



π -Conjugated polymers based on flexible heteroatom-containing complexes for precise control of optical functions

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Abstract

Controlling the optical properties of π -conjugated polymers is a relevant strategy to satisfy growing demands for the development of next-generation optoelectronic devices and luminescent materials. Generally, planar and rigid monomers have been used to improve the performance of polymers by enhancing intermolecular electronic interactions and delocalizing π -electrons with polymer main chains. In contrast, we demonstrate that introducing flexible monomeric units with heteroatom-containing complexes into the polymer main chains provides unique functions and the ability to precisely control their optical properties. Due to the slightly bent and asymmetric structures against the π -surface created by boron and O,N,O-type tridentate ligands, large structural relaxation in the excited state occurs with bending motion. This relaxation leads to stimuli-responsive solid-state emission, such as aggregation-induced emission (AIE) and crystallization-induced emission (CIE) properties. Through these structures, π -conjugation and electronic interactions between polymer chains are extended. The resulting π -conjugated polymers show bright emission even in the near-infrared (NIR) region, sensitive stimuli-responsiveness, and high carrier mobility. Our strategy could provide novel insights for improving the functionality of conventional π -conjugated polymers and provide a breakthrough in the development of polymer-based material science.

Introduction

Current industries are supported by various luminescence phenomena. Information can be clearly visualized by luminescence, especially in the dark. To control luminescence and manufacture luminescent devices, many light-emitting materials composed of inorganic and organic substances have been developed thus far, and they help make our lives more prosperous [1, 2]. Among them, organic-based π -conjugated polymers have received much attention owing to their excellent luminescence properties and other useful properties, such as conductivity, processability, chemical and thermal stability, thinness, lightness, and designability [3, 4]. For example, π -conjugated polymers can be applied as ink to a roll-to-roll process, which is useful technology for saving costs and energy when

fabricating large-surface luminescent and optoelectronic devices [5].

The optical properties of π -conjugated polymers are largely dependent on their chemical structures [6]. Hence, design guidelines for controlling their properties are constantly needed to develop tailor-made functional materials. Generally, an increase in the planarity and rigidity of π -conjugated scaffolds can enhance their luminescence performances in solution owing to highly delocalized π -electrons through the π -conjugated system, as observed from boron dipyrromethene (BODIPY) derivatives (Fig. 1) [7–10]. The improvement in planarity can promote electronic interactions among polymer chains via intermolecular π – π interactions in solids and can help enhance carrier mobility and stimuli responsiveness. However, nonspecific intermolecular interactions in the condensed state simultaneously accelerate nonradiative deactivation processes by the formation of nonemissive excimers or the diffusion of excitons [11]. This annihilation process is called concentration quenching or aggregation-caused quenching (ACQ). Conversely, sterically crowded luminescent molecules, such as 1,1,2,3,4,5-hexaphenylsilole (HPS), hardly show emission in solution, whereas the emission is enhanced in aggregation [12]. This behavior is called the aggregation-induced emission (AIE) property [13, 14]. When the emission

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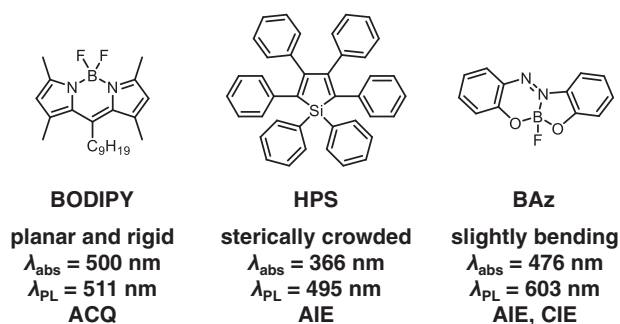


Fig. 1 Optical properties and behaviors of luminophores, λ_{abs} and λ_{PL} for BODIPY in solution from ref. [10], λ_{abs} and λ_{PL} for HPS in solution and aggregation, respectively, from ref. [12], λ_{abs} and λ_{PL} for BAz in solution and aggregation, respectively, from ref. [27]

intensity is greatly improved by crystallization, the emission dyes are classified as crystallization-induced emission (CIE)-active molecules [15]. Thus, π -conjugated polymers composed of AIE (or CIE)-active monomers should be promising candidates that possess solid-state emission properties.

As mentioned above, introducing conventional solid-state luminescent dyes, including AIE and CIE-active molecules, is a promising strategy for obtaining luminescent solid and/or film materials. However, there is another problem with this strategy. The sterically hindered and twisted structures disturb the consecutive connection of π -electrons through the polymer main chains [16]. Therefore, it is difficult to both expand π -conjugation with electronic interactions through polymer chains and achieve solid-state emission based on conventional material designs. This issue is critical, especially in the design of near-infrared (NIR) luminescent materials. NIR-luminescent devices are among the next targets in the development of optoelectronic materials because NIR light exhibits various advantageous properties, such as high transparency to skin/water and invisibility to human eyes, which is useful for medical and security applications. However, to obtain NIR emission, a narrow energy gap between frontier molecular orbitals is necessary, and extending the π -conjugated system is a major strategy for realizing the desired electronic states. Thus, very large obstacles remain in the development of highly efficient NIR light-emitting materials, especially in solids, due to ACQ [17, 18].

