed emission annihilation (Table 1 and Figure 3B). By incorporating the BAz unit into the polymer main chain, molecular motions would be effectively suppressed, followed by emission in the solution. It should be emphasized that the film of **P-BAz** also exhibited efficient NIR emission ($\lambda_{PL}$ = 821 nm, $\Phi_{PL}$ = 0.038). These $\Phi_{PL}$ values were relatively-high in the NIR-emissive organic materials,[22] especially in the polymers.[23] To gather further information on the effect of polymerization on electronic properties of BAzs, photochemical mechanism was investigated. It was found from the comparison of optical properties between the model compounds and polymers that the values of $\lambda_{PL}$s and $\Phi_{PL}$s increased (Table 1). It is likely that extension of π-conjugated system through the polymer main chain contributed to narrowing the energy gap in the $S_0$−$S_1$ transition. According to the solvatochromism of emission bands and subsequently Lippert−Mataga plots, it was revealed that the emission bands of **P-BAz**, **BAz-M1** and **BAz-M2** should be from the charge transfer (CT) state (Figures S37 and S39, Table S4). From the calculation of the kinetic parameters with a PL lifetime measurement (Table 1 and Figure S36), it was shown that increase in the radiative rate constants ($k_r$s) and decrease in the non-radiative rate constants ($k_{nr}$s) were simultaneously induced by polymerization. Because structural relaxation would be disturbed in the polymer main chain, enhancement to the radiation process should be induced. Additionally, using the fluorene unit as the different comonomer, the similar behavior was observed with polymerization, and it was found that BT unit was more effective in enhanmcement of the PL

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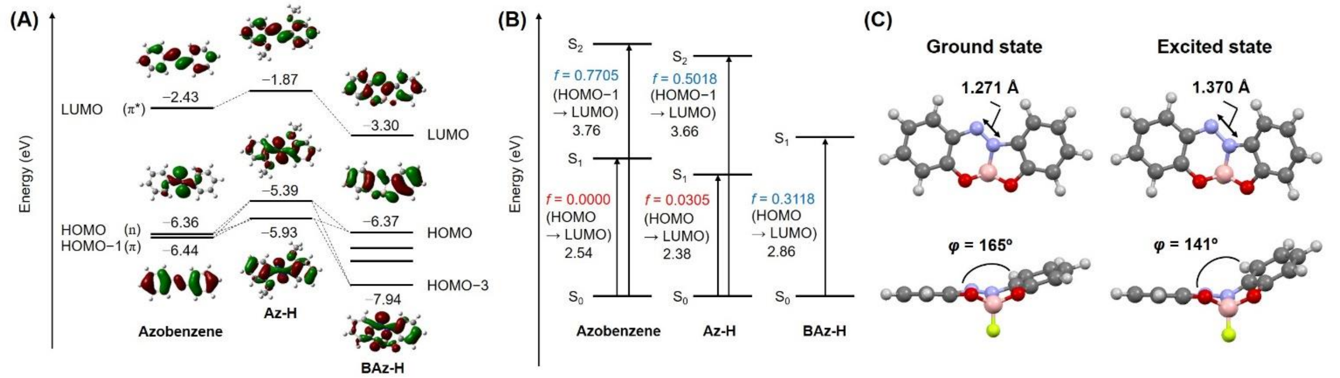

**Figure 4.** The results of quantum calculation. (A) Energy diagram, selected MOs and (B) oscillator strength (*f*) of selected transition bands of azobenzene, **Az-H** and **BAz-H** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) level (isovalue = 0.03). (C) Optimized structures both in the ground and excited states of **BAz-H** with DFT and TD-DFT calculations at the B3LYP/6-311G(d,p) and TD-B3LYP/6-311+G(d,p) levels, respectively.

performance than fluorene one (Figures S38 and S39, Tables S3 and S4). On the other hand, no emission was obtained from the pristine azobenzene-containing polymer **P-Az**, indicating that the B–N coordination and formation of the fused structure are necessary for presenting luminescence.

LUMO levels of the azobenzene moieties were estimated from the onset potentials with electrochemical analyses. Cyclic voltammetry (CV) was carried out in dichloromethane ($1.0\times10^{-3}$ M of samples and 0.1 M of tetrabutylammonium hexafluorophosphate ($NBu_4PF_6$)). The results are shown in Figure S40 and Table S5. It was shown that the **Az-H** possesses the similar LUMO level (−3.00 eV) with that of the conventional electron-acceptor, benzothiadiazole (−2.86 eV). The LUMO levels of **BAz-H** (−3.87 eV) and **P-BAz** (−3.98 eV) were lower by approximately 0.8 eV than that of **Az-H** and **P-Az** (−3.20 eV) indicating that the azobenzene derivatives intrinsically worked as a strong electron-acceptor and the boron complexation is responsible for further enhancement of electron-accepting ability. Thus, the D–A type copolymer composed of BT and BAz can exhibit the narrow band-gap property with the NIR emission.

