

**Development of Functional Organic Materials
with an Intramolecular B–N Coordination Bond
as a Key Scaffold**

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Table of Contents

General Introduction	1
Chapter 1 Effects of Dibenzo- and Dithieno-Fused Structures at the <i>b</i> , <i>g</i> Bonds in the BODIPY Skeleton	21
Chapter 2 NIR Dye Using BF ₂ -Bridged Azafulvene Dimer as an Electron-Accepting Unit	37
Chapter 3 4,7-Bis[3-(dimesitylboryl)thien-2-yl]benzothiadiazole: Solvato-, Thermo-, and Mechanochromism Based on the Reversible Formations of an Intramolecular B–N Bond	65
Chapter 4 D– π –A Dyes Using an Intramolecular B–N Coordination Bond as a Key Scaffold for Electronic Structural Tuning and Their Application in Dye-Sensitized Solar Cells	93
Chapter 5 D– π –A Dyes Containing Diketopyrrolopyrrole and Boryl-Substituted Thienylthiazole Units for Dye-Sensitized Solar Cells with High J_{sc} Values	135
List of Publications	163
Acknowledgement	165

General Introduction

For the molecular design of new π -electron materials, the incorporation of main group elements into π systems is one of the powerful methodologies. Among the main group elements, boron, a group 13 element possessing a vacant p-orbital, is particularly interesting because boron has several characteristic structural and electronic features (Figure 1).¹⁻⁸ The first feature is a structural one. That is, trivalent boron has the trigonal planar geometry (Figure 1b). For example, the combination of boron with nitrogen readily results in the formation of borazine, a six-membered ring, which is also known as inorganic benzene and may be used as a scaffold to build boron-containing molecules.^{3,4} The second feature is an effective orbital interaction with the π -conjugated frameworks through the vacant p-orbital. The incorporation of boron into π -conjugated systems induce a unique interaction between π^* orbitals in the π -conjugated framework and the vacant p-orbital of boron, namely p- π^* interactions, which take place to provide π -electron systems with high electron-accepting abilities (Figure 1c).⁵ The third feature is the electron-accepting properties of the trivalent boron moiety in the excited state. The combination of the electron-accepting boryl group with an electron-donating unit, such as an amino group in a π -conjugated system, results in intriguing fluorescence properties with large Stokes shifts arising from the intramolecular charge-transfer (ICT) transition (Figure 1d).⁶ The forth feature is the Lewis acidity of trivalent boron derived from its vacant p-orbital. Trivalent boron compounds exhibit considerable Lewis acidity and thus readily form a coordination bond between the Lewis acidic boron center and the Lewis bases, in which the vacant p-orbital of the boron is occupied with the lone pair on Lewis bases to form a tetrahedral borate skeleton (Figure 1e).^{2,7} The exploitation of these characteristic features of boron in the molecular design enables us to produce sophisticated π -functional materials with attractive photophysical and electronic properties.¹⁻⁸ Among these characteristic features of boron, the formation of a coordination bond is particularly of interest in terms of the application to functional materials. This is because the formation of a coordination bond between trivalent boron and Lewis base can stabilize the boron-containing π system effectively due to the inhibition of the reactivity regarding p-orbital of boron center, as well as can endow such π system with the electronic impacts. This methodology would be useful for structural and electronic modifications of π -conjugated systems to form stable

boron-containing compounds.

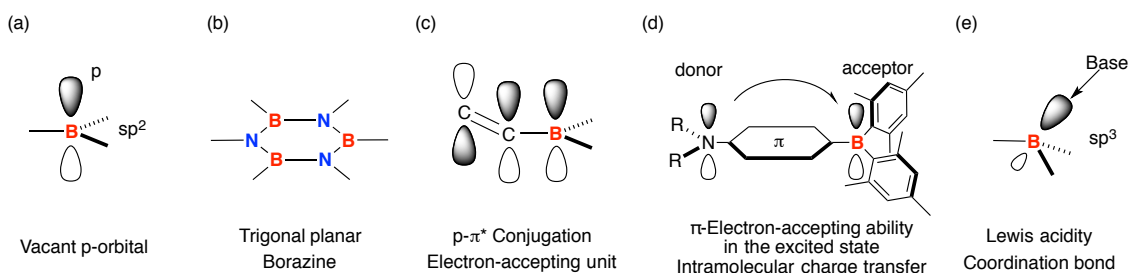


Figure 1. The characteristics of boron atom: (a) Vacant p-orbital, (b) trigonal planar geometry, (c) p- π^* conjugation through a vacant p-orbital, (d) the π -electron-accepting ability of the trivalent boron moiety in the excited state, and (e) Lewis acidity.