To develop π -conjugated polymers that show bright emission both in solution and solid, even in the NIR region, we focused on designing polymer materials based on an “element-block”, which is a minimum functional unit containing heteroatoms [19–22]. Through combination with element blocks, such as toy blocks, π -conjugated polymers could be created with unprecedented functions. Boron-fused azobenzene (BAz) and azomethine (BAM) complexes are typical example of element blocks [23]. We used these complexes as monomers because their π -conjugated systems can be

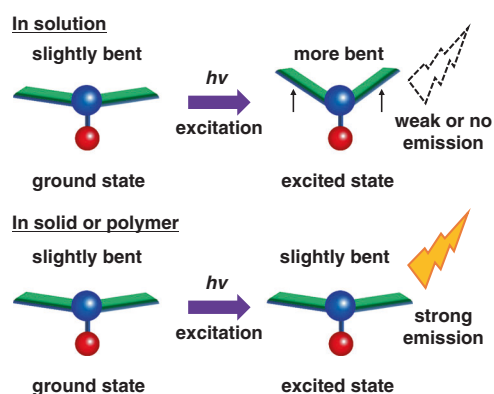


Fig. 2 Schematic illustration of the concept based on precise control of the optical functionalities of flexible heteroatom-containing complexes

expanded by their structures through nitrogen–nitrogen double (N=N) bonds in BAz and carbon–nitrogen double (C=N) bonds in BAM, and the nitrogen atoms can be used as a coordination point (Fig. 1). In addition, the boron-fused structures have slightly bent and asymmetric scaffolds with substituents that protrude perpendicularly at boron (Fig. 2). The structures can electronically interact with each other at the opposite side of the protruded substituent, which prevents ACQ caused by excess intermolecular π – π interactions. The unique structures are bent after photoexcitation and hardly show emission in solution. On the other hand, the emissions are recovered in solid and crystal, which are categorized as AIE and CIE properties, respectively. Moreover, we will mention their luminescent properties in the polymer main chains. Since bending motions in the excited state are restricted when incorporated into π -conjugated main chains, π -conjugated polymers exhibit highly efficient emission in solution and solid. We have reported many examples of light-emitting materials based on π -conjugated polymers composed of BAz and BAM monomers [23]. More recently, the concept has been extended to the other elements in Group 14, such as germanium and tin [24–26]. We will provide design guidelines that are useful for solving problems in conventional polymeric materials by examining areas beyond common knowledge. Our findings will contribute to the development of polymer-based material science.

Fundamental properties of BAz complexes

BAz scaffolds are prepared by condensation reaction with O,N,O-type azobenzene tridentate ligands and boron sources, such as halogenated boron or boronic acid [27, 28]. The fundamental structure of BAz (BAz-H) was synthesized from commercially available 2,2'-dihydroxyazobenzene (LAz) and boron trifluoride etherate (BF₃·Et₂O) in the presence of triethylamine (Et₃N) in toluene at 100 °C (Fig. 3a) [27]. After the color changes from yellow to red,

