

New Strategy for Lowering Energy Levels of One of Frontier Molecular Orbitals of Conjugated Molecules and Polymers Based on Aza-substitution at the Isolated HOMO or LUMO

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Keywords: conjugated polymer; near infrared; aggregation-induced emission; boron complex; luminescence

Running head: Selective modulation of molecular orbital level

Abstract: The new method to control the electronic states of conjugated polymers without extending the π -conjugated system is described. In the distribution of frontier molecular orbitals (FMOs), if one of FMOs is distributed on the skeletal carbon, we defined each of them as the isolated highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO). By replacing carbon to nitrogen (aza-substitution) at the isolated FMO, we found that efficient and selective lowering of the energy level of one of FMOs can be realized. Based on this principle, we obtained blue and near-infrared emitting materials. Moreover, aggregation-induced emission (AIE) and/or crystallization-induced emission (CIE)-active complexes with longer wavelength emission were also obtained through the similar protocols. Furthermore, solid-state luminescent polymers were obtained. Various types of conjugated polymers with near-infrared (NIR) luminescent properties were also developed through the selective lowering of the LUMO level by aza-substitution. In this review, we explain that aza-substitution in isolated FMOs is a new method for controlling the electronic state of conjugated polymers.

Introduction

Conjugated polymers are recognized as a versatile material for organic electronic devices because of not only superior optical and electronic properties but also physical properties such as film-formability and solubility in conventional solvents. By polymerization, there are various advantages not only for modulating optical properties but also for enhancing processability. It is possible to realize narrower energy gaps followed by NIR absorption and emission. Moreover, these optical properties can be precisely tuned by selecting the type of comonomers by employing electron-donating and accepting units in the alternating polymer structures. Furthermore, since light absorption properties are caused each component in electron-donor and acceptor units, it is difficult to show light absorption in the NIR region. In contrast, conjugated polymers can show efficient light absorption properties in the longer wavelength region. Regarding physical properties, because of enhanced solubility and film-formability, it is easy to prepare homogenous films which are favorable for manufacturing electronic devices. Therefore, many researchers have devoted their much effort to develop new molecular skeletons for obtaining further functions. On the other hand, there are still unresolved issues. In general, luminescent properties of conventional organic dyes are often critically spoiled in solid due to concentration quenching due to non-specific intermolecular interactions in the condensed state. In particular, conjugated polymers, which have a conjugated system through the main chain, tend to cause inter-chain interactions and tend to lower their light-emitting ability in the film state due to concentration quenching. In order to obtain sensitive chemical sensors and efficient organic light-emitting devices, it is essential to avoid concentration quenching and receive intense solid-state emission.

In recent years, the development of polymeric materials that absorb and emit NIR light is also a hot topic. NIR light has been utilized in a wide variety of application fields including information communication and bio-imaging because of its unique and useful physical properties, such as high permeability through various media. One of recent applications of NIR dyes with high relevance is organic photodetectors [1–5]. Since NIR photodetectors can be a key material for realizing advanced technologies such as medical imaging, night vision, remote temperature sensing, and optical communication [6–8], development of NIR dyes with desired optical properties and high processability is still required [9,10]. To obtain NIR light, it is necessary to realize a narrow energy gap between FMOs, and the extension of π -conjugation is one of the promising strategies to receive appropriate properties [11]. However, there are difficulties in the development of practical NIR materials, especially in light-emitting materials, due to the concentration quenching problem described above, which causes a critical loss of device efficiency, because non-specific intermolecular interactions are easily formed through extended π -conjugated systems. In addition, the solubility of the molecule may be reduced due to the enlargement of molecular planarity, which may make it impossible to apply the molecule as a monomer to the polymerization reaction and may also cause loss of film-formability. Hence, it can be said that the new design strategy for realizing narrower energy gaps without extending the conjugated system has the potential to solve the various problems mentioned above and is expected to make a breakthrough in the development of new generation of functional conjugated polymers.

Concept of isolated FMOs and selective lowering of energy levels by aza-substitution

Under such circumstances, we found that the energy gap can be tuned without

extending the π -conjugated system by using the unique electronic structure of “isolated FMOs” [12]. If the position where there is only either HOMO or LUMO on the skeletal carbon is found, we defined this position as an isolated HOMO or isolated LUMO, respectively (Figure 1a). As an initial example on the conjugated system having isolated FMOs, we have previously reported pentaazaphenalene (5AP) derivatives (Figure 1b) [13]. At each side and vertex, the isolated HOMOs and LUMOs are located in the triangular molecular skeleton. By introducing electron-withdrawing/donating groups at each site, we found that only one of energy level of the isolated FMOs was perturbed. For instance, when the electron-donating and/or withdrawing groups were introduced into the isolated HOMOs and LUMOs in the single molecule, the absorption bands were observed from **1a–e** in the far red (FR) or NIR region (Figure 1c) [14]. It is because that the elevating HOMO and the lowering LUMO were simultaneously induced, respectively. Consequently, the narrowest energy gap was observed from **1e** ($\lambda_{\text{onset}} = 875$ nm). It is noted that the resulting 5AP derivative showed light absorption property in the longer wavelength region despite the fact that it has a relatively small conjugated system.

