

Development of Near-Infrared Light-Emitting π -Conjugated Polymers Based on Hypervalent Silicon(IV)-Fused Azobenzene Compounds as a Strong Electron Acceptor

Ippei Kanetani¹, Masayuki Gon^{1,2}, and Kazuo Tanaka^{1,2*}

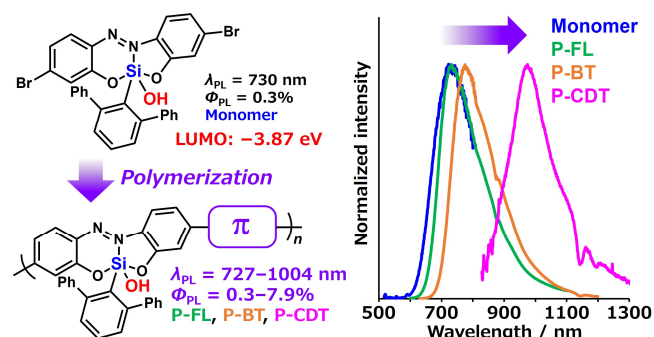
¹ Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Katsura, Kyoto 615-8510, Japan.

² Department of Technology and Ecology, Graduate School of Global Environmental

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp

Keywords: hypervalent silicon; azobenzene; near-infrared emission; π -conjugated polymer, solid-state emission

Table of Contents



Abstract

Near-infrared (NIR) light-emitting materials have attracted attention in the fields of optical communication and bioimaging. To improve the utility of NIR light-emitting materials, it is significant to increase their chemical stability and solubility in common solvents. In this study, we synthesize hypervalent silicon(IV)-fused azobenzene (SAz) compounds and their π -conjugated polymers exhibiting NIR emission both in solution and film (maximum photoluminescence (PL) wavelength: $\lambda_{\text{PL}} = 727\text{--}1004$ nm, absolute PL quantum yield: $\Phi_{\text{PL}} = 0.3\text{--}7.9\%$). The introduction of a bulky terphenyl group on silicon ensures sufficient chemical stability of the SAz backbone and solubility of the compounds in common solvents. The SAz compounds have a strong electron-accepting ability reaching -3.87 eV in the lowest unoccupied molecular orbital (LUMO) energy level owing to the combination of the five-coordinated hypervalent silicon and the azobenzene tridentate ligand. By constructing donor–acceptor systems based on π -conjugated polymers, the optical properties are dramatically improved not only by increasing the radiative transition probability but also by suppressing the structural relaxation in the SAz moiety. Our results reveal that hypervalent silicon compounds are a promising candidate for the development of advanced NIR light-emitting materials.

Introduction

Near-infrared light (NIR, 700–2500 nm) is invisible to the human eye and known for low-scattering property in the air and high permeability to various materials.^{1,2} In particular, the wavelength range from 1,000 to 1,700 nm is called the second optical window (NIR-II), and the light in the NIR-II region has superior deep penetration depth into biotissues.^{3,4} Therefore, the demand for NIR light-emitting materials is increasing in the fields of optical communications and bioimaging.^{5–9}

Recently, donor–acceptor (D–A) type π -conjugated polymers have attracted much attention as the molecular design to achieve absorption/PL in the NIR region.^{10–14} The highest occupied molecular orbitals (HOMOs) of the electron donor units and the lowest unoccupied molecular orbitals (LUMOs) of the electron acceptor units play a significant role in determining the energy gap (E_g) of D–A type π -conjugated polymers. Therefore, this strategy can be a powerful tool for narrowing the energy gap, leading to the bathochromically-shifted absorption and PL wavelengths. The development of strong donor molecules has been limited by concerns that their high HOMO energy levels reduce their stability against oxidation in air.^{15,16} In contrast, the development of strong acceptor molecules with low LUMO energy levels can overcome such limitations. However, there are few examples of strong acceptor skeletons, and the design and development of novel acceptor molecules are desired.^{17–20} In addition, the extension of the π -conjugation with polymerization can improve optical performances by increasing the molar extinction coefficient and radiative transition probability. Meanwhile, it often decreases solid-state emission efficiency due to aggregation-caused quenching (ACQ) originating from strong nonspecific interchain π – π interactions.²¹ Therefore, it is necessary to incorporate

molecular designs that can disturb interchain π - π stacking among conjugation units to suppress ACQ followed by highly-efficient solid-state emission.

To lower the LUMO energy level of the π -conjugated units, the strategy of introducing heteroatoms into their molecular skeletons is effective.²²⁻²⁶ We have suggested the concept of “aza-substitution”, in which a nitrogen replaces a skeletal carbon atom that has a large contribution of the HOMO or LUMO orbital for the π -framework based on the frontier molecular orbital (FMO) theory.^{27,28} The “aza-substitution” enables selective reduction of the energy level of the π -conjugated systems, leading to drastic modulation of the energy gap. As an example, azobenzene (Ph-N=N-Ph), in which the two central carbons of stilbene (Ph-CH=CH-Ph) are replaced with nitrogen, has been found to have a lower LUMO energy level and a narrower energy gap compared to stilbene.^{29,30} Since the azobenzene is generally non-emissive due to the *cis-trans* photoisomerization and the forbidden S_0 - S_1 transition assigned to the n - π^* transition,^{31,32} chemical modifications to the azobenzene skeletons are required to obtain the emission.

Recently, it was reported that the bright emission can be observed from a series of azobenzene compounds by coordinating Lewis acidic boron and the lone-pair electrons of nitrogen in the azobenzene moiety.³³⁻³⁶ This is because the coordination not only suppresses the *cis-trans* photoisomerization of the azobenzene but also converts the S_0 - S_1 transition to the allowed π - π^* transition. We also developed excellent novel acceptor molecules with boron-fused azo/azomethine complexes (BAz/BAm) composed of azo/azomethine tridentate ligands.³⁷⁻⁴⁰ It was found that the boron-fused azo/azomethine complexes (BAz/BAm) show very weak emission in the diluted solution state, meanwhile they exhibit intense emission in the aggregated and crystalline states. These phenomena called aggregation-induced emission (AIE)^{37,41-43} and crystallization-induced emission

enhancement (CIEE)^{41,44–46}, respectively. According to the mechanistic studies, it is proposed that the emission quench in the dilute solution state should be due to the bending motion of the BAz/BAm skeletons caused by the elongation of the nitrogen–nitrogen double (N=N) bond in the excited state.⁴⁷ The aggregated and crystalline states suppresses such structural relaxation, and subsequently the emission efficiency increases by closing the nonradiative decay channel. By incorporating the BAz/BAm units into the π -conjugated polymers, similar restriction of the molecular motion is also obtained, and their extended π -conjugation also enhances the optical properties accompanied by the bathochromically-shifted absorption and emission wavelengths. Additionally, the interchain π – π stacking can be suppressed by the substituent on the boron that protrudes orthogonally to the π -conjugated systems, leading to highly-efficient NIR emission in the solid state.^{37,47–53}

More recently, we developed the molecules incorporating heavy group 14 elements such as tin (Sn) and germanium (Ge) into azobenzene tridentate ligands (TAz and GAz).^{54–56} Unlike the coordination with the empty p orbital of boron, the group 14 elements are coordinated to form the hypervalent state, in which more than eight electrons are formally observed around the central element based on the Lewis octet rule.⁵⁷ Compared to BAz, these hypervalent compounds show absorption and emission in the longer wavelength region and proved to be applicable as a platform for the development of NIR-emitting π -conjugated polymers.^{58–62} In the case of silicon (Si), the strongest electron-accepting ability with low LUMO energy level is expected owing to the small atom size of silicon compared to the tin and germanium. Although several hypervalent silicon compounds with azo/azomethine tridentate ligands were synthesized,^{63–65} π -conjugated polymers including them as repeating units have never been realized. This

should be because the five-coordinated silicon-fused azo/azomethine (SAz/SAm) compounds are not considered stable enough to withstand the polymerization conditions. Our research group reported the blue and NIR light-emitting π -conjugated polymers including stable five-coordinated silicon compounds based on benzo[*h*]quinoline-based organosilicon,⁶⁶ dibenzosilepin⁶⁷ and silicon formazanate scaffolds⁶⁸. From these reports, we expected that increasing chemical stability of the SAz/SAm compounds should be a key factor for preparing their π -conjugated polymers.⁶⁹