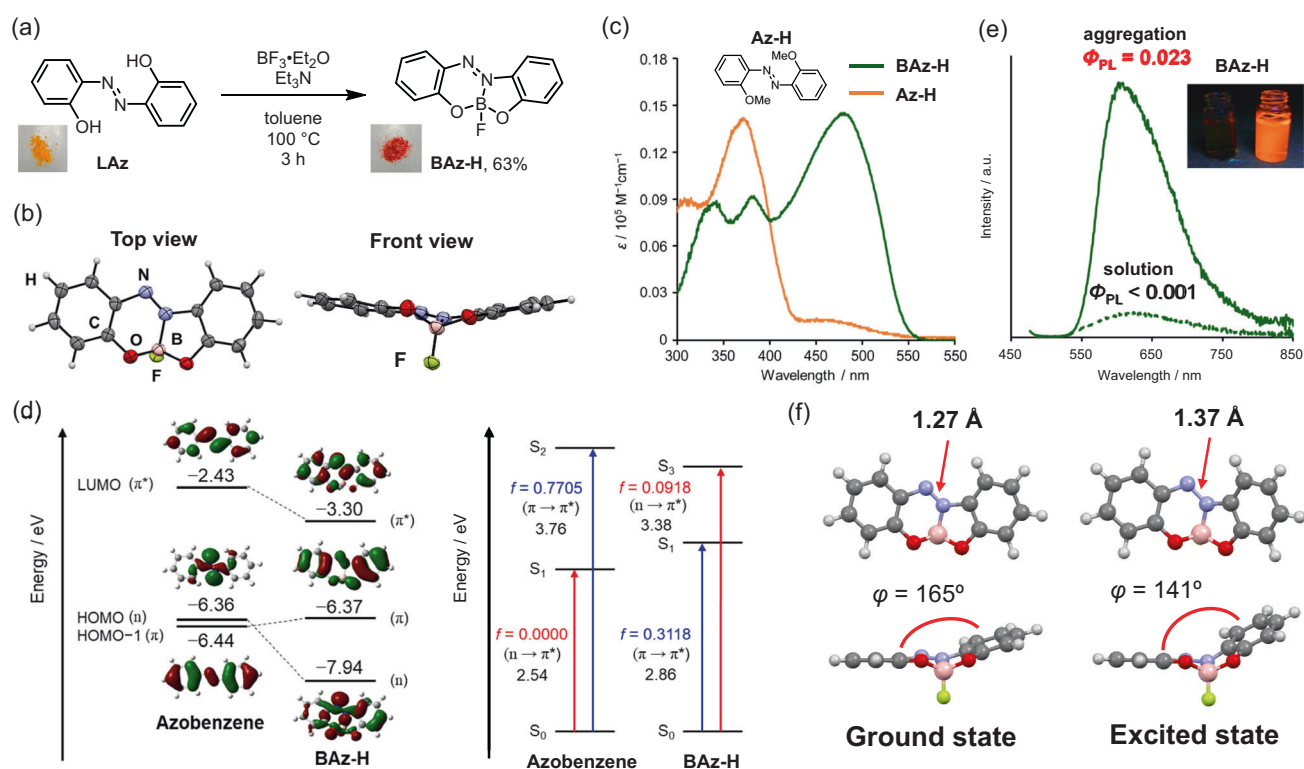


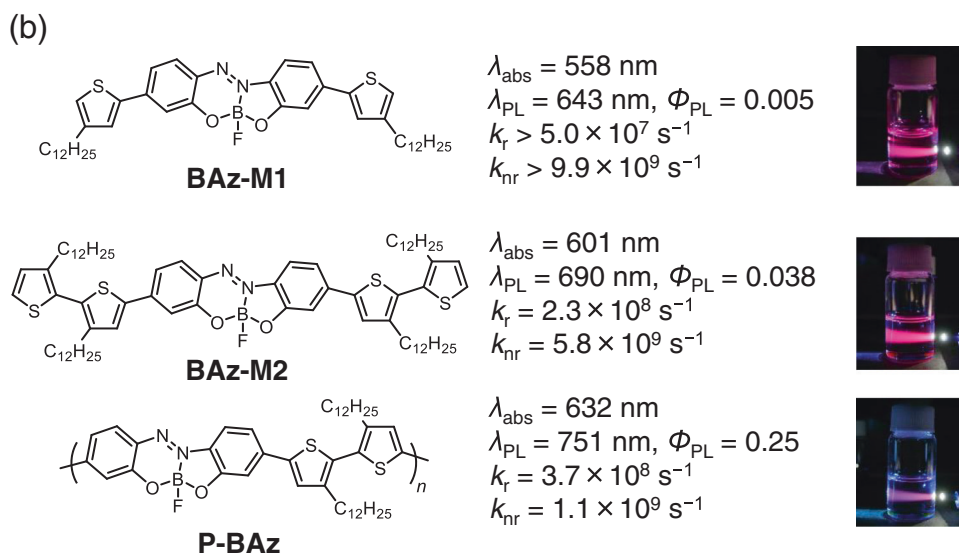
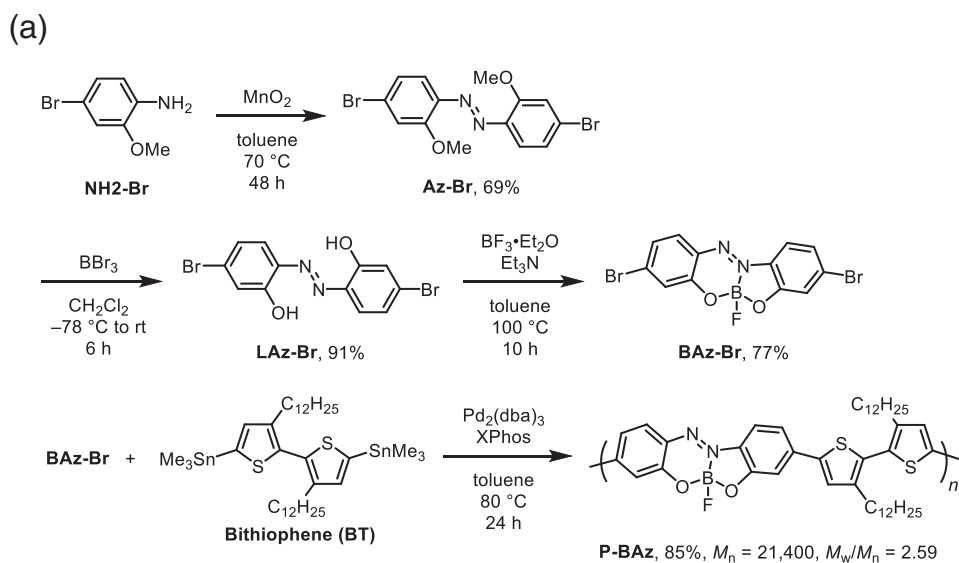
Fig. 3 The functionalities of **BAz-H**. **a** Synthesis of **BAz-H** from **LAz** and their colors. **b** ORTEP drawings of **BAz-H** from the results of single-crystal X-ray structural analysis. **c** UV-vis absorption spectra of **BAz-H** and **Az-H** in toluene ($1.0 \times 10^{-5}\text{ M}$). **d** Energy diagram, selected MOs, and oscillator strength (f) of selected transition bands of azobenzene 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).

the reaction progress can be easily checked on a thin layer chromatography (TLC) plate; in contrast to the ligand, the target compound should generate a new reddish spot at a lower polar area. **BAz-H** can be purified by silica gel column chromatography and is highly stable under ambient conditions. Although partial decomposition in **BAz-H** is caused by photoirradiation or the addition of strong bases, such as a fluoride ion, stability can be enhanced by introducing substituents or polymerization. Incomplete ring fusion with similar reagents was reported in the 1980s by Hohaus and coworkers [29]. Therefore, our case suggested that a high temperature should be necessary for constructing a completely boron-fused structure, such as **BAz-H**. The single crystal X-ray structural analysis with **BAz-H** revealed the tightly ring-fused structure and the perpendicularly protruding fluorine against the π -surface (Fig. 3b). In the UV-vis absorption spectra, a large new absorption band for **BAz-H** was generated in the long-wavelength region ($\lambda_{\text{abs}} = 479\text{ nm}$) compared to the weak absorption band of the azobenzene derivative (**Az-H**) in the similar wavelength region ($\lambda_{\text{abs}} = 400\text{--}500\text{ nm}$) (Fig. 3c). In this case, **LAz** is not suitable for evaluating the fundamental properties of the nonfused azobenzene compound because the two hydrogen

PL spectra of **BAz-H** in 1,4-dioxane ($1.0 \times 10^{-4}\text{ M}$) (solution, dotted line) and 1,4-dioxane/ $\text{H}_2\text{O} = 1/99\text{ v/v}$ ($1.0 \times 10^{-4}\text{ M}$) (aggregation, solid line). **f** Optimized structures 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. Reprinted with permission from ref. [27]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

bonds between nitrogen atoms and hydroxy groups also moderately enhance the intensity of the broad absorption band in the long wavelength region, similar to **BAz-H** [27]. Theoretical calculations with density functional theory (DFT) and time-dependent (TD) DFT supported the dramatic alteration of electronic states by boron complexation. The fundamental mechanism was originally proposed by Kawashima and coworkers with similar luminescent boron-fused azobenzene scaffolds [30]. Accordingly, the boron-nitrogen coordination highly stabilized the non-bonding highest occupied molecular orbital (HOMO) of azobenzene. Then, the π -bonding molecular orbital became HOMO in **BAz-H** (Fig. 3d). Therefore, the weak absorption band assigned to the forbidden $S_0 \rightarrow S_1$ ($n \rightarrow \pi^*$) transition of azobenzene was transformed to the strong absorption band assigned to the allowed $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition. Despite the large oscillator strength (f) of the $S_0 \rightarrow S_1$ transition, **BAz-H** hardly showed emission in solution (absolute photoluminescence quantum efficiency (Φ_{PL}) < 0.001) (Fig. 3e). Our result was opposite to the previously reported azobenzene-boron complexes that showed bright emission in solution [31]. Interestingly, emission enhancement was monitored in aggregation ($\Phi_{\text{PL}} = 0.023$) and in crystal