Introduction of electron-withdrawing substituents to the lone LUMO of 5AP can effectively lower the energy level of the LUMO. On the other hand, the HOMO was affected to some extent because the conjugated system was also extended by the substituents. In order to demonstrate the selective lowering of the energy level of LUMO, we converted the skeletal carbon with the isolated LUMO to nitrogen (aza-substitution). Nitrogen has a higher electronegativity than carbon. Therefore, it is suggested that aza-substitution of the carbon atom in a conjugated system can be expected to lower the energy level through the inductive effect. As a result, LUMO-selective perturbation can

be presumed. Moreover, molecular stability can be enhanced by the aza-substitution [15,16]. In the previous report with boron dipyrromethene (BODIPY), it has been known from the results of quantum chemical calculations that the isolated LUMO exists at the *meso* position of BODIPY (Figure 2a) [17]. We have also reported that azaBODIPY, which is the aza-substituted compound, can exhibit light absorption and emission bands in the longer wavelength region ($\lambda_{\text{abs}} = 692 \text{ nm}$, $\lambda_{\text{em}} = 738 \text{ nm}$) than the BODIPY ones ($\lambda_{\text{abs}} = 603 \text{ nm}$, $\lambda_{\text{em}} = 648 \text{ nm}$) [18]. In particular, these optical properties are obtained without extending the conjugated system. Therefore, the sharp spectral shape which is the characteristic of BODIPY was maintained after aza-substitution.

Figure 2

In the case of BODIPY dyes, selective lowering of the LUMO level was observed by the aza-substitution, while the aza-substitution at the bridge position in the boron complex induced intense blue emission in other boron complexes (Figure 2b) [19–22]. This means that opposite results were obtained. These behaviors can be clearly explained and theoretically predicted based on the idea of isolated FMOs. As a representative example, initially, position dependent lowering of one of FMOs with 5AP is illustrated. According to our previous reports, it has been shown that there are isolated LUMO and isolated HOMO at the 8 and 7 positions of 5AP, respectively (Figure 1b) [14]. Therefore, we designed and synthesized analogs **2a** (aza-substituted at 8-position) and **2b** (aza-substituted at 7-position), which were aza-substituted at each position and compared their electronic structures (Figure 3a) [23]. First, electrochemical measurements showed that only the reduction potential of **2a** was lower than that of 5AP (Figure 3b). In contrast, a

decrease in oxidation potential was observed with **2b**. These results directly indicate that only one of the isolated FMOs can be selectively lowered by modulating the position of the aza-substitution. Corresponding to these results, from UV-vis absorption measurements, it was shown that **2a** has the absorption band in the longer wavelength region than 5AP, while **2b** has in the shorter wavelength region (Figure 3c). Because the isolated LUMO in **2a** and the isolated HOMO in **2b** were selectively lowered, the energy gaps between FMOs were widened and narrowed, respectively. From the above data, it was shown that the energy level of one of FMOs can be lowered more selectively by using aza-substitution than by modifying substituents at the isolated FMOs.

Figure 3

Development of blue luminescent materials by the selective lowering of the isolated HOMO

As briefly mentioned in Figure 2b, next, we explain the development of designed luminescent materials by regulating the energy level of conjugated polymers by aza-substitution at the isolated FMOs. As mentioned above, conjugated molecules tend to show poor luminescent properties in the condensed state due to concentration quenching. To solve this problem, we have focused on AIE properties [24]. AIE-active dyes hardly show emission in solution because the excited state is deactivated by intramolecular motions, while in solids, these motions would be suppressed. Moreover, by avoiding concentration quenching using steric substituents, enhanced emission can be observed even in aggregation. Hence, AIE is realized by the combination of these solution annihilation and solid-state emission behaviors.

We have so far discovered several complexes exhibiting AIE properties [25,26]. Among these AIE-active complexes, we focused on boron ketoiminates as a platform for developing polymeric materials (Figure 4a) [27,28]. We presumed that constant emission might be obtained in both solution and solid states by immobilizing the molecular skeleton, and highly-efficient luminescent polymers can be generated by using the fixed complexes as a monomer. Based on this idea, we designed and synthesized the series of fused boron ketoiminates (FBKIs) consisting of a pyridine ring for immobilizing molecular motions by introducing the fused ring structure at the imine site, which is proposed to be prone to energy-consumable molecular motions (Figure 4b) [29,30]. As we presumed, it was shown that FBKIs showed similar luminescence efficiency in both solution and solid states, and luminescent films can be fabricated with conjugated polymers involving FBKI in the main chain [31,32]. Based on solid-state luminescent properties, we aimed to develop pure blue color materials.

Figure 4

Blue is one of the three primary colors of light and a blue-luminescent device is one of the components of organic EL displays. Commonly, when a dye is incorporated into the π -conjugated system, electron conjugation causes narrowing of the gap, and subsequently the emission wavelength would shift in the longer wavelength region. Additionally, in films of conjugated polymers, interchain interactions such as π -stacking are likely to occur, which tends to cause the peak shift of luminescent bands to the longer wavelength region. Therefore, there is still a great need to obtain a blue color with high purity from

polymer films.