In this study, we synthesized the hypervalent SAz compounds and observed highly-efficient NIR emission from their D–A type π -conjugated polymers incorporating the SAz units as an electron acceptor. Hypervalent SAz derivatives were stabilized by introducing a terphenyl group which sterically protects the silicon center from nucleophilic attack. Consequently, the introduction of the terphenyl group provides sufficient stability and solubility for polymerization. Furthermore, the optical properties can be modulated by variable substituents (phenyl, methyl, and hydroxyl groups) at the apical position of the hypervalent silicon. Finally, the SAz compound was used as an acceptor unit to construct D–A type π -conjugated polymers. Consequently, its π -conjugated polymers not only showed the bathochromically-shifted absorption and emission in the NIR region but also enhanced the emission efficiency compared to the monomer. In addition, these polymer films also exhibited solid-state emission owing to the presence of the bulky terphenyl group that can disturb interchain interaction. In particular, the emission wavelength in the film state reached the NIR-II region. These results suggest the usefulness of SAz compounds as a novel acceptor unit to create NIR light-emitting polymer materials.

Results and Discussion

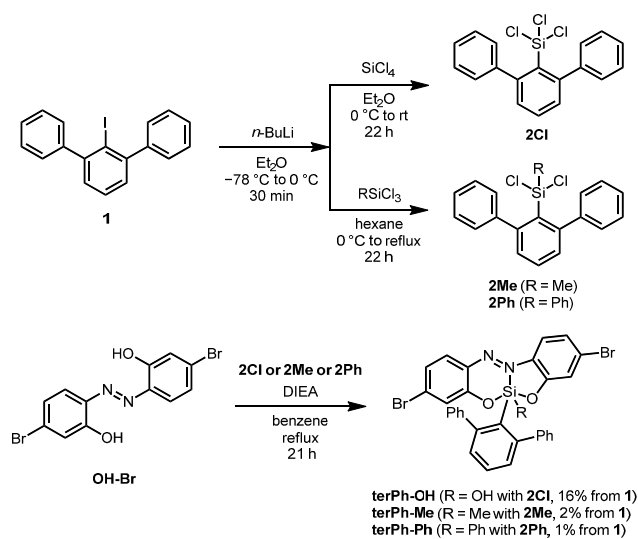
Synthesis

The outline of the synthesis of SAz derivatives is shown in Scheme 1. After the reaction of 2-iodo-1,1:3,1-terphenyl (terPh, **1**) with *n*-butyllithium (*n*-BuLi) in diethyl ether (Et₂O), the corresponding chlorosilane derivatives were added to prepare crude products of terPh silane derivatives (**2Cl**, **2Me**, and **2Ph**). The crude products were filtrated followed by removing the solvent of the filtrate *in vacuo*, then **OH-Br** and *N,N*-diisopropylethylamine (DIEA) were added and reacted at 60 °C in benzene to afford SAz derivatives with terPh groups, **terPh-OH**, **terPh-Me**, and **terPh-Ph** in 16%, 2%, and 1% isolated yields, respectively. Notably, the chlorine on silicon from **2Cl** was converted to the OH group to provide **terPh-OH** during purification process. All compounds are stable enough to be purified by silica gel column chromatography at ambient condition. The low product yields should be caused by the low reactivity of the silicon center covered with the steric terPh groups.

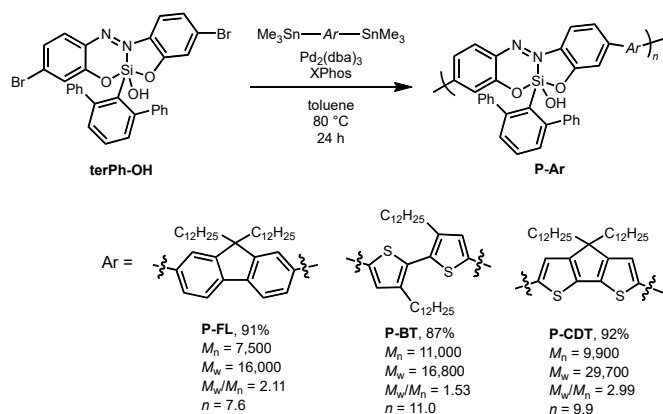
By using **terPh-OH** as an electron acceptor, D–A type π -conjugated polymers (**P-FL**, **P-BT**, and **P-CDT**) were synthesized by the Migita–Kosugi–Stille cross-coupling reaction^{70,71} in the catalytic system of Pd₂(dba)₃ (dba=dibenzylideneacetone) using 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) as a phosphine ligand (Scheme 2). As commoners, fluorene (FL) for **P-FL**, bithiophene (BT) for **P-BT**, and cyclooctadithiophene (CDT) for **P-CDT** were used as weak, moderate, and strong donor units, respectively. The production of polymers was confirmed from the data with gel permeation chromatography (GPC), and the number- and weight-average molecular weights (M_n and M_w) of the polymers were determined as a relative value toward the polystyrene standards (Figure S1 and Table S1). Moreover, to confirm the effect of

extension of π -conjugation on the optical properties, a model compound (**M-BT**) was also synthesized (Scheme 3). All polymers had good solubility in common organic solvents such as toluene, tetrahydrofuran (THF), CHCl_3 , and dichloromethane (CH_2Cl_2) owing to the bulky terPh groups sterically covering the π -conjugated system and suppressing interchain interactions.

The chemical structures of the synthesized compounds in this study were confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{29}Si NMR spectroscopy and high-resolution mass spectrometry (Charts S1–S24). The ^{29}Si NMR signals of the SAz derivatives were observed from -70 to -110 ppm, suggesting that the five-coordinated silicon should be formed in the solution.⁶⁵ From the $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, it was clearly revealed that the two benzene rings of the azobenzene skeleton cannot be distinguished. It is probably because of pedal motion of the azobenzene skeleton.^{64,65,72,73} In the single-crystal X-ray diffraction analysis of **terPh-OH**, the structure was confirmed to be five-coordinated silicon with square pyramidal (SP) geometry (Figure S2 and Table S2).

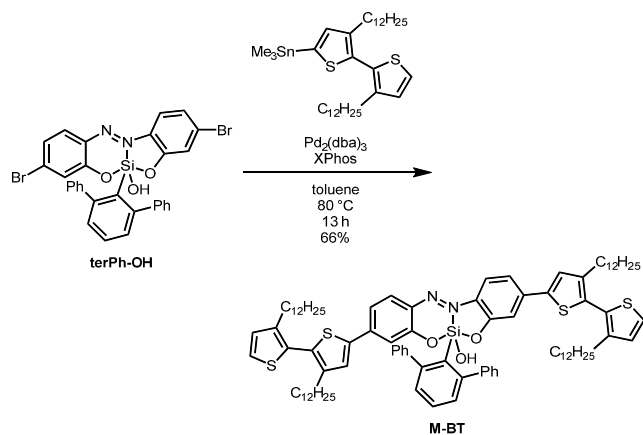


Scheme 1. Synthesis of SAz derivatives.



Scheme 2. Synthesis of D–A type π -conjugated polymers (**P-FL**, **P-BT**, and **P-CDT**).

The regiorandom polymers were obtained, and this certain structure is shown here.



Scheme 3. Synthesis of a model compound (**M-BT**).