Fig. 4 a Syntheses of monomer **BAz-Br** and polymer **P-BAz**.
b Optical properties of oligomers and a polymer in toluene (1.0×10^{-5} M per repeating unit for a polymer). Photographs of oligomers and a polymer irradiated by white light from ref. [27]



($\Phi_{\text{PL}} = 0.06$) [27, 32]. These results indicate that **BAz-H** is the AIE- and CIE-active molecule. Theoretical calculations indicated that bending motion occurred in the excited state, in which the structure was more bent, which was probably occurred because the N=N bond was elongated by 0.10 Å compared to the optimized structure in the ground state and the structure against the π -surface was asymmetric (Fig. 3f). In aggregation, this molecular motion should be restricted, leading to an enhancement in emission. Recently, Hori, Tomita, Sohma, Kanai and coworkers obtained unique properties by combining AIE behavior and efficient light-absorption ability in the long wavelength region despite small molecules, which were used for biochemical applications [33]. The BAz derivative worked as a photo-oxygenation catalyst that permeated the blood–brain barrier owing to its small molecular weight; in addition, the catalyst selectively and directly degraded an extracellular

Alzheimer's disease-related undruggable protein, amyloid- β protein. BAz derivatives are sufficiently resistant to water and photobleaching for biological applications.

π -Conjugated polymers based on BAz complexes

The monomers of BAz are synthesized from brominated anisidine derivatives as starting compounds (Fig. 4a) [27]. The condensation reaction with manganese dioxide (MnO_2) provides azobenzene derivatives. Then, the methyl groups can be deprotected by boron tribromide (BBr_3) to afford O,N,O-type tridentate ligands. After boron complexation with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, brominated BAz monomers can be obtained. For example, **BAz-Br** is highly useful as a strong electron acceptor (LUMO energy level: ca. -4.0 eV from cyclic

voltammetry (CV)), and gram-scale synthesis is available without any column chromatography during purification processes. The BAZ derivatives show high redox stability, and the LUMO energy levels can be easily determined from onset reduction potentials in the reversible cyclic voltammograms. The π -conjugated copolymer (**P-BAz**) with **BAz-Br** and the bithiophene unit (BT) as a strong electron donor was prepared by the Migita–Kosugi–Stille cross coupling reaction [34, 35]. The reaction can be executed under neutral conditions and is useful for conducting polymerization with heteroatom-containing monomers without decomposition (Fig. 4a) [27]. After purification, the optical properties were evaluated. Accordingly, **P-BAz** showed highly efficient NIR emission (Fig. 4b). The drastic changes in optical properties were confirmed by investigations on the oligomer models of mono-thiophene (**BAz-M1**) and bithiophene (**BAz-M2**). The oligomers showed both gradual emission enhancement and bathochromic shifts as the number of π -conjugated units increased. These were attributable to both an increase in the radiative constant (k_r) and a decrease in the nonradiative constant (k_{nr}) from the monomer to the polymer. These kinetics changes were relevant to expanded π -conjugation restricting the molecular motion. The first discovery of BAZ complexes strongly suggests that tightly fused but slightly bent π -conjugated structures play important roles in creating novel functional materials, such as stimuli-responsive materials with AIE and NIR emission. These results clearly indicate that BAZ complexes should be promising element blocks for achieving incompatible properties, such as stimuli-responsiveness and solid-state emission properties.

Recently, transient absorption measurements were obtained that provided detailed information on the bending motion in the excited state with similar boron complexes composed of two six-membered rings (Fig. 5) [36]. The structural deformation of **monoBAzM** occurred after photoexcitation, nonradiative deactivation from the structure occurred within 20 ps, and motion was prohibited under restricted conditions, such as in viscous solutions, polymer films, and aggregation. Furthermore, extension of π -conjugation suppressed the deformation in the excited state, leading to strong emission both in solution and solid. Finally, we obtained highly efficient solid-state NIR emission from the totally fused bisboron complex (**bisBAzM**) with CIE properties.

Precise energy control with substituents

The optical properties of BAZ can be precisely controlled by introducing substituents at the azobenzene moiety and boron. We prepared fluorinated BAZ derivatives (**BAz-3F**, **BAz-5F**, **BAz-35F**) at the 3,3' and 5,5' positions of the azobenzene moiety (Fig. 6a) [37]. The energy gaps of

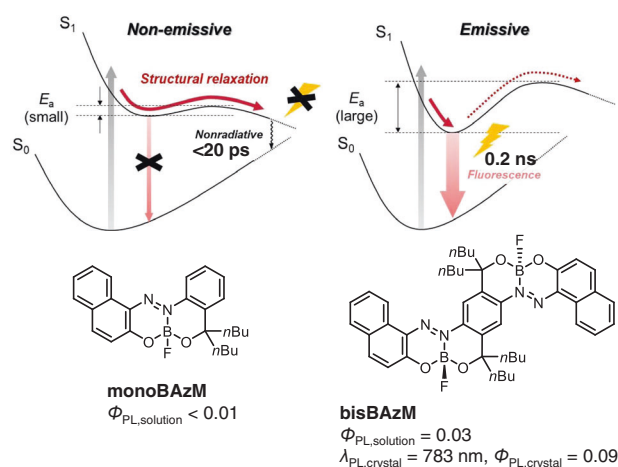


Fig. 5 Schematic illustrations of the S_0 and S_1 energy diagrams and optical properties of **monoBAzM** and **bisBAzM**. Reprinted with permission from ref. [36]. Copyright 2021 The Royal Society of Chemistry

BAz-H and **BAz-3F** or **BAz-5F** and **BAz-35F** were almost the same, and **BAz-5F** and **BAz-35F** showed narrower energy gaps than those of **BAz-H** and **BAz-3F**. These substituent effects occurred because the HOMO energy level should be elevated by the resonance effect from lone pairs of the fluorine atoms, as the HOMO is largely distributed at the 5,5' positions (Fig. 6a). In addition, all BAZ derivatives are AIE active ($\Phi_{\text{PL}} < 0.01$ in solution). The resulting π -conjugated polymers **P-BAz-3F**, **P-BAz-5F**, and **P-BAz-35F** had low-lying LUMO energy levels (-4.09 eV , -4.08 eV , and -4.25 eV from CV, respectively) and showed bright NIR emission in toluene. The emission bands were highly bathochromic-shifted in spin-coated films ($\lambda_{\text{PL}} = 924 \text{ nm}$, 916 nm , 980 nm with $\Phi_{\text{PL}} < 0.01$). The π -electron delocalization of the polymers effectively occurred by connecting at 4,4' positions due to positions *para* to the N=N bond, which enhances absorbance and emission efficiency. In contrast, extension of the π -conjugation hardly induced emission enhancement when connected at the 5,5' positions (*meta*-positions to the N=N bond) in **P-BAz-5BT** (Fig. 6b) [32].