According to the FMOs of FBKI **3a** estimated by quantum chemical calculations, it was suggested that the isolated HOMO should exist (Figure 4b) [33]. Therefore, it was assumed that the aza-substitution at this site induces selective lowering of the energy level of the HOMO followed by the wide energy gap. Actually, as mentioned in Figure 2b, these complexes showed pure blue emission [19–22]. In addition, considering the solid-state luminescent properties of FBKIs, it was expected that efficient practical polymeric materials possessing intense blue luminescence could be obtained only by regulating the energy gap.

According to the previous report [31], it was showed that **3a** has an emission band with the peak at 497 nm ($\Phi_{\text{PL}} = 0.25$) in the crystalline state, meanwhile the aza-substituted FBKI **3b** has a significantly shorter emission band at around 431 nm with good emission efficiency ($\Phi_{\text{PL}} = 0.82$) (Figure 4c) [33]. Next, by using **3b** as a monomer, the polymer **3c** was designed (Figure 4d). We adopted a homopolymer structure for suppressing the effect of charge transfer due to electron withdrawing and donating interactions which are dominant in copolymer-type conjugated polymers [34]. The synthesizing polymer **3c** had the emission band with the peak at 422 nm ($\Phi_{\text{PL}} = 0.42$) in solution and 440 nm ($\Phi_{\text{PL}} = 0.48$) in film, clearly indicating that short-wavelength emission and emission efficiency can be maintained even after film preparation as well as polymerization. In addition, the color coordinates of (0.19, 0.18) were obtained from the CIE diagram, suggesting that this polymer is practically useful as a blue luminophore.

NIR-luminescent polymers with formazane complexes

Next, NIR luminescent polymers having the lowered LUMO energy levels by the aza-substitution at the isolated LUMO are described. As mentioned above, conventional luminescent boron complexes having diketonate structures were able to be transformed into AIE-active molecules by replacing one of oxygen atoms with nitrogen. Based on this fact, we designed diiminate complexes containing dual imine structures instead of ketones (Figure 4a) [35–40]. According to optical measurements, it was found that the resulting complexes and the polymers involving diiminate structures exhibit CIE and AIE properties, respectively.

Similarly to the previous example on FBKIs, we surveyed electronic distributions in FMOs of the diiminate derivative **4a** and found that there are two isolated LUMOs in the six-membered ring involving boron (Figure 5a). Therefore, we designed the aza-substituted complexes, known as formazane, by replacing carbon to nitrogen at both positions and prepared boron complexes and polymers (Figure 5b) [41]. The synthesized boron formazanate exhibited FR emission ($\lambda_{em} = 630$ nm), and by the combination with a fluorene comonomer, the NIR-luminescent conjugated polymer **4b** ($\lambda_{em} = 751$ nm) was obtained.

Figure 5

Based on the NIR-luminescent property of the boron formazanate polymer, we constructed the wavelength conversion materials [41]. We initially prepared the ligand polymer consisting of the formazane unit with a fluorene comonomer (Figure 5c). Boron

complexation was accomplished through the polymer reaction with the boronate reagent, boron trifluoride diethylether complex ($\text{BF}_3 \cdot \text{OEt}_2$). Especially, by modulating stoichiometry between the formazane unit and $\text{BF}_3 \cdot \text{OEt}_2$, it was demonstrated that the series of polymers with variable complexation ratios with boron at the formazane unit. Among them, it was found that the black color polymer **4c** can absorb relatively-shorter and longer wavelength light in the visible region at the formazane ligand and boron formazanate unit in the polymer main chain, respectively (Figure 5d). After photo-excitation, excited energy is accumulated at the boron formazanate unit through energy transfer, and significant emission can be observed in the NIR region. This means that the polymer **4c** can work as a wavelength converter from all visible to NIR light.

Optical properties of diiminate complexes were able to be modulated by changing the central element [42–45]. We attempted to shift the emission band to the longer wavelength region by employing silicon element. Silicon complexes often show NIR emission originating from low LUMO caused by $\sigma^*-\pi^*$ conjugation with silicon. Therefore, by introducing silicon into the formazane unit, we expected that narrower energy gaps can be realized. We synthesized the polymer **4d** involving silicon formazanate and detect the absorption and emission bands with the peak at 870 nm and 944 nm, respectively (Figure 5e) [46]. It should be emphasized that the significant emission band was observed from the film sample in the NIR-II region ($\lambda_{\text{em}} = 1,080$ nm). These data represent that aza-substitution is orthogonal toward other conventional methods for lowering energy levels of molecular orbitals. By the combination with aza-substitution and conventional design strategies, such superior materials can be received.