Optical property

To investigate the substituent effect at the apical position of the synthesized hypervalent silicon compounds, UV–vis absorption and PL spectra measurements of **terPh-OH**, **terPh-Me**, and **terPh-Ph** were performed (Figure 1 and Table 1). As a result, not only the electronic state of the π -conjugated system in the ground state but also the degree of structural relaxation in the excited state can be tuned by the substituents at apical position. In UV–vis absorption spectra, the maximum absorption wavelengths (λ_{abs}) were longer for **terPh-OH**, **terPh-Me**, and **terPh-Ph** in that order (Figure 1a). This means that the energy levels of FMOs in the ground state can be modulated by the substituents at the apical position. On the other hand, similar PL spectra were observed in the NIR region regardless of the substituents (Figure 1b). This fact means that they have similar electronic states in the excited state. The Stokes shifts ($\Delta\tilde{\nu}$) were smaller for **terPh-OH**, **terPh-Me**, and **terPh-Ph** in that order. These data represent that the substituents on silicon can affect the degree of structural relaxation in the excited state, and the smaller substituents at the apical position tend to show larger structural relaxation. The higher quantum efficiency can be obtained by suppressing structural relaxation although the Φ_{PL} values were low.

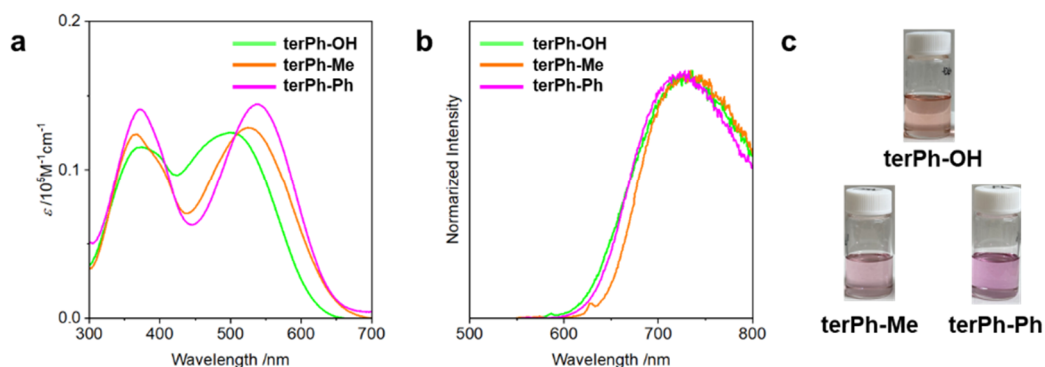


Figure 1. a) UV–vis absorption and b) PL spectra of SAz derivatives excited at each absorption maximum wavelength in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$). c) Photographs of the CHCl_3 solutions of SAz derivatives under room light.

Table 1. Optical data of SAz derivatives in the diluted solution state

	$\lambda_{\text{abs}}^a / \text{nm}$	$\epsilon^a / \text{cm}^{-1} \text{ M}^{-1}$	$\lambda_{\text{PL}}^a / \text{nm}$	$\Delta\tilde{\nu}^b / \text{cm}^{-1}$	$\Phi_{\text{PL}}^{a,c} / \%$
terPh-Ph	372, 538	14,400	725	4790	0.9
terPh-Me	367, 526	12,900	732	5350	0.5
terPh-OH	372, 501	12,500	730	6260	0.3

^a In CHCl_3 ($1.0 \times 10^{-5} \text{ M}$), excited at λ_{abs} for PL, ϵ : molar extinction coefficient. ^b Stokes shift; $\Delta\tilde{\nu} = 1/\lambda_{\text{abs}} \times 10^7 - 1/\lambda_{\text{PL}} \times 10^7$. ^c Absolute PL quantum yield, excited at λ_{abs} .

Next, the optical properties of each compound in the solid state were evaluated (Figure S3 and Table S3). PL measurements revealed that the emission efficiency in the solid state was slightly enhanced compared to that in the diluted solution state (Figure S3a). Similar behavior was also observed from the BAz derivatives,^{37,41} suggesting that the structural relaxation of SAz derivatives in the excited state is partially suppressed in

the solid state. To obtain further insight into the molecular motion, we measured the PL spectra and the emission efficiency of SAz derivatives under cryogenic conditions (Figure S3b). Consequently, a significant increase in the emission efficiencies accompanied by hypsochromic shifts of the emission bands were observed in all compounds at 77 K. In particular, **terPh-OH** showed the more hypsochromically-shifted wavelength and the higher emission efficiency than **terPh-Me** and **terPh-Ph**. Considering that the molecular motion is strongly restricted at glass-forming solvent at 77 K, these results support that the emission efficiency should be affected by the degree of structural relaxation in the excited state. Therefore, to impart excellent NIR light-emitting properties to the SAz derivatives, it is necessary to design molecules that suppress such structural relaxation.

As the strategy for suppressing the structural relaxation, the effect of extension of π -conjugation was investigated by comparing the optical properties of the monomer (**terPh-OH**), oligomer (**M-BT**), and polymer (**P-BT**) based on the backbone of **terPh-OH** which has the highest emission intensity in the cryogenic state. The results are shown in Figure S4 and Table S4. In summary, it was found that the extension of π -conjugation is effective in suppressing the structural relaxation of the hypervalent silicon compounds, followed by enhancing the optical properties. By expanding the π -conjugated system, larger bathochromic shifts in absorption and PL wavelengths were observed accompanied by increases in emission efficiencies. We determined the kinetic parameters such as a radiative rate constant (k_r) and a non-radiative rate constant (k_{nr}) from a PL lifetime measurement (Figure S5 and Table S4). It was suggested from the data that the increase in emission efficiency is attributed to both the elevation of the radiative rate constant and the reduction of non-radiative constant. These are involved in the enhancement of radiative transition probability and restriction of structural relaxation, respectively, owing

to the delocalized π -electron through the main-chain π -conjugated system.

To evaluate the utility of the polymers whose optical properties can be modulated by the selection of comonomers, UV-vis-NIR absorption and PL spectra of the polymers, **P-FL**, **P-BT**, and **P-CDT**, were measured (Figure 2 and Table 2). From the PL measurements, it was shown that strong NIR emissions can be obtained from these polymers at wavelengths ranging from 700 to 1,000 nm depending on the strength of the donor units (donor strength: FL < BT < CDT). **P-FL** showed the bathochromic shift of the absorption band compared to the monomer. This should be attributed to the smaller energy gap because of the extension of the π -conjugated system. Furthermore, the emission intensity in diluted solution was confirmed to be 4.0%. This result means that a significant increase in emission efficiency can be accomplished by polymerization. It is because the expansion of π -conjugation should contribute to suppression of structural relaxation in the excited state and enhancement of radiative transition probability. This effect on optical properties by polymerization is also supported by the smaller Stokes shift of **P-FL** compared to the monomer (**terPh-OH**).

In addition, further bathochromic shifts of the absorption and emission bands were observed in **P-BT**. This should be attributed to the construction of the strong D-A interactions between BT and SAz units reducing the energy gap in addition to the expansion of the π -conjugation. A further increase in emission efficiency was also detected in **P-BT**. This should be because of the D-A interaction in the more rigid π -conjugated system and the increase in the radiative transition probability originating from the introduction of the electron-donating BT unit. Therefore, the D-A type π -conjugated polymerization is a valid strategy for realizing excellent PL properties in the NIR region.

In **P-CDT**, the maximum absorption and PL wavelengths were found to be over 800

nm and close to 1,000 nm in the diluted solution, respectively, owing to the CDT donor unit, which is expected to extend the π -conjugated system because of its high planarity and superior electron-donating property compared to FL and BT units. Although the emission intensity was lower than that of **P-FL** and **P-BT**, high emission efficiency can be obtained in the near NIR-II region. In the previous our reports, the D–A type π -conjugated polymers including CDT units showed a small Stokes shift ($\Delta\tilde{\nu} < 1000\text{ cm}^{-1}$) and large self-absorption.^{49,50} On the other hand, **P-CDT** exhibited the larger Stokes shift ($\Delta\tilde{\nu} > 2000\text{ cm}^{-1}$) compared to the previous CDT polymers. The SAz unit with flexible and strong electron-accepting properties plays an significant role in achieving the efficient NIR emission with reduced excited energy loss caused by self-absorption.