The perpendicularly protruding substituent at boron is effective for enhancing solid-state emission, even in polymers. We synthesized a series of BAZ polymers, **P-BAzC6F5**, **P-BAzPh** and **P-BAzMes**, with perpendicularly protruding aryl derivatives at the boron atom toward π -conjugated systems (Fig. 6c) [28]. The polymers showed efficient NIR luminescence both in solution and film. The substituents at boron affected the energy levels of the molecular orbitals (MOs) of the polymer main chains. Electron-withdrawing and electron-donating groups decreased (-3.92 eV for **P-BAzC6F5** from CV) and increased (-3.79 eV for **P-BAzPh** and -3.82 eV for **P-BAzMes** from CV) the LUMO energy levels of BAZ

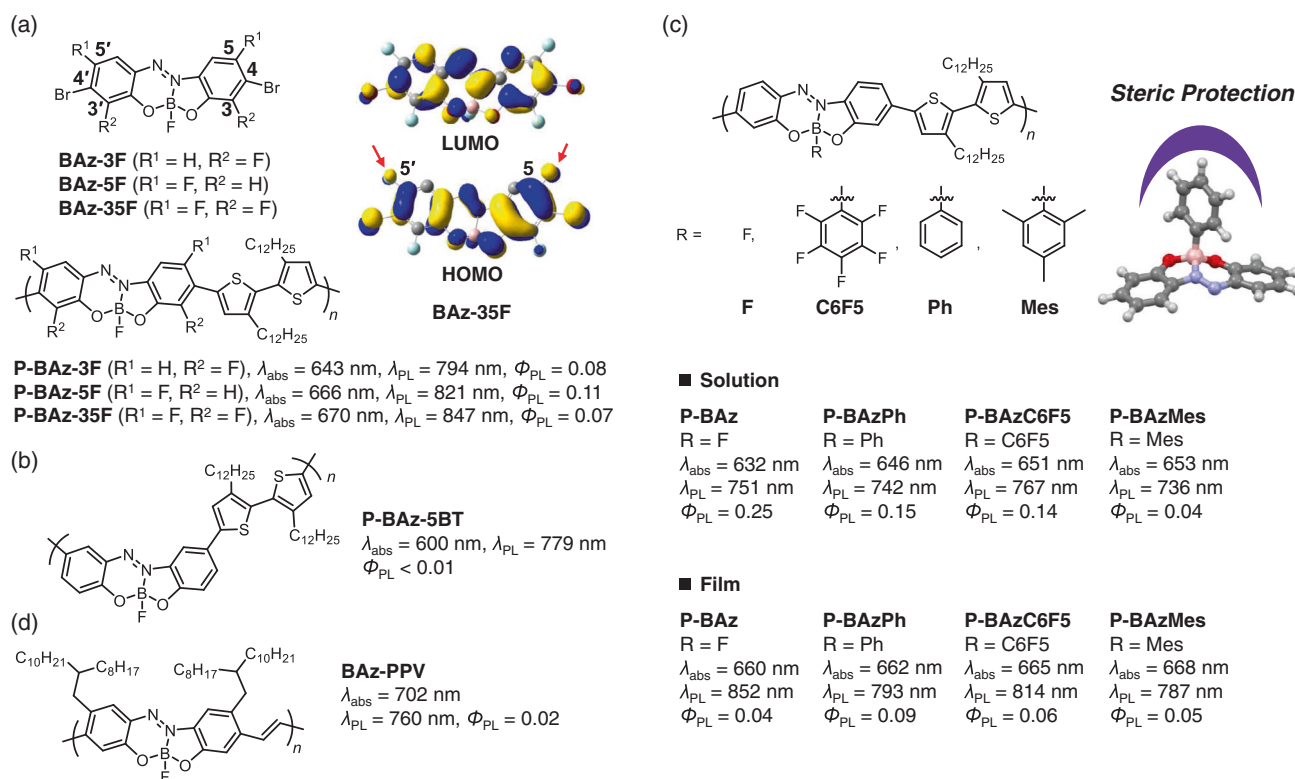


Fig. 6 Chemical structures and optical properties of BAZ polymers; (a) fluorinated BAZ polymers and selected Kohn-Sham orbitals of **BAz-35F** from ref. [37], (b) a BAZ polymer connected at 5,5' positions from ref. [32], (c) BAZ polymers having aryl substituents at boron from ref. [28, 37], (d) a BAZ polymer connected with a vinylene linker from ref. [38]

moieties, respectively. This indicates that the energy gaps are tunable by the substituents at the boron atom.

NIR absorptive and emissive π -conjugated polymers

The extension of the π -conjugated system without the D–A system is much more suitable for evaluating the effect of π -electron delocalization through the BAZ units. We selected vinylene linkers to connect BAZ units and prepared an alternating copolymer (**BAz-PPV**; PPV = poly(*p*-phenylene vinylene)) by the Migita–Kosugi–Stille cross coupling reaction (Fig. 6d) [38]. In this case, long branched alkyl chains were introduced into the azobenzene moiety to ensure sufficient solubility in common organic solvents. Interestingly, it was confirmed from optical measurements that the peak-top wavelengths of absorption and emission reached the NIR region. The effective conjugation length was calculated to be over $n = 50$ by using molecular weight-dependent absorption spectra of the fractionated polymers with high-performance liquid chromatography (HPLC) [39]. In addition, we found that these polymers showed sufficient carrier-transport ability, and both holes and electrons flew to the same degree (10^{-2} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), as estimated from the

time-of-flight (TOF) technique [40, 41]. Based on our data, perpendicularly protruded substitution at boron could less significantly disturb the carrier transport pathway.