Development of NIR-luminescent AIE-active complexes and polymers based on boron azobenzene complexes

AIE-active NIR luminescent materials have attracted attention especially as a bioprobe and a photo-active medicine [47]. The design of NIR-luminescent luminophores with AIE properties from a scratch with quantum chemical calculations is illustrated here based on selective lowering of LUMO energy levels by aza-substitution at the isolated LUMO. Moreover, the development of solid-state NIR-luminescent polymers are also explained [48].

Emission annihilation in solution in AIE behaviors is caused by molecular motions in the excited state. We previously presumed that the degree of molecular motions is estimated by the comparison of the most stable structures between ground and excited states which were able to be obtained from DFT and TD-DFT calculations, respectively [29,49]. Based on this speculation, we explored boron azomethine complexes and found their CIE properties as we expected (Figure 6a) [50–52]. According to a series of mechanistic studies, it is suggested that molecular motion occurs for relaxing the intrinsic structural distortion around boron in the excited state. Indeed, solid-state emission efficiencies were observed from the polymers having azomethine units in the main chains where molecular motions would be highly restricted [53–57].

Figure 6

We examined molecular orbital distributions of boron azomethine complexes and found the isolated LUMO (Figure 6a). Similarly to the above examples, we designed the

aza-substituted structure, named as boron azobenzene complexes, and evaluated optical properties [58]. From the comparison of emission properties in solution, it was clearly indicated that narrower energy gap should be realized in the azobenzene complex **5b** than the azomethine complex **5a** although both complexes showed AIE behaviors (Figure 6b). In the crystalline state, **5a** has two types of polymorphs and the emission bands were observed at around 552 nm or 566 nm, whereas **5b** exhibited emission with the peak over 600 nm in crystal. Next, we designed binuclear complexes containing the azobenzene structure for obtaining NIR emission [59]. Accordingly, significant CIE properties in the NIR region were observed from the complex **5c** (Figure 6c) [59]. It is proposed that NIR luminescence is obtained by the combination with the extension of the conjugated system and selectively lowering of the LUMO energy level by aza-substitution.

As mentioned above, since concentration quenching is caused by intermolecular interactions, it is generally difficult to obtain solid-state luminescence especially from NIR-emitting dyes which have expanded π -conjugated systems. On the other hand, the azobenzene complexes obtained by aza-substitution have a compact π -conjugated system and exhibit solid-state luminescence as shown by AIE and CIE. Therefore, it can be expected to obtain NIR-luminescent polymers by using the azobenzene complexes as a monomer. We synthesized the series of conjugated polymers and were able to find significant emission bands in the NIR region (Figure 6d). As a representative example, polymer **5d** containing **5b** and bithiophene comonomer showed NIR emission both in solution and film [58]. The emission efficiency in film was able to be enhanced by introducing the phenyl group on the boron atom as observed from **5e** [60]. The polymer **5f** in which the azobenzene units are connected with the vinylene linker showed superior

electron-transporting ability as well as NIR emission (electron mobility, $\mu = 10^{-2}\sim 10^{-3}$ cm² V⁻¹ s⁻¹) [61]. As shown in the above examples, by modifying the substituents and changing the copolymer, we were able to tune not only the optical properties but also electronic functions [62–64]. More recently, it has been demonstrated that it is possible to modulate electronic properties by replacing from boron to different elements, such as tin [65–69] and bismuth [70].

We explain another advantage of selective lowering of LUMO levels by aza-substitution except for electronic state controls. It is reported that the materials having the HOMO energy level over -5.06 eV (-0.658 V vs SCE) can be oxidized by oxygen [71]. NIR-emitting dyes, however, have a higher HOMO energy level to realize a narrow energy gap structure. Therefore, they tend to be easily oxidized and often show poor stability. In the present method based on aza-substitution, narrow energy gaps are realized only by lowering the LUMO energy level, and the HOMO is hardly affected. That is, it is assumed that the aza-substituted materials might possess high oxidation resistance and higher durability than conventional dyes. To prove this speculation, we investigated durability of the aza-substituted materials against UV irradiation.

We prepared NIR-luminescent protein complexes utilizing **5e** and indocyanine green (ICG) which is the typical NIR luminescent dye used in a wide variety of bioassays [72]. The modification of protein molecules with **5e** can be easily accomplished by a simple mixing process in an aqueous buffer, followed by purification using filtration and freeze drying. The resulting **5e**-adsorbed protein complex exhibited remarkable NIR emission in the buffer and possess high dispersibility. Particularly, from the photostability test, it

was clearly shown that the **5e**-adsorbed protein complexes exhibited superior resistance to photobleaching (Figure 6e). Absorption and emission properties of the ICG-adsorbed protein critically decreased by approximately 90% within 20 min under UV irradiation. In contrast, the **5e**-adsorbed complexes displayed remarkable photostability, maintaining nearly identical levels of absorption and emission properties even after 60 min of irradiation. These findings indicate the significant advantage of utilizing polymer-modified protein complexes as compared to conventional ICG for applications requiring sustained NIR luminescence over extended periods. As mentioned above, the aza-substitution hardly influences HOMO energy levels. Moreover, in the case of **5e**, the perpendicular phenyl substitution and alkyl chains could disturb the access of reactive oxygen species. Therefore, stability in aqueous media can be improved. Furthermore, we investigated the applicability of the NIR-luminescent protein complexes with a different type of protein. By utilizing lipase as a scaffold, we found that enzymatic activity can still be detected after polymer modification, indicating that the functionality of proteins is retained throughout the process. The outstanding photostability should be originated from the low HOMO energy level and make these complexes potential candidates for a wide range of bioimaging and biomedical applications.