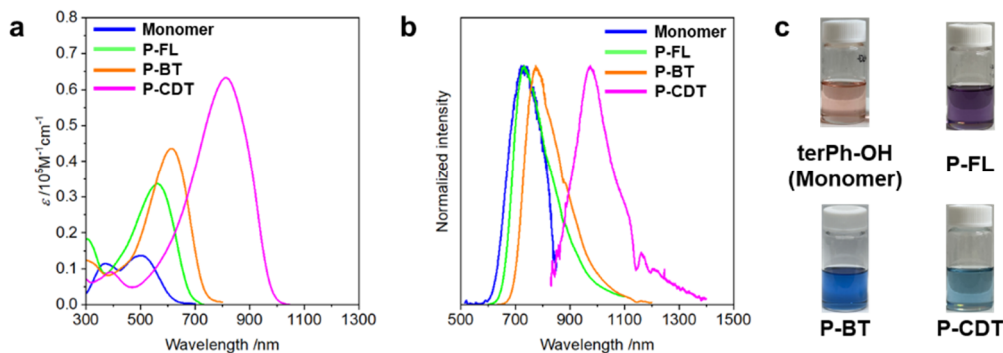


Figure 2. a) UV–vis–NIR absorption and b) PL spectra of polymers excited at each absorption maximum in toluene (1.0×10^{-5} M per repeating unit). c) Photographs of the toluene solutions of polymers under room light.

Table 2. Optical data of polymers in the diluted solution state

	λ_{abs}^a /nm	ε^a / $\text{cm}^{-1} \text{M}^{-1}$	λ_{PL}^a /nm	$\Delta\tilde{\nu}^b$ / cm^{-1}	$\Phi_{\text{PL}}^{a,c}$ / %
P-FL	561	33,600	727	4070	4.0
P-BT	615	43,600	775	3360	7.9
P-CDT	814	63,300	975	2030	1.0 ^d

^a In toluene (1.0×10^{-5} M per repeating unit), excited at λ_{abs} for PL. ^b Stokes shift; $\Delta\tilde{\nu} = 1/\lambda_{\text{abs}} \times 10^7 - 1/\lambda_{\text{PL}} \times 10^7$. ^c Absolute PL quantum yield excited at λ_{abs} . ^d Absolute PL quantum yield, excited at 525 nm.

Next, we measured the UV–vis–NIR absorption and PL spectra in four different solvents (toluene, chlorobenzene (PhCl), CHCl_3 , and CH_2Cl_2) to investigate the solvent effect involved in charge-transfer (CT) characters of each polymer (Figures S6 and S7, Table S5). The solvatochromic behavior of a general D–A type π -conjugated polymer is

known to cause positive solvatochromism, in which only the emission wavelength changes while the absorption wavelength hardly changes, because the CT state in the excited state is stabilized by polar solvents.¹⁰ On the other hand, all the polymers synthesized in this study showed not only a change in the emission wavelength but also a change in the absorption wavelength. In **P-FL**, the emission wavelength hardly changed, and only the absorption wavelength changed depending on the polarity of the solvent. This should be attributed to the effect of the monomer (**terPh-OH**) property which showed the similar behavior both in the absorption and emission wavelengths (Figure S8 and Table S6). This might be due to the hydroxy group having an acidic proton that should be more sensitive to solvents. In **P-BT** and **P-CDT**, in addition to a change in the absorption wavelength, a change in the emission wavelength was also observed. This suggests that **P-BT** and **P-CDT** show emission from the CT states because of the strong D–A interactions.

Solid-state emission is an essential optical function for applications on fabricating light-emitting devices. Therefore, we investigated the solid-state PL property of each polymer with the spin-coated film on the quartz substrate (Figure 3 and Table 3). From the measurements, it was confirmed that all polymers can exhibit the NIR emission even in the film. The absorption and PL bands of each polymer film were observed in the longer wavelength region than those in the diluted solution. Interestingly, **P-FL** maintained the emission intensity in the film state compared with the diluted solution. That is probably because the bulky terPh groups suppress interchain interactions leading to ACQ. In **P-BT** and **P-CDT**, although the emission efficiencies were partially reduced, NIR emissions were still observed. Focusing on the emission wavelength of **P-CDT** in the film, we found that it reached the NIR-II region, suggesting SAz is useful as an excellent acceptor unit

that can provide the tunable NIR emission.

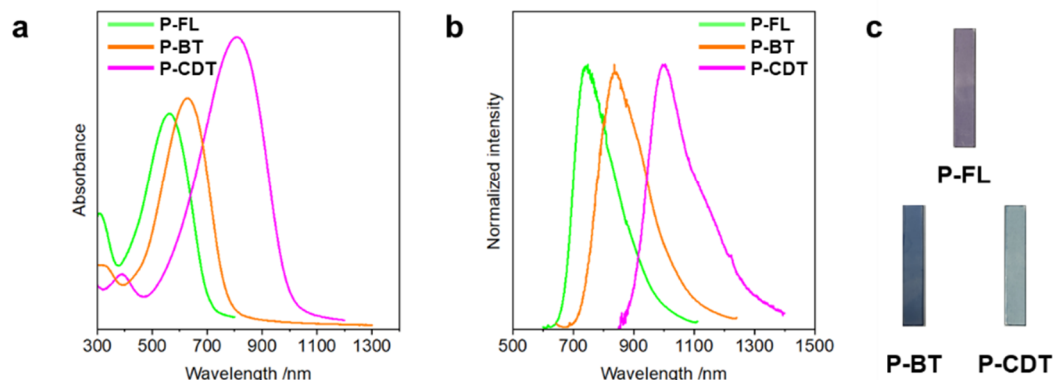


Figure 3. a) UV–vis–NIR absorption and b) PL spectra of polymers excited at each absorption maximum in film. c) Photographs of the films of obtained polymers under room light.

Table 3. Optical data of polymers in the film state

	$\lambda_{\text{abs}}^a/\text{nm}$	$\lambda_{\text{PL}}^a/\text{nm}$	$\Phi_{\text{PL}}^{a, b}/\%$
P-FL	564	741	4.1
P-BT	628	836	2.1
P-CDT	812	1004	0.3 ^c

^a spin-coated film on the quartz substrate (0.9 cm × 5 cm) prepared from CHCl₃ solution (0.10 mL, 1000 rpm, concentration: 1.0 mg / 0.30 mL), excited at λ_{abs} for PL. ^b Absolute PL quantum yield excited at λ_{abs} . ^c Absolute PL quantum yield, excited at 525 nm.

Cyclic voltammetry

Cyclic voltammetry (CV) measurements were conducted to estimate the energy levels of FMOs of SAz compounds. Accordingly, SAz derivatives exhibited low LUMO energy level reaching -3.87 eV. This means SAz derivatives work as a strong electron acceptor in D–A π -conjugated polymers.¹⁷ The LUMO and HOMO energy levels (E_{LUMO} and E_{HOMO}) were calculated from the onsets of the first reduction curves and from the starting point of the first oxidation curve with ferrocene/ferrocenium (Fc/Fc^+) as a standard (-4.8 eV), respectively.^{74,75} The results are summarized in Figure 4 and Table S7, and the voltammograms are shown in Figure S9.

Regarding the monomers, both the HOMO and LUMO energy levels were lower for **terPh-Me**, **terPh-Ph**, and **terPh-OH** in that order, implying that the strong inductive effect of the substituent at the apical position mainly reduces the energy levels of FMOs of the hypervalent compounds, since inductive substituent constants (σ_I) are higher methyl (-Me), phenyl (-Ph), and hydroxy (-OH) in that order.⁷⁶ Focusing on the energy gaps between HOMO and LUMO, we found that **terPh-OH** had narrower energy gap than **terPh-Me** and **terPh-Ph**, which is not opposite results from the UV–vis absorption spectra. This might be attributed to the sensitive property of the hydroxy group to the measurement environment. In polymers, a slight increase in the LUMO energy level was observed compared to **terPh-OH**. This should be attributed to the destabilization of the energy levels induced by the electron donation from the donor comonomer. On the other hand, the HOMO energy level tended to increase depending on the electron-donating strength of the donor units. This effect dominantly leads to a smaller energy gap between the FMOs of the D–A type π -conjugated polymers, which is consistent with the longer absorption wavelengths observed in the optical properties.