Boron-Containing π -Conjugated System with an Intramolecular Coordination Bond

Upon taking a view of the tetracoordinated boron-containing compounds with an intramolecular coordination bond, boron dipyrromethenes (BODIPYs)^{9–12} and boron β -diketonates^{13–16} derivatives are known to represent such π systems (Figure 2). In addition to these examples, boron pyridylphenolate¹⁷ and boryl-substituted thienylthiazole,¹⁸ have been reported (Figure 2). In these systems, π -conjugated units are fixed by the boron-bridge to give a planar structure. The examples of such compounds possessing intramolecular boron coordination bonds can be classified by the binding modes via boron, such as N–B–N, O–B–O, O–B–N and C–B–N bridges, respectively. According to this classification, several representative examples of the functional π -electronic systems containing the intramolecular coordination bond are introduced as follows.

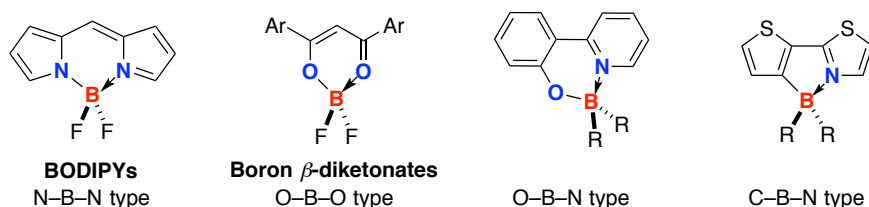


Figure 2. Examples of boron-containing π systems with an intramolecular coordination bond.

1. Boron Dipyrromethenes (BODIPYs)

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) derivatives exhibit intriguing photophysical properties. For example, tetramethyl derivative **1** shows an intense absorption peak at 509 nm with a large extinction coefficient ($\epsilon = 80,000 \text{ M}^{-1} \text{ cm}^{-1}$) and a sharp fluorescence at 517 nm with high quantum yield ($\Phi_F = 0.92$) (Figure 3a). The first example of this class of compound was reported by Treibs and Kreuzer in 1968.¹⁰ Since then, the large numbers of BODIPY derivatives exhibiting attractive photophysical properties have been developed so far. Based on such properties, some of BODIPY derivatives have been applied to the materials for fluorescent indicators, energy transfer cassettes, photovoltaics, and medical applications, etc.⁹

In general, the nitrogen-containing π systems show two different types of electronic character depending on the bonding mode of nitrogen. The nitrogen-containing π systems, in which nitrogen has three single bonds, such as pyrrole and triarylaminines, work as the electron-donating group on account of the mesomeric effect of the lone pair of nitrogen. Conversely, the other π systems, in which nitrogen has double bond and single bond, such as pyridine and azafulvene, work as the electron-accepting group due to the inductive effect of the high electronegativity of nitrogen atom (Figure 3b). BODIPY can be regarded as the π -conjugated system consisted of an electron-donating pyrrole unit and an electron-accepting azafulvene unit, which are fixed by N–B–N bridge. The characteristic electrochemical and photophysical properties of BODIPY derivatives should be attributed to the results of effective resonance structures between pyrrole and azafulvene units as well as an intramolecular B–N bond formation.

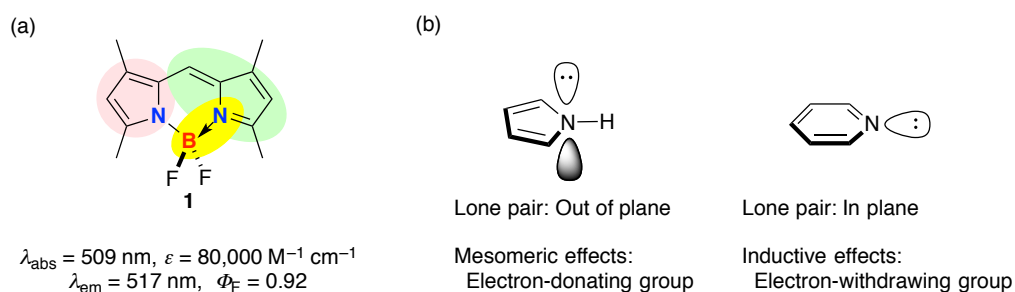


Figure 3. (a) Structure of tetramethyl BODIPY derivative **1