Conclusion

In this review, the new method to control the electronic state of conjugated polymers without extending the π -conjugated system is explained, and typical examples were demonstrated. When isolated FMOs can be discovered by quantum chemical calculations, it is possible to efficiently and selectively lower the energy level of one of FMOs by aza-substitution. By lowering the HOMO and LUMO levels, blue and near-infrared emitting

materials were obtained, respectively. In particular, since the π -conjugation area is not expanded, concentration quenching caused by intermolecular interactions can be avoided, and subsequently intense luminescence can be obtained even from crystalline states of small molecules and polymer films. It was also found that the NIR luminescent materials obtained by aza-substitution are resistant to photobleaching. This method is orthogonal to the conventional design for tuning the electronic properties of conjugated systems, such as expansion of π -conjugation, electron-donor and acceptor interaction and atom coordination. Therefore, further physical properties can be expressed by the combination with design strategies. More recently, we accomplished to observe additional lowering of LUMO levels by coordinating boron at the aza-substituted position although this issue is not described due to lack of space [73]. Thus, our protocol is useful for the creation of next-generation optoelectronic materials.

ACKNOWLEDGEMENT

This work is partially supported by a Grant-in-Aid for Scientific Research (B) (JP21H02001).

The authors declare that there is no conflict of interest.

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Figure legends

Figure 1. (a) Illustration of the concept for selective lowering of LUMO energy level by the aza-substitution at the isolated LUMO. (b) Chemical structures and isolated FMOs (indicated by arrow) of 5AP. (c) Light absorption properties of 5AP derivatives in CHCl₃. The picture is the CHCl₃ solution of 1e (1 mM). Reprinted with permission from ref 14. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 2. (a) Isolated LUMO in BODIPY and molecular design for NIR emission by the aza-substitution and (b) blue luminescent molecule.

Figure 3. (a) Chemical structures, (b) redox potentials and (c) absorption properties of aza-substituted derivatives at the isolated FMOs. Reprinted with permission from ref 23. Copyright 2022 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 4. (a) Chemical structures of boron complexes reported in our studies. (b) Chemical structure, optical properties, and molecular orbitals of FBKI **3a** reported in ref. 31. (c) Chemical structure and optical properties of aza-substituted FBKI **3b** and (d) polymer **3c**.

Figure 5. (a) Chemical structure and molecular orbitals of diiminate derivative **4a**. (b) Structure and optical properties of boron formazanate-containing conjugated polymer **4b**. (c) Schematic reaction for partially boronated polymer **4c** and (d) absorption and emission spectra in toluene. The picture is the solution of **4c** in toluene. Reprinted with permission from ref 41. Copyright 2021 American Chemical Society. (e) Structure and optical properties of silicone formazanate-containing conjugated polymer **4d**.

Figure 6. (a) Isolated LUMO in the boron azomethine complex **5a**. (b) Chemical structure and optical properties of the boron azobenzene complex **5b**. (c) AIE-active complex **5c** with NIR emission consisting of the azobenzene structure. (d) Representative NIR-luminescent polymers containing boron azobenzene complexes. (e) Photostability tests with the protein complexes with ICG or polymer **5e** under UV irradiation (254 nm).