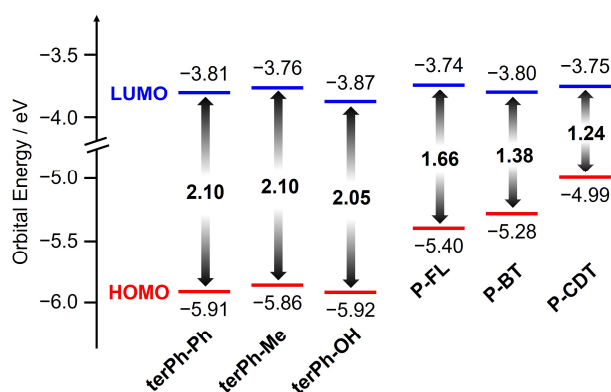


Figure 4. Energy diagrams of monomers and polymers prepared with the data from CV measurements (Table S7).

DFT calculation

To obtain further insight into the optical properties of the SAz derivatives, density functional theory (DFT) and time-dependent (TD)-DFT calculations were executed. The detailed calculation methods are shown in the Supporting Information. In monomers, the geometry of the optimized structure of each compound was categorized into the SP geometry, and significant structural differences were hardly observed (Figure S10). This result is different from the previous report in which the shortening of the distance between silicon–nitrogen (Si–N) was induced by the introduction of electron-withdrawing substituents.⁶⁵ In our case, the Si–N distance might be highly dependent on the bulky substituent at silicon (terPh group) since there were little differences in the Si–N distances in **terPh-Me**, **terPh-Ph**, and **terPh-OH**.

Next, focusing on the FMOs, we found that the LUMO shapes of each compound are similar, while the HOMOs are spread to the apical position in the **terPh-Me** and **terPh-Ph** compared to **terPh-OH** (Figure 5). The larger orbital contribution at the apical position should destabilize the HOMO energy level. These should be responsible for the

change in absorption wavelengths as described above (Table S8).

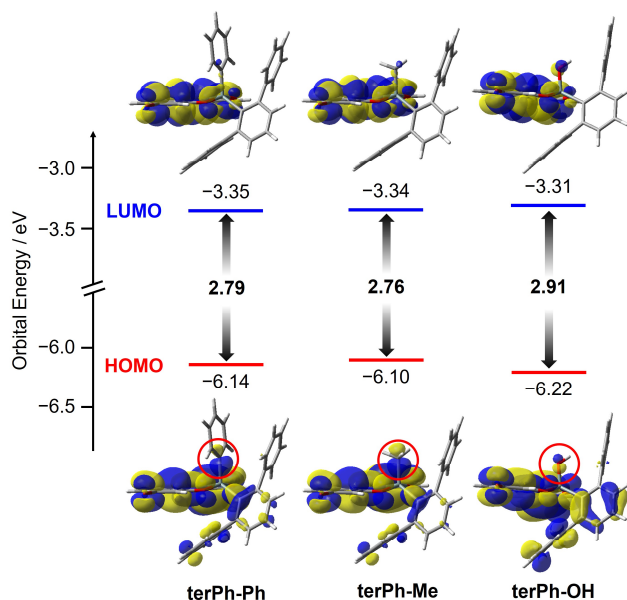


Figure 5. Kohn-Sham orbitals (HOMO and LUMO) and energy diagrams of SAz derivatives with DFT calculations (isovalue = 0.02).

To obtain information on the excited states of the hypervalent silicon compounds, we calculated the optimized structures of each compound with TD-DFT calculations (Figure S11). As a result, large structural deformation was observed in all compounds, and the optimized structures in the excited states were similar, which are in good agreement with the observation of the large Stokes shifts and the similar PL spectra in optical measurements. It was shown that the N=N bonds of azobenzene were elongated compared to the optimized structures in the ground state. This trend is consistent with the previously reported other azobenzene compounds.^{37,41} Furthermore, the Si-N distances were shortened, and the N-Si-X bond angles (X: the atoms in the apical position) were widened. The change value of the N-Si-X bond angle of **terPh-OH** was larger than those of **terPh-Me** and **terPh-Ph**, supporting the experimentally observed larger Stokes shift

of **terPh-OH**. In addition, the $S_1 \rightarrow S_0$ transition was assigned to a ligand (azobenzene) to a ligand (terPh group) transition (Figure S12 and Table S9). It should cause small oscillator strength, large non-radiative deactivation, and low emission efficiency in the SAz derivatives.

P-FL, **P-BT**, and **P-CDT** were calculated to investigate the effect of polymerization on optical properties. The model compounds having two repeating units and methyl groups at thiophene rings instead of long alkyl chains were used for the calculation to save computation costs (Figure 6). Accordingly, the shorter Si–N distance was observed after polymerization in the ground state (Figure S13). The shortening of the Si–N bond should be attributed to the substitution of the donor comonomer which increases the electron-donating ability of the lone-pair electrons on the nitrogen followed by a larger interaction with the silicon. This might enhance the rigidity of the SAz scaffold and subsequently suppress the structural relaxation in the excited state, leading to an increase in the emission efficiency. Furthermore, the $S_0 \rightarrow S_1$ transition was assigned to the π – π^* transition of the polymer main chain, where the HOMO–LUMO transition is more dominant compared to the monomer (Tables S8 and 10). In addition, increase in the oscillator strength by polymerization should lead to the enhancement of the molar extinction coefficient in polymers. Focusing on the FMOs in each polymer, we found that the HOMO is delocalized throughout the polymer main chain, whereas the LUMO is relatively localized to the SAz moiety (Figure 6). These results support the existence of the D–A interaction between the SAz acceptor and comonomer donor units with a significant increase in the HOMO energy level. This result is consistent with the modulation of the emission wavelengths in the optical measurements.

To obtain further information on the increase of the emission efficiency of **P-BT**

compared with the monomer, we calculated the excited state of the model compound of **M-BT** with TD-DFT (Figure S14). As a consequence, the $S_1 \rightarrow S_0$ transition was assigned to the $\pi-\pi^*$ transition of the main-chain π -conjugated system in contrast to **terPh-OH**. These data mean that the expansion of the π -conjugation should be effective in increasing the emission efficiency.