CIE property and thermal effect from BAm complexes

BAm derivatives can be prepared by a condensation reaction with O,N,O-type tridentate ligands composed of an azomethine (Schiff base, C=N) moiety, such as *o*-salicylideneaminophenol derivatives and boron sources (Fig. 7a) [42]. Although more BAm derivatives have been reported than azobenzene derivatives, their optical properties remain unclear [43, 44]. Initially, we prepared the BAm derivative with a diethylamino group (**Et2N-BAm**) (Fig. 7a) [42]. The diethylamino group was introduced to enhance the emission property. The BAm derivatives also show high stability under ambient conditions and are potentially decomposed by strong bases, similar to BAZ derivatives. **Et2N-BAm** exhibits a slightly bent structure similar to the BAZ derivatives. The structural flexibility provided two polymorphic crystals during a recrystallization process in THF under a hexane atmosphere. The crystals exhibited different colors and shapes, and we named a yellow needle-like crystal the

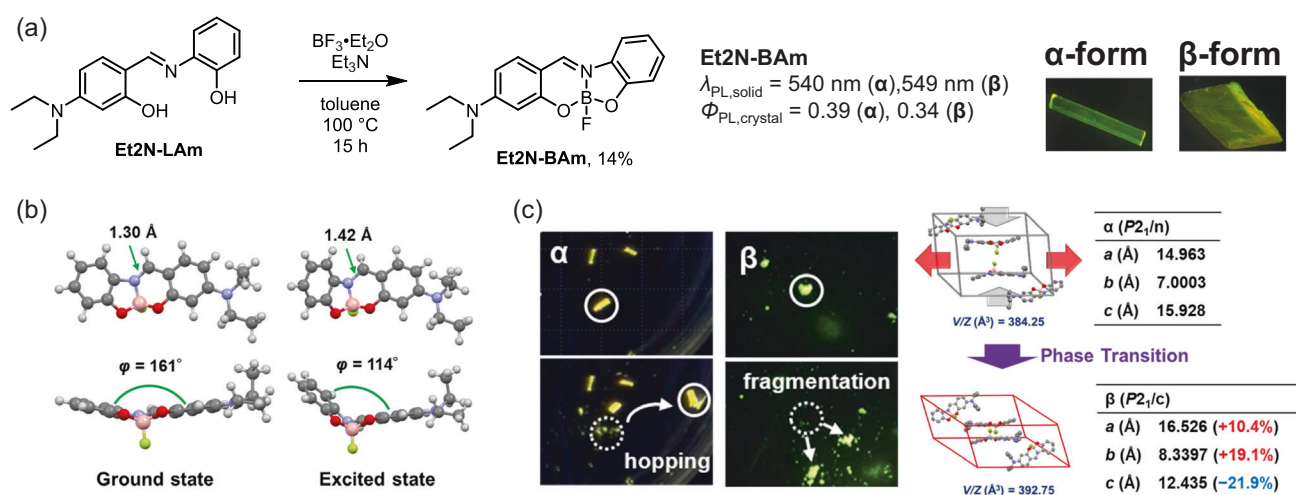


Fig. 7 **a** Synthesis and optical properties of crystal polymorphs of **Et2N-BAm**. **b** Optimized structures in the ground and excited states of **Et2N-BAm** with DFT and TD-DFT calculations at the B3LYP/6-311G(d,p) and TD-B3LYP/6-311+G(d,p) levels, respectively. **c** Snapshots of thermal and photo-induced behaviors irradiated by a UV lamp

(365 nm) and anisotropic deformation of unit cells of α and β during the $\alpha \rightarrow \beta$ crystal-crystal transition. Reprinted with permission from ref. [42]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

α -form and an orange block crystal the β -form (Fig. 7a). Both crystals showed highly efficient emission, whereas the emission was totally annihilated in solution. Theoretical calculations supported that the distinct CIE property from **Et2N-BAm** occurred with bendable motions in the excited state similar to the BAz derivatives (Fig. 7b). Additionally, we observed the thermal effect, in which crystals jump by temperature changes; [45] this effect is triggered by reversible crystal-crystal phase transitions by both heating and cooling accompanied by emission color changes (Fig. 7c). The number of crystals showing the thermal effect with emission color changes is still limited [46–48]. The flexible and tightly fused conformation should be responsible for these unique physical functions.

Crystal polymorphs are intentionally created by applying different crystal packing structures originating from racemic and homochiral products. We synthesized **Et2N-BAm-Cl** and separated the enantiomers by chiral HPLC (Fig. 8a) [49]. In this case, crystallinity decreased after the separation, and chlorine was necessary to compensate for the sufficient crystallinity. As expected, different space groups, $P2_1/c$ and $P3_2$, were obtained from the crystals of *rac*-**Et2N-BAm-Cl** and (*R*)-**Et2N-BAm-Cl**, respectively. In addition, we observed different optical properties depending on the conformation and crystal packing structures. The inherent flexible structure of BAm should allow for flexible arrangement in both racemic and homochiral crystals. As a result, we succeeded in converting the information of chirality to that of luminescence, which is more easily detectable. Furthermore, the chiral products showed weak circularly polarized luminescence (CPL, dissymmetry factor

in luminescence ($g_{\text{lum}} = \text{ca. } 10^{-4}$; $g_{\text{lum}} = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$ (I_{left} , I_{right} : PL intensities of left- and right-handed CPL, respectively)) in crystal and had large specific rotation values ($[\alpha]_{\text{D}}^{23} = \text{ca. } \pm 1200$) in solution.