Figures

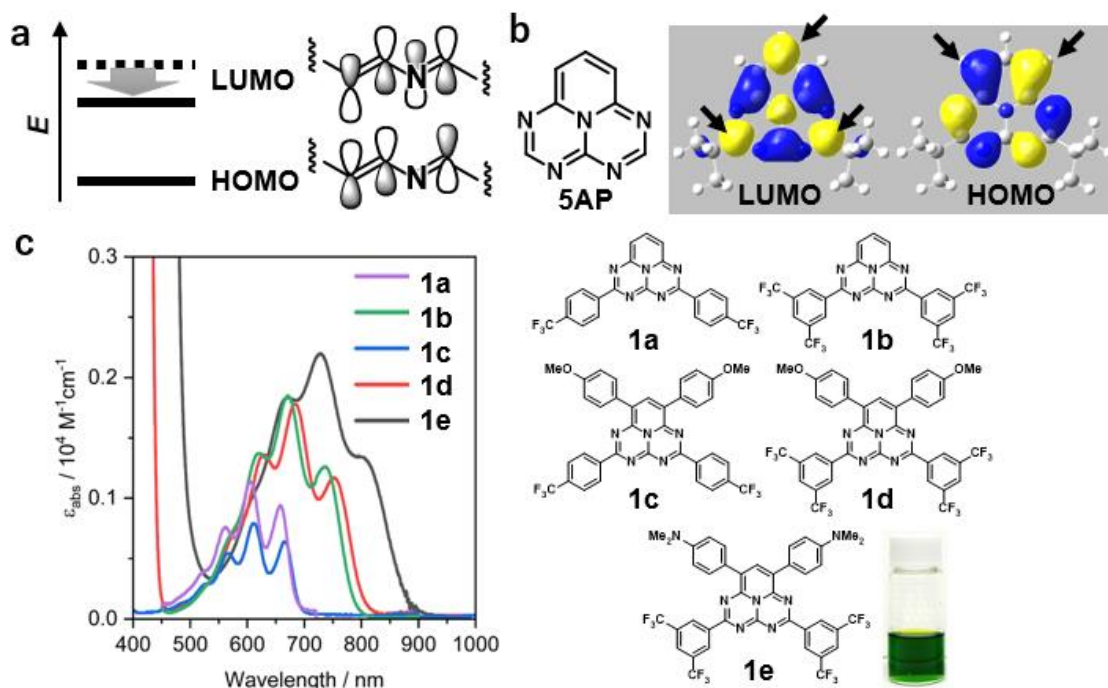


Figure 1

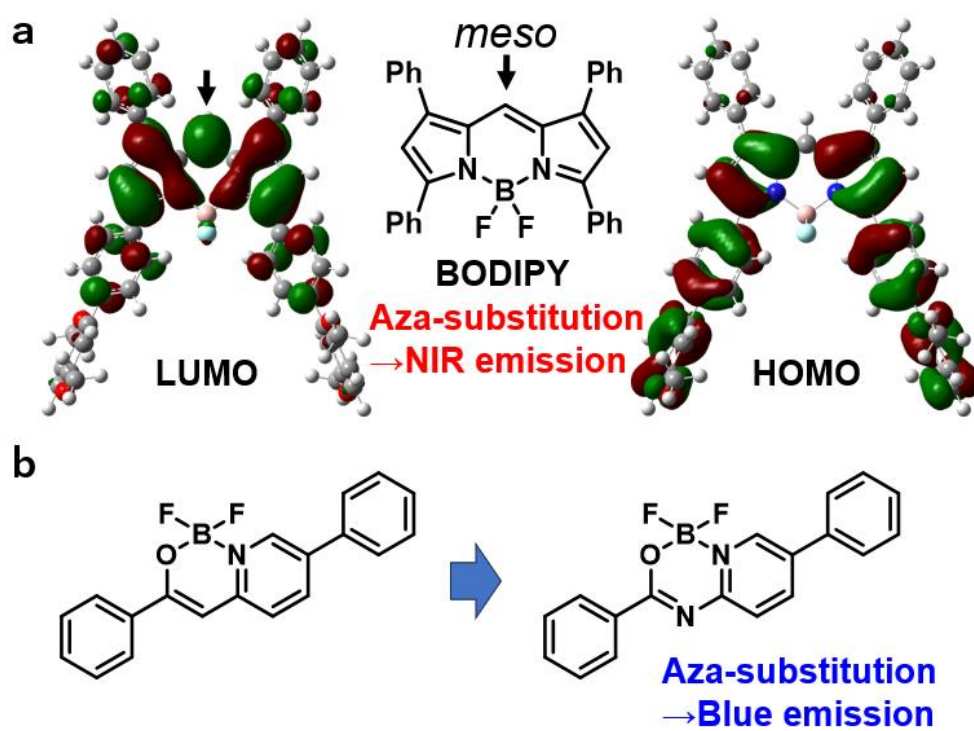


Figure 2

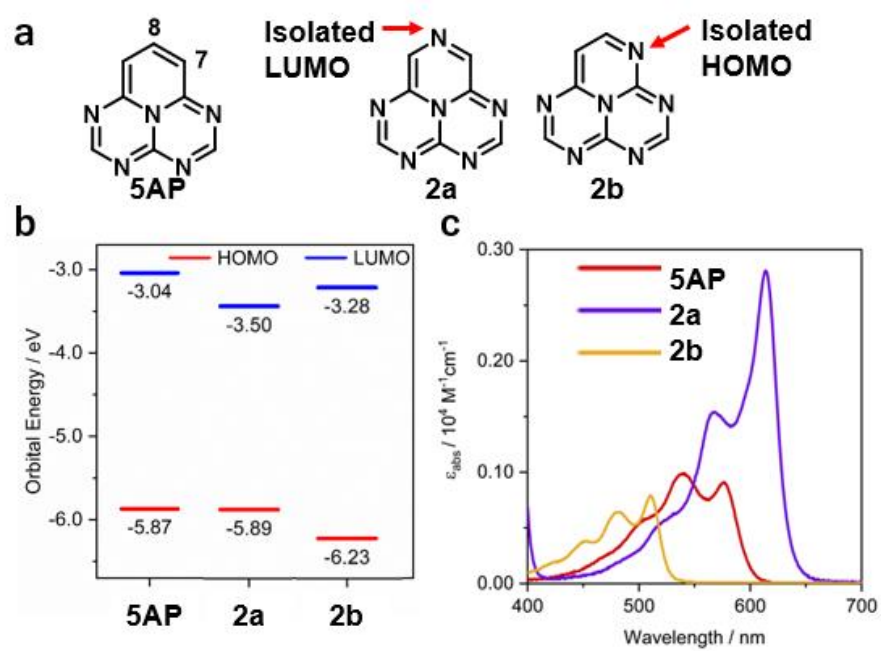


Figure 3

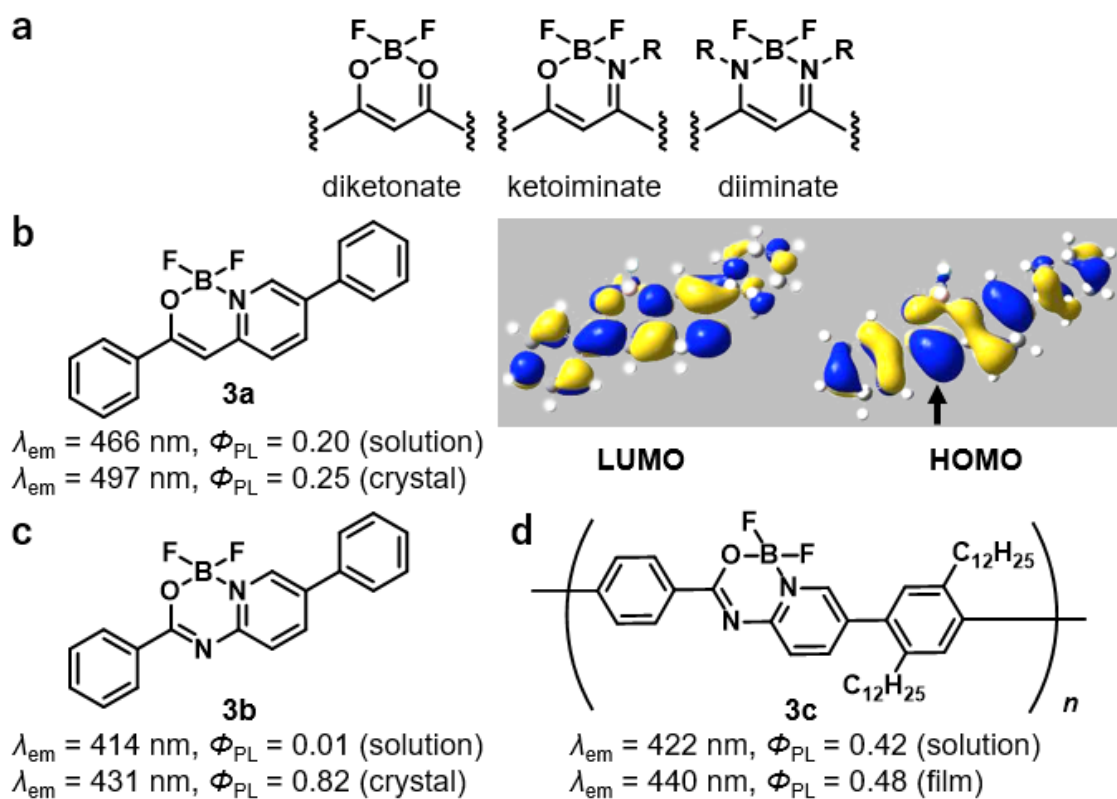


Figure 4

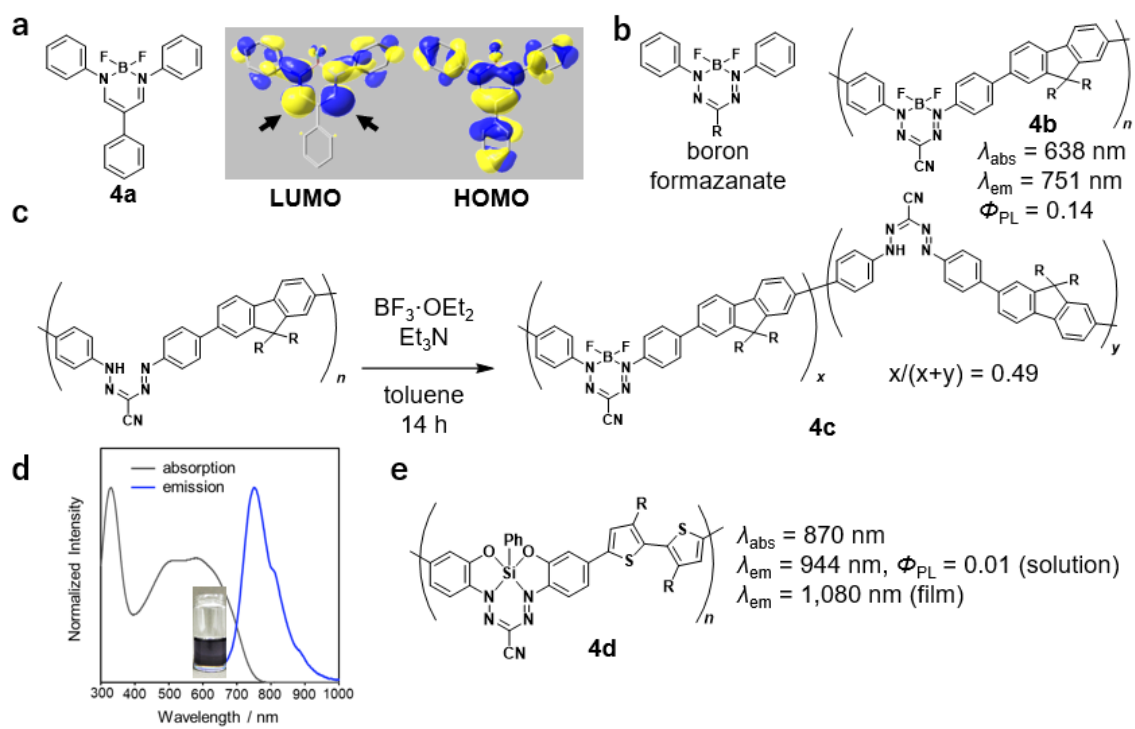


Figure 5

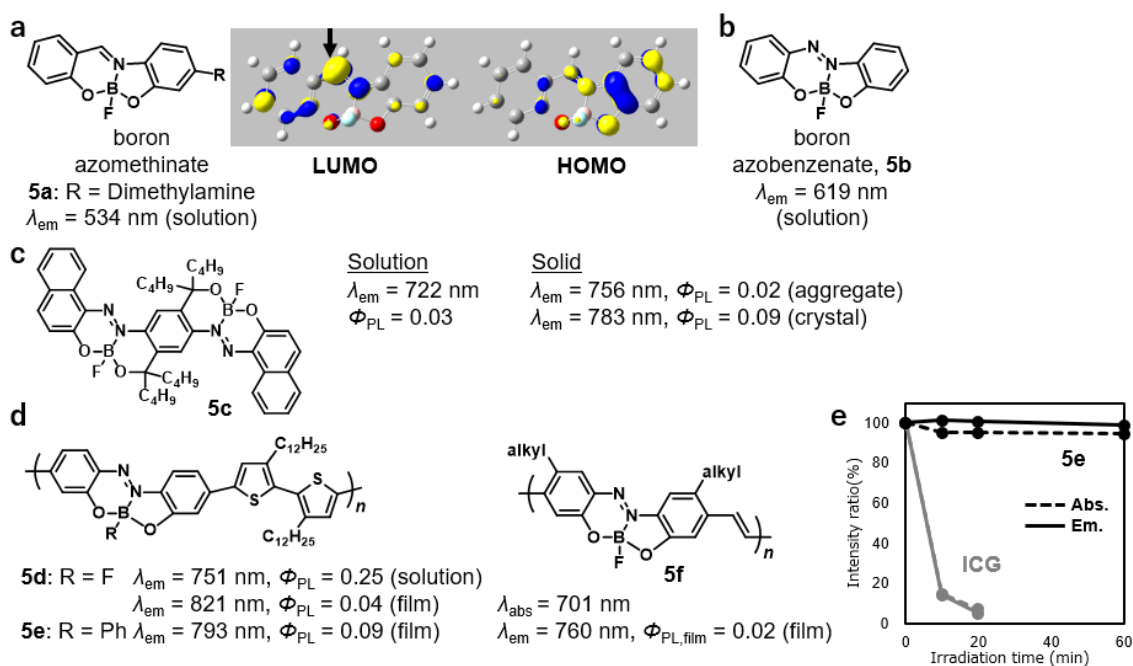
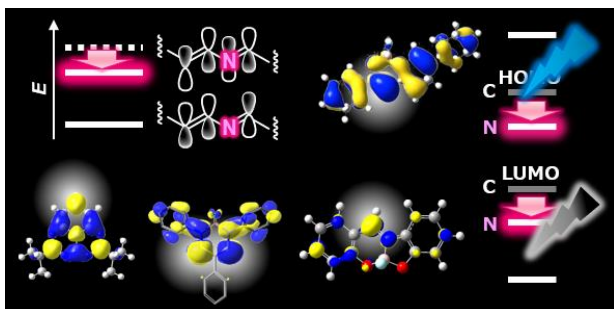


Figure 6

Graphical abstract:



The new concept for controlling the energy level of conjugated materials without extending the π -conjugated system is described. By the aza-substitution at the “isolated frontier molecular orbitals (FMOs)”, which are defined in this manuscript, one of energy level of FMOs can be selectively and efficiently lowered. Based on this protocol, advanced conjugated polymers with pure-blue or near infrared luminescent properties were obtained.



Kazuo Tanaka

Kazuo Tanaka received his Ph.D. degree in 2004 from Kyoto University, and worked in Stanford University, USA, Kyoto University, and RIKEN as a postdoctoral fellow. In 2007, he has moved to the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, and in 2018, he was promoted to Professor. His research projects especially focus on design of new functional materials relating optics and nanotechnology based on the heteroatom-containing conjugated polymers and organic-inorganic polymer hybrids.