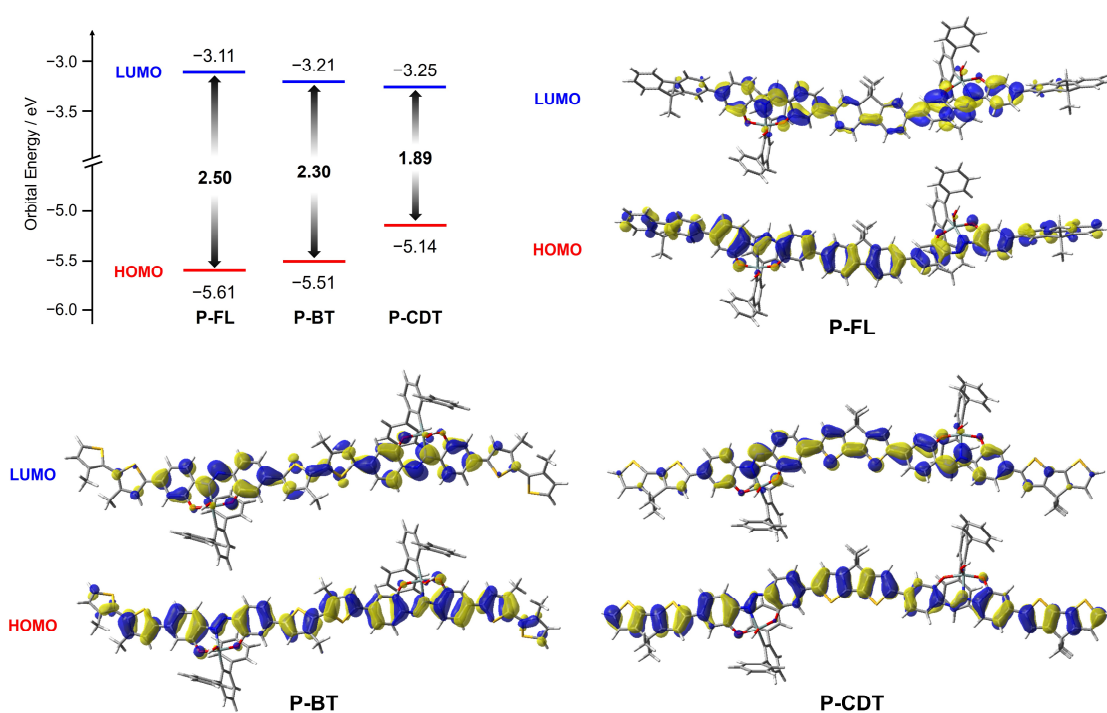


Figure 6. Energy diagrams and Kohn-Sham orbitals (HOMO and LUMO) of **P-FL**, **P-BT**, and **P-CDT** obtained with DFT calculations (isovalue = 0.02).

Conclusion

We developed NIR light-emitting hypervalent silicon(IV)-fused azobenzene compounds with sufficient stability and strong electron-accepting properties. The introduction of the bulky terPh group on silicon improved stability of the SAz backbone. Furthermore, the electronic properties of the hypervalent silicon compounds can be modulated by the substituents at the apical position. While the monomers showed very weak emission, the D–A π -conjugated polymers extremely enhanced emission efficiency accompanied by bathochromic shifts of the absorption and PL wavelengths in the NIR region. In particular, the emission wavelength of **P-CDT** reached the NIR-II region in the film state, suggesting that SAz has excellent electron-accepting ability. From CV measurements, it was found that the LUMO energy level should be lowered by the inductive effect of the substituent at apical position, and the strongest electron-accepting ability was achieved with the OH group among the SAz derivatives. From quantum chemical calculations with DFT, it is suggested that the electron delocalization in HOMO and LUMO through the polymer main chain should play a role in the strong NIR emission from D–A π -conjugated polymers. Our finding that SAz units have strong electron-accepting properties showing NIR emissions should provide useful insight into the development of highly-functional materials based on heteroatom-containing conjugation systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

This work was partially supported by the Toshiaki Ogasawara Memorial Foundation (for M.G.), Japan Society for the Promotion of Science (JSPS), a Grant-in-Aid for Scientific Research (B) (JP23K23398) (for M.G.) and (JP24K01570) (for K.T.).

References

1. Gon, M.; Ito, S.; Tanaka, K.; Chujo, Y. Design Strategies and Recent Results for Near-Infrared-Emissive Materials Based on Element-Block π -Conjugated Polymers. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2290–2301.
2. Zampetti, A.; Minotto, A.; Cacialli, F. Near-Infrared (NIR) Organic Light-Emitting Diodes (OLEDs): Challenges and Opportunities. *Adv. Funct. Mater.* **2019**, *29*, 1807623.
3. Chen, Y.; Xue, L.; Zhu, Q.; Feng, Y.; Wu, M. Recent Advances in Second Near-Infrared Region (NIR-II) Fluorophores and Biomedical Applications. *Front. Chem.* **2021**, *9*, 750404.
4. Smith, A. M.; Mancini, M. C.; Nie, S. Second window for in vivo imaging. *Nat. Nanotechnol.* **2009**, *4*, 710–711.
5. Wu, J.; Shi, Z.; Zhu, L.; Li, J.; Han, X.; Xu, M.; Hao, S.; Fan, Y.; Shao, T.; Bai, H.; Peng, B.; Hu, W.; Liu, X.; Yao, C.; Li, L.; Huang, W. The Design and Bioimaging Applications of NIR Fluorescent Organic Dyes with High Brightness. *Adv. Opt. Mater.* **2022**, *10*, 2102514.
6. Li, T.; Zhang, Y.; Wu, F.; Chen, G.; Li, C.; Wang, Q. Rational Design of NIR-II Ratiometric Fluorescence Probes for Accurate Bioimaging and Biosensing In Vivo. *Small Methods* **2025**, *9*, 2400132.
7. Xie, Y.; Li, Z.; Zhao, C.; Lv, R.; Li, Y.; Zhang, Z.; Teng, M.; Wan, Q. Recent Advances in Aggregation-Induced Emission–Active Type I Photosensitizers with Near-Infrared Fluorescence: From Materials Design to Therapeutic Platform Fabrication. *Luminescence* **2024**, *39*, e4621.
8. Tan, Y.; Sun, Y.; Huang, W.; Zhu, D.; Yan, D.; Wang, D.; Tang, B. Z. Thiophene

π -Bridge-Based Second Near-Infrared Luminogens with Aggregation-Induced Emission for Biomedical Applications. *Luminescence* **2024**, *39*, e4606.

9. Khan, Y.; Han, D.; Pierre, A.; Ting, J.; Wang, X.; Lochner, C. M.; Bovo, G.; Yaacobi-Gross, N.; Newsome, C.; Wilson, R.; Arias, A. C. A Flexible Organic Reflectance Oximeter Array. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, E11015–E11024.
10. Kim, B.-G.; Ma, X.; Chen, C.; Je, Y.; Coir, E. W.; Hashemi, H.; Aso, Y.; Green, P. F.; Kieffer, J.; Kim, J. Energy Level Modulation of HOMO, LUMO, and Band-Gap in Conjugated Polymers for Organic Photovoltaic Applications. *Adv. Funct. Mater.* **2013**, *23*, 439–445.
11. Su, Y.-W.; Lin, Y.-C.; Wei, K.-H. Evolving Molecular Architectures of Donor–Acceptor Conjugated Polymers for Photovoltaic Applications: from One-Dimensional to Branched to Two-Dimensional Structures. *J. Mater. Chem. A* **2017**, *5*, 24051–24075.
12. Shao, X.; Wang, J.; Marder, T. B.; Xie, Z.; Liu, J.; Wang, L. N–B $\leftarrow$ N Bridged Bithiophene: A Building Block with Reduced Band Gap to Design n-Type Conjugated Polymers. *Macromolecules* **2021**, *54*, 6718–6725.
13. Modicano, P.; Neumann, P. R.; Schüller, M.; Holthof, J.; Kyrilis, F. L.; Hamdi, F.; Kastiris, P. L.; Mäder, K.; Ann Dailey, L. *Eur. J. Pharm. Biopharm.* Enhanced Optical Imaging Properties of Lipid Nanocapsules as Vehicles for Fluorescent Conjugated Polymers. **2020**, *154*, 297–308.
14. Rodrigues, A. C. B.; Eckert, A.; Pina, J.; Scherf, U.; Seixas de Melo, J. S. Polymeric Near Infrared Emitters with Bay-Annulated Indigo Moieties. *Mater. Adv.* **2021**, *2*, 3736–3743.