As described in BAz derivatives, the molecular flexibility, especially in the excited state, strongly affected the degree of electronic interaction in the π -conjugated system. The bisboron complex with an extended BAm system (**bisBAmM**) was prepared to evaluate the relevance between π -conjugation and emission (Fig. 8b) [50]. Diastereomers of **bisBAmM** (*syn*- and *anti*-**bisBAmM**) were present due to the two stereogenic boron centers, and they were successfully separated by a reprecipitation method with different solubilities of soluble *syn*-**bisBAmM** and insoluble *anti*-**bisBAmM** in diethyl ether. Interestingly, **bisBAmM** showed efficient NIR emission both in solution and as a solid owing to its robust fully fused structure. Moreover, *anti*-**bisBAmM** also exhibited the CIE property of BAm. Three bulky phenyl groups around boron should help prevent π - π stacking, leading to ACQ.

The AIE or CIE and ACQ properties can be switched by controlling structural flexibility. In quinoline-based BAm derivatives, we prepared a slightly bent and tightly ring-fused structure (**BPhQ**) and a planar and loosely ring-fused structure with a methylene spacer (**BPhQM**) (Fig. 8c) [51]. Accordingly, it was revealed that **BPhQ** showed AIE and CIE properties, whereas **BPhQM** exhibited ACQ properties. The methylene spacer promoted ACQ by eliminating structural distortion and close and consecutive π - π interactions. Understanding monomeric properties is useful for designing π -conjugated polymers with solid-state emission properties.

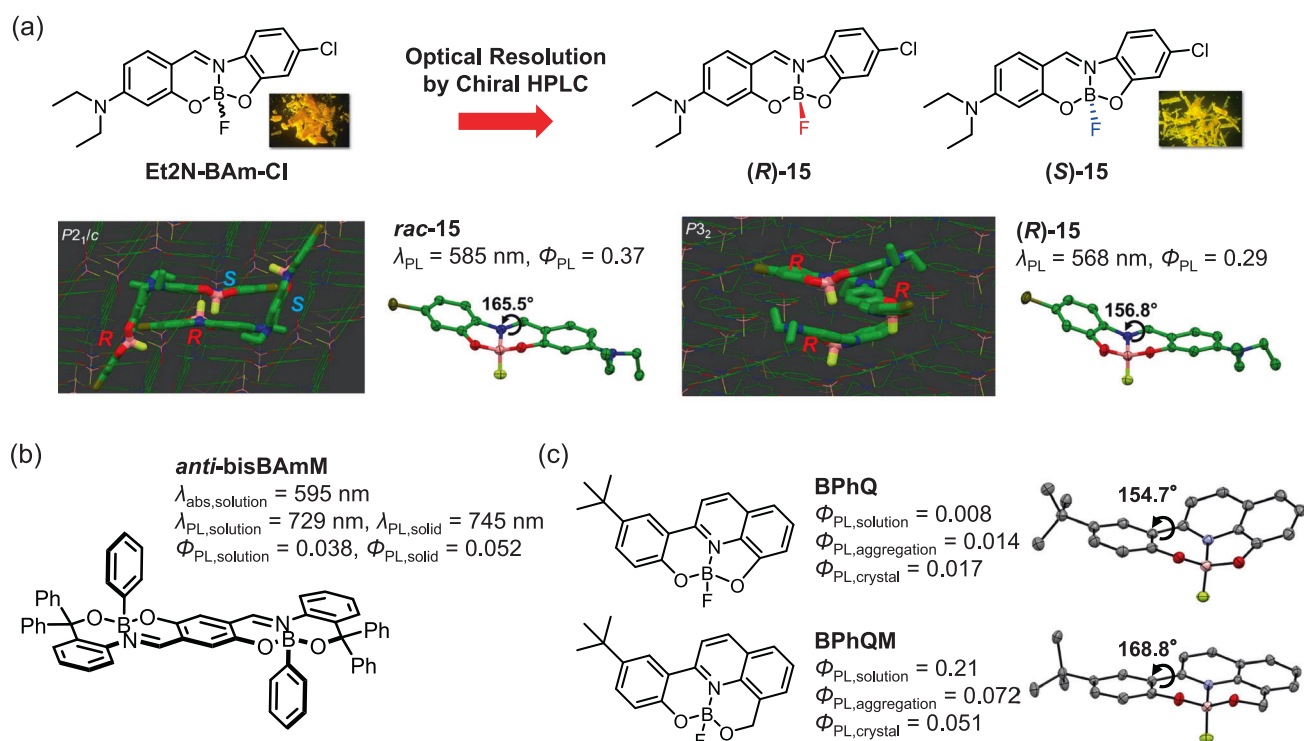


Fig. 8 **a** Chemical structures, separation of enantiomers, optical properties in crystal, ORTEP drawings from results of single crystal X-ray structural analysis and packing structures of **BAm-Et₂N-Cl**. Reprinted with permission from ref. [49]. Copyright 2020 The Royal Society of Chemistry. **b** Chemical structures and optical properties of

anti-bisBAmM from ref. [50]. **c** Chemical structures, optical properties, and ORTEP drawings from the results of single crystal X-ray structural analysis of **BPhQ** and **BPhQM**. Reprinted with permission from ref. [51]

π -Conjugated polymers based on BAm complexes

In the above sections, we introduced the monomer properties of BAm derivatives, and their emission bands tended to be located at higher energy areas than those of BAZ derivatives. Additionally, in polymers, it is predicted that converting the N=N bond to the C=N bond in the PPV system provides wide energy gaps with an increase in HOMO and LUMO energy levels [52]. Therefore, we expected that excellent emission both in solution and solid in the visible region can be obtained from π -conjugated polymers based on BAm. We synthesized D-A-type π -conjugated copolymers with BAm and fluorene (**BAmP-F**) and bithiophene (**BAmP-T**) units by the Migita–Kosugi–Stille cross coupling reaction (Fig. 9a) [53]. We adopted a scaffold with two six-membered rings to ensure sufficient solubility by introducing two long alkyl chains at the methylene spacer. Interestingly, efficient yellow and red emissions were observed both in solution and film from **BAmP-F** and **BAmP-T**, respectively. LUMO energy levels were experimentally estimated to be -3.18 eV for **BAmP-F** and -3.31 eV for **BAmP-T** from CV, and therefore, emission in the visible region was attributed to the weaker electron-accepting ability of the BAm units compared to the BAZ

units. In addition, BAm derivatives also exhibit high redox stability in reversible cyclic voltammograms, similar to BAZ derivatives. The model copolymers without boron hardly showed emission, and boron coordination is critical for obtaining bright emission from nitrogen-containing π -conjugated polymers in the main chain. These results suggest that the emission color can be tuned from the visible to NIR region by selecting flexible electron-accepting comonomers based on BAm and BAZ.