The electronic states of the azobenzene derivatives were supported by quantum calculation. Density functional theory (DFT) and time-dependent DFT (TD-DFT) were performed, and the resulting molecular orbitals (MOs) were examined (Figures 4A and S41). The HOMO−1s, HOMOs and LUMOs of azobenzene were assigned to π, n and π* orbitals, respectively. In **Az-H**, the HOMO−1 and HOMO consisted of the mixture of the n and π orbitals derived from azobenzene because the optimized structure was not planar due to the methoxy groups. The $S_0$–$S_1$ transitions were assigned to the forbidden transitions ($f$ = 0.0000 for azobenzene and $f$ = 0.0305 for **Az-H**, $f$: oscillator strength), and the $S_0$–$S_2$ transitions were permitted ones ($f$ = 0.7705 for azobenzene and $f$ = 0.5018 for **Az-H**) (Figure 4B). Conversely, in **BAz-H**, the energy level of the MO derived from n orbital was lowered after the boron complexation (HOMO−3), and instead of the n orbital, the π orbital became the HOMO. Thereby, the $S_0$–$S_1$ transition was the permitted transition ($f$ = 0.3118). These results are similar with those from the Kawashima's reports on 2-borylazobenzene derivatives.[12] Although the HOMO and LUMO levels of azobenzene were lifted up by modification with the methoxy groups, the LUMO level was strikingly lowered by the boron complexation. The results of the TD-DFT calculation of **BAz-M1** and **BAz-M2**, where dodecyl groups were changed to methyl groups for simplification in the caluculation, clearly showed the extension of π-conjugation in the ground state (Figure S42). Increase in the oscillator strengths and decrease in the enegy gaps of $S_0$–$S_1$ transitions of the model compounds compared with those of the monomer **BAz-H** (Table S6) were in good agreement with the results of the UV–vis absorption spectra measurements (Figure S37). Those should lead to enhamcement of PL performances with increase in $k_r$ and decrease in $k_{nr}$.

To evaluate validity of the plausible mechanism of AIE in **BAz-H** via large structural relaxation in the excited state, optimized structures of **BAz-H** both in the ground and excited states were compared by (TD-)DFT calculations (Figure 4C). The optimized structure in the ground state had the four-coordinated boron atom and the slightly-bent azobenzene moiety ($\varphi_{(C–N=N–C)}$ = 165°) which showed good agreement with the crystallographic data (Figure 1). On the other hand, the calculated structure in the excited state was obviously bent ($\varphi_{(C–N=N–C)}$ = 141°). Increase in the length of the N=N double bond (1.271 Å for the ground state and 1.370 Å for the excited state) was detected. It was implied that extension of the bond length could cause the bending of **BAz-H** by excitation. Based on these structural changes, the AIE behavior of **BAz-H** can be clearly explained. As proposed in the optical measurements, emission annihilation should occur during structural alteration in the solution after excitation, meanwhile, since there is hardly room to show structural relaxation in the condensed state, emission can be recovered.[17]

Finally, the photostability was evaluated as the change of the UV–vis absorption spectra with irradiation by transilluminator (365 nm, 6,500 $\mu$W cm$^{-2}$) and white room light (the spectrum is shown in Figure S47) in the diluted solution ($1.0\times10^{-5}$ M in chloroform). The results are summarized in Figures S43, S44 and S45. The pristine azobenzene moieties, **Az-H** and **P-Az**, rapidly showed the typical spectral changes caused by *cis*–*trans* photoisomerization. In contrast, the absorption spectrum of **BAz-H** was slightly altered by UV irradiation. The spectral changes reached a plateau after 2 h for **BAz-H** (Figure S46). The obtained spectrum was completely identified with that of the corresponding ligand **1**, indicating that the spectral changes were caused not by *cis*–*trans* photoisomerization but by boron elimination. Meanwhile, the spectrum of **P-BAz** was preserved even after irradiation with UV and the white room light (Figure S44B). The photostability of the model compounds **BAz-M1** and **BAz-M2** also increased. These results indicate that the extension of π-conjugation contributed to improving photostability. Considering the fact that **P-BAz** showed more efficient emission property than **BAz-H**, it was reasonable that the bending was restricted by extension of π-conjugation and increasing the rigidity of the polymer main chain.

In conclusion, fused azobenzene–boron complexes and their copolymers were successfully synthesized. By the B–N coordination, the forbidden S$_0$–S$_1$ transition in **BAz-H** was transformed to the permitted transition. It was suggested that elongation of the N=N double bond occurred by photoexcitation, resulting in distortion of molecular frameworks. Based on this structural relaxation in the excited state, AIE behaviors were obtained. Owing to the strong electron-accepting ability of BAzs and extension of the π-conjugation by copolymerizaition, the D–A type copolymer **P-BAz** exhibited highly-efficient NIR emission in both of the solution and the film states. The extension of the π-conjugation effectively increased $k_r$ and decreased $k_{nr}$ both of which were essential for obtaining good PL performances. In addition, **P-BAz** had higher photostability than the other azobenzene derivatives. Those unique and useful properties were attributed to the N=N double bond including fused structure with B–N coordination. This concept shuold be applicable for fabricating advanced optically-functional materials utilizing the heteroatom-coordinated azobenzene as a key element-block.

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**Keywords:** boron • conjugated polymer • near-infrared • luminescence • azobenzene

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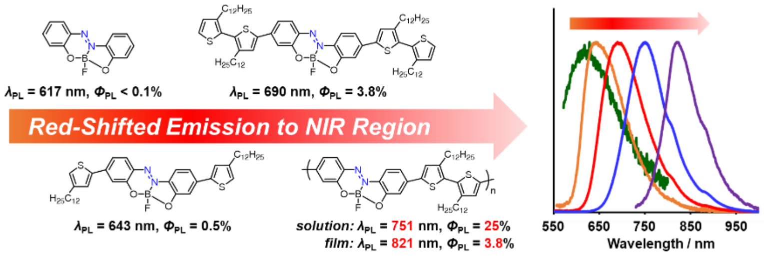
## Entry for the Table of Contents

## COMMUNICATION



**N=N double bond:** A nitrogen–nitrogen double bond (N=N) containing π-conjugated copolymer showed a highly-efficient near-infrared (NIR) emission. The N=N double bond should be a new element-block for realizing narrow band-gap π-conjugated polymers.

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**A Highly-Efficient Near-Infrared-Emissive Copolymer with N=N Double-Bond π-Conjugated System Based on a Fused Azobenzene–Boron Complex**