15. Viswanathan, V. N.; Rao, A. D.; Pandey, U. K.; Kesavan, A. V.; Ramamurthy, P. C. Molecular-Level Architectural Design Using Benzothiadiazole-Based Polymers for Photovoltaic Applications. *Beilstein J. Org. Chem.* **2017**, *13*, 863–873.
16. de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. Stability of *n*-Type Doped Conducting Polymers and Consequences for Polymeric Microelectronic Devices. *Synth. Met.* **1997**, *87*, 53–59.
17. Zhang, Z.-G.; Wang, J. Structures and Properties of Conjugated Donor–Acceptor Copolymers for Solar Cell Applications *J. Mater. Chem.* **2012**, *22*, 4178–4187.
18. Zheng, Y. Q.; Lei, T.; Dou, J. H.; Xia, X.; Wang, J. Y.; Liu, C. J.; Pei, J. Strong Electron-Deficient Polymers Lead to High Electron Mobility in Air and Their Morphology-Dependent Transport Behaviors. *Adv. Mater.* **2016**, *28*, 7213–7219.
19. Huang, J.; Mao, Z.; Chen, Z.; Gao, D.; Wei, C.; Zhang, W.; Yu, G. Diazaisoindigo-Based Polymers with High-Performance Charge-Transport Properties: From Computational Screening to Experimental Characterization. *Chem. Mater.* **2016**, *28*, 2209–2218.
20. Li, C.; Un, H. I.; Peng, J.; Cai, M.; Wang, X.; Wang, J.; Lan, Z.; Pei, J.; Wan, X. Thiazoloisoindigo: A Building Block that Merges the Merits of Thienoisindigo and Diazaisoindigo for Conjugated Polymers. *Chem. Eur. J.* **2018**, *24*, 9807–9811.
21. Jenekhe, S. A.; Osaheni, J. A. Excimers and Exciplexes of Conjugated Polymers. *Science* **1994**, *265*, 765–768.
22. Ito, S.; Gon, M.; Tanaka, K. Effects of Heavy p-Block Elements on Photophysical Properties of π -Conjugated Complexes and Organoelement Compounds. *Eur. J. Inorg. Chem.* **2024**, *27*, e202400180.

23. Matsumura, Y.; Tanudjaja, A.; Fukushima, M.; Higuchi, M.; Ogino, S.; Ishidoshiro, M.; Irie, Y.; Imoto, H.; Naka, K.; Hifumi, R.; Inagi, S.; Tomita, I. Parallel Synthesis of Donor-Acceptor π -Conjugated Polymers by Post-Element Transformation of Organotitanium Polymer. *Des. Monomers Polym.* **2023**, *26*, 190–197.
24. Matsumura, Y.; Ishidoshiro, M.; Irie, Y.; Imoto, H.; Naka, K.; Tanaka, K.; Inagi, S.; Tomita, I. Arsole-Containing π -Conjugated Polymer by the Post-Element-Transformation Technique. *Angew. Chem. Int. Ed.* **2016**, *55*, 15040–15043.
25. Adachi, Y.; Matsuura, R.; Ohshita, J. Conjugated Building Blocks Based on Electron-Deficient Thiaborin S-Oxides. *Organometallics* **2024**, *43*, 829–839.
26. Adachi, Y.; Ooyama, Y.; Ren, Y.; Yin, X.; Jäkle, F.; Ohshita, J. Hybrid Conjugated Polymers with Alternating Dithienosilole or Dithienogermole and Tricoordinate Boron Units. *Polym. Chem.* **2018**, *9*, 291–299.
27. Tanaka, K. New Strategy for Lowering the Energy Levels of One Frontier Molecular Orbital in Conjugated Molecules and Polymers Based on Aza-Substitution at the Isolated HOMO or LUMO. *Polym. J.* **2024**, *56*, 61–70.
28. Watanabe, H.; Tanaka, K.; Chujo, Y. Position Dependent Effects of the Aza-Substitution on the Electronic Properties and Crystal Structures Based on Hexaazaphenylene Isomers. *Asian J. Org. Chem.* **2022**, *11*, e202200221.
29. Liu, C. L.; Tsai, F. C.; Chang, C. C.; Hsieh, K.-H.; Lin, J.-L.; Chen, W. C. Theoretical Analysis on the Geometries and Electronic Structures of Coplanar Conjugated Poly(azomethine)s. *Polymer* **2005**, *46*, 4950–4957.
30. Wang, Y.; Ma, J.; Jiang, Y. Tuning of Electronic Structures of Poly(*p*-phenylenevinylene) Analogues of Phenyl, Thienyl, Furyl, and Pyrrolyl by Double-

Bond Linkages of Group 14 and 15 Elements *J. Phys. Chem. A*. **2005**, *109*, 7197–7206.

31. Cembran, A.; Bernardi, F.; Garavelli, M.; Gagliardi, L.; Orlandi, G. On the Mechanism of the *cis*–*trans* Isomerization in the Lowest Electronic States of Azobenzene: S_0 , S_1 , and T_1 *J. Am. Chem. Soc.* **2004**, *126*, 3234–3243.
32. Fujino, T.; Arzhantsev, S. Y.; Tahara, T. Femtosecond Time-Resolved Fluorescence Study of Photoisomerization of *trans*-Azobenzene. *J. Phys. Chem. A* **2001**, *105*, 8123–8129.
33. Yoshino, J.; Kano, N.; Kawashima, T. Synthesis of the Most Intensely Fluorescent Azobenzene by Utilizing the B–N Interaction. *Chem. Commun.* **2007**, 559–561.
34. Yoshino, J.; Kano, N.; Kawashima, T. Fluorescent Azobenzenes and Aromatic Aldimines Featuring an N–B Interaction. *Dalton Trans.* **2013**, *42*, 15826–15834.
35. Kano, N.; Furuta, A.; Kambe, T.; Yoshino, J.; Shibata, Y.; Kawashima, T.; Mizorogi, N.; Nagase, S. 2,2'-Diborylazobenzenes with Double N–B Coordination: Control of Fluorescent Properties by Substituents and Redox Reactions *Eur. J. Inorg. Chem.* **2012**, *2012*, 1584–1587.
36. Yoshino, J.; Furuta, A.; Kambe, T.; Itoi, H.; Kano, N.; Kawashima, T.; Ito, Y.; Asashima, M. Intensely Fluorescent Azobenzenes: Synthesis, Crystal Structures, Effects of Substituents, and Application to Fluorescent Vital Stain. *Chem. Eur. J.* **2010**, *16*, 5026–5035.
37. Gon, M.; Tanaka, K.; Chujo, Y. A Highly Efficient Near-Infrared-Emissive Copolymer with a N=N Double-Bond π -Conjugated System Based on a Fused Azobenzene–Boron Complex. *Angew. Chem. Int. Ed.* **2018**, *57*, 6546–6551.
38. Gon, M.; Tanaka, K.; Chujo, Y. Discovery of Functional Luminescence Properties

- Based on Flexible and Bendable Boron-Fused Azomethine/Azobenzene Complexes with O,N,O-Type Tridentate Ligands. *Chem. Rec.* **2021**, *21*, 1358–1373.
39. Gon, M.; Tanaka, K.; Chujo, Y. π -Conjugated Polymers Based on Flexible Heteroatom-containing Complexes for Precise Control of Optical Functions. *Polym. J.* **2023**, *55*, 723–734.
40. Gon, M.; Wakabayashi, J.; Nakamura, M.; Tanaka, K.; Chujo, Y. Controlling Energy Gaps of π -Conjugated Polymers by Multi-Fluorinated Boron-Fused Azobenzene Acceptors for Highly Efficient Near-Infrared Emission. *Chem. Asian J.* **2021**, *16*, 696–703.
41. Nakamura, M.; Gon, M.; Tanaka, K. Contribution of radiative rate constants to crystallization-induced emission enhancement in boron-fused azobenzene complexes. *Dalton Trans.* **2025**, *54*, 1079–1086.
42. Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
43. Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole. *Chem. Commun.* **2001**, 1740–1741.
44. Ohtani, S.; Gon, M.; Tanaka, K.; Chujo, Y. A Flexible, Fused, Azomethine–Boron Complex: Thermochromic Luminescence and Thermosensitive Behavior in Structural Transitions between Crystalline Polymorphs. *Chem. Eur. J.* **2017**, *23*, 11827–11833.
45. Ohtani, S.; Takeda, Y.; Gon, M.; Tanaka, K.; Chujo, Y. Facile Strategy for

Obtaining Luminescent Polymorphs Based on the Chirality of a Boron-Fused Azomethine Complex. *Chem. Commun.* **2020**, 56, 15305–15308.