Next, we successfully observed stimuli-responsiveness from the BAm polymers upon exposure to solvent vapor while retaining their bright emission in film by tuning the length of the alkyl side chains [54]. Six kinds of polymers, **BAm_aBT_b** ($a = 2, 8, 12$, $b = 0, 2, 6, 12$), were prepared to investigate the stimuli-responsiveness depending on the length of the alkyl side chains (Fig. 9b). All polymers showed efficient emission, and the shorter alkyl chains at the bithiophene unit ($b = 0, 2$) dramatically decreased their emission efficiencies both in solution and film. The emission behavior of two types of polymers, **BAm₂BT₁₂** and **BAm₈BT₂**, with combinations of shorter and longer alkyl chains, changed after exposure to dichloromethane (DCM) vapor. In particular, **BAm₂BT₁₂** showed a distinct bathochromic shift in emission spectra without a loss of efficiency ($\lambda_{\text{PL}} = 644 \rightarrow 685 \text{ nm}$, $\Phi_{\text{PL}} = 0.37 \rightarrow 0.36$). This study suggests that

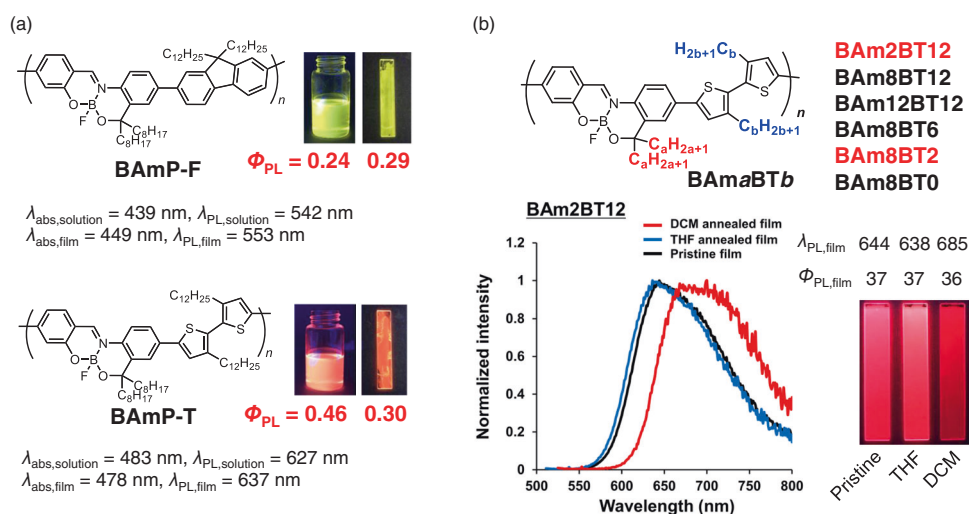


Fig. 9 a Chemical structures and optical properties of **BAMp-F** and **BAMp-T** with photographs in solution and film states irradiated by a UV lamp (365 nm). Reprinted with permission from ref. [53]. Copyright 2020 American Chemical Society. **b** Chemical structure of **BAMaBTb**, PL spectra, and optical properties of **BAM2BT12** in film

before and after exposure to solvent vapors with photographs irradiated by a UV lamp (365 nm). The polymers showing vapo-chromism are marked in red. Reprinted with permission from ref. [54]. Copyright 2021 The Royal Society of Chemistry

alkyl chains support stimuli-responsiveness in films, including flexible comonomers with bright emission.

Conclusion and future research outlook

In this study, we demonstrated examples of unique optical functions based on flexible heteroatom-containing complexes. The flexibility of the complexes is derived from the slightly bent and asymmetric structure against the π -surface, and the distinctive structural formation is created by the combination of heteroatoms. Flexible monomers as a part of the PPV backbone, including the N=N and C=N bonds, were designed to modulate the optical properties by regulating the degree of electronic interaction with the monomer units in the main-chain conjugation. The resulting polymers achieved highly efficient emission in the visible to NIR region in solution and as a solid. The molecular orbital energy can be easily controlled by introducing substituents at the π -surface of the main-chain conjugation and at boron. In particular, the substituent at boron is effective for preventing ACQ caused by intermolecular π - π interactions, and the polymer film can show high carrier mobility. Furthermore, various types of stimuli-responsiveness, such as the thermal effect and vapo-chromism, are observed owing to the structural flexibility.

The electron-accepting ability of BAZ monomers can be greatly enhanced by chemical modification. Additionally, BAZ polymers are promising candidates for inducing NIR-II (1000–1700 nm) absorption and emission, which are very necessary for biomedical applications. The perpendicularly

protruding substituent at boron is useful for introducing functional groups independently without affecting the electronic properties of the polymer main chains. The substituent at boron can be released through decomposition in the boron complex by base photoirradiation and neutron irradiation. In particular, the reactivity of boron with neutrons can be utilized for boron neutron capture therapy (BNCT), which is applicable to medical treatment with a combination of NIR absorption/emission and other properties. Carrier mobility and solid-state luminescent properties are available for polymer-based electroluminescence (EL) devices from the visible to NIR region. Furthermore, the concept based on flexible heteroatom-containing complexes can be expanded to use other group elements. Indeed, we recently observed vapo-chromism from tin-fused azobenzene with a coordination-number change of hypervalent bonds. As another instance, germanium-fused azobenzene showed a larger degree of bathochromic-shifted absorption and emission than that of tin- and boron-fused azobenzene complexes. Now, we aim to expand this system to Group 15 heavy elements, such as bismuth. Heteroatom-containing π -conjugated systems show the potential to produce unprecedented features beyond expectations. The construction of conjugated systems involving element blocks should synergistically create advanced functional materials for future technology.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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