46. Dong, Y.; Lam, J. W. Y.; Qin, A.; Li, Z.; Sun, J.; Sung, H. H.-Y.; Williams, I. D.; Tang, B. Z. *Chem. Commun.* **2007**, 40–42.
47. Nakamura, M.; Gon, M.; Natsuda, S.; Tamai, Y.; Ohkita, H.; Tanaka, K.; Chujo, Y. Development of NIR Emissive Fully-Fused Bisboron Complexes with π -Conjugated Systems Including Multiple Azo Groups. *Dalton Trans.* **2022**, 51, 74–84.
48. Gon, M.; Wakabayashi, J.; Nakamura, M.; Tanaka, K.; Chujo, Y. Preparation of Near-Infrared Emissive π -Conjugated Polymer Films Based on Boron-Fused Azobenzene Complexes with Perpendicularly Protruded Aryl Substituents. *Macromol. Rapid Commun.* **2021**, 42, 2000566.
49. Nakamura, M.; Gon, M.; Tanaka, K.; Chujo, Y. Solid-State Near-Infrared Emission of π -Conjugated Polymers Consisting of Boron Complexes with Vertically Projected Steric Substituents. *Macromolecules* **2023**, 56, 2709–2718.
50. Nakamura, M.; Kanetani, I.; Gon, M.; Tanaka, K. NIR-II Absorption/Fluorescence of D–A π -Conjugated Polymers Composed of Strong Electron Acceptors Based on Boron-Fused Azobenzene Complexes. *Angew. Chem. Int. Ed.* **2024**, 63, e202404178.
51. Nakamura, M.; Yamauchi, M.; Gon, M.; Tanaka, K. UV-to-NIR Wavelength Conversion of π -Conjugated Polymers Based on Pyrene-Substituted Boron-Fused Azobenzene Complexes. *Macromolecules* **2023**, 56, 7571–7578.
52. Ohtani, S.; Yamada, N.; Gon, M.; Tanaka, K.; Chujo, Y. The Effect of Alkyl Chain Lengths on the Red-to-Near-Infrared Emission of Boron-Fused Azomethine

Conjugated Polymers and Their Film-State Stimuli-Responsivities. *Polym. Chem.* **2021**, *12*, 2752–2759.

53. Ohtani, S.; Gon, M.; Tanaka, K.; Chujo, Y. Construction of the Luminescent Donor-Acceptor Conjugated Systems Based on Boron-Fused Azomethine Acceptor. *Macromolecules* **2019**, *52*, 3387–3393.
54. Gon, M.; Tanaka, K.; Chujo, Y. Vapochromic Luminescent π -Conjugated Systems with Reversible Coordination-Number Control of Hypervalent Tin(IV)-Fused Azobenzene Complexes. *Chem. Eur. J.* **2021**, *27*, 7561–7571.
55. Gon, M.; Yaegashi, M.; Tanaka, K. Enhancement of Near-infrared Emission Based on Hypervalent Germanium(IV)-Fused Azobenzene Compounds with Electron-donating Groups. *Bull. Chem. Soc. Jpn.* **2023**, *96*, 778–784.
56. Gon, M.; Tanaka, K. Utilization of Hypervalent Bonds as a Novel Strategy for Manipulating Energy Levels of π -Conjugated Systems. *Eur. J. Org. Chem.* **2024**, *27*, e202400738.
57. J. I. Musher, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 54–68.
58. Gon, M.; Tanimura, K.; Yaegashi, M.; Tanaka, K.; Chujo, Y. PPV-type π -conjugated polymers based on hypervalent tin(IV)-fused azobenzene complexes showing near-infrared absorption and emission. *Polym. J.* **2021**, *53*, 1241–1249.
59. Gon, M.; Yaegashi, M.; Tanaka, K.; Chujo, Y. Near-Infrared Emissive Hypervalent Compounds with Germanium(IV)-Fused Azobenzene π -Conjugated Systems. *Chem. Eur. J.* **2023**, *29*, e202203423.
60. Gon, M.; Morisaki, Y.; Tanimura, K.; Tanaka, K.; Chujo, Y. Vapochromic Films of π -Conjugated Polymers Based on Coordination and Desorption at Hypervalent Tin(IV)-Fused Azobenzene Compounds. *Mater. Chem. Front.* **2023**, *7*, 1345–

1353.

61. Gon, M.; Morisaki, Y.; Tanimura, K.; Tanaka, K. Preparation of Seven-Coordinated Hypervalent Tin(IV)-Fused Azobenzene and Applications for Stimuli-Responsive π -Conjugated Polymer Films. *Dalton Trans.* **2024**, 53, 11858–11866.
62. Gon, M.; Tanimura, K.; Okazaki, K.; Kato, T.; Nakauchi, D.; Kawaguchi, N.; Yanagida T.; Tanaka, K. Liquid and Film-Type Organic Scintillators Based on Near-Infrared Fluorescent π -Conjugated Polymers Containing Hypervalent Tin(IV) Compounds. *Polym. J.* **2025**, 57, 567–573.
63. Wagler, J. *Organometallics* **2007**, 26, 155–159.
64. Bohme, U.; Jähnigen, S. Dynamic Disorder in a Pentacoordinate Silicon Complex with 2,2'-Diazenediylldiphenol. *Acta Cryst. C* **2008**, 64, o364–o366.
65. Soldatenko, A. S.; Sterkhova, I. V.; Lazareva, N. F. Pentacoordinate Silicon Compounds Based on 2,2'-Dihydroxyazobenzene Ligand. *J. Organomet. Chem.* **2019**, 903, 120997.
66. Tokoro, Y.; Yeo, H.; Tanaka, K.; Chujo, Y. Synthesis and Tuning of Optical Properties of Conjugated Polymers Involving Benzo[h]quinoline-Based Neutral Pentacoordinate Organosilicon Complexes in the Main Chain. *Polym. Chem.* **2013**, 4, 5237–5242.
67. Tokoro, Y.; Tanaka, K.; Chujo, Y. Synthesis of π -Conjugated Polymers Containing Dibenzosilepin Moieties with Pentacoordinate Silicon. *Bull. Chem. Soc. Jpn.* **2015**, 88, 1350–1355.
68. Ito, S.; Ito, Y.; Kazuo, T.; Chujo, Y. Near-infrared-emissive π -conjugated polymers based on five-coordinated silicon formazanate complexes. *Polymer* **2022**, 239,

124463.

69. Gon, M.; Dekura, S.; Akutagawa, T.; Tanaka, K. Geometry-Dependent Energy-Gap Modulation of π -Conjugated Systems Based on Hypervalent Silicon(IV)-Fused Azomethine Compounds. *Chem. Eur. J.* **2025**, *31*, e202500506.
70. Kosugi, M.; Sasazawa, K.; Shimizu, Y.; Migita, T. Reactions of Allyltin Compounds III. Allylation of Aromatic Halides with Allyltributyltin in the Presence of Tetrakis(Triphenylphosphine)Palladium(0) *Chem. Lett.* **1977**, *6*, 301–302.
71. Milstein, D.; Stille, J. K. A General, Selective, and Facile Method for Ketone Synthesis from Acid Chlorides and Organotin Compounds Catalyzed by Palladium *J. Am. Chem. Soc.* **1978**, *100*, 3636–3638.
72. Harada, J.; Ogawa, K. Pedal Motion in Crystals. *Chem. Soc. Rev.* **2009**, *38*, 2244–2252.
73. Tanimura, K.; Gon, M.; Tanaka, K. Effects of Hypervalent Bismuth on Electronic Properties of the Azobenzene Tridentate Ligand and Roles of Lewis Acidity in Controlling Optical Properties. *Inorg. Chem.* **2023**, *62*, 4590–4597.
74. Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. Efficient Two Layer Leds on a Polymer Blend Basis. *Adv. Mater.* **1995**, *7*, 551–554.
75. Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, *23*, 2367–2371.
76. Charton, M. Electrical Effect Substituent Constants for Correlation Analysis. In

Progress in Physical Organic Chemistry, Vol.13; (Ed.: R. W. Taft), Wiley: New York, **1981**, pp. 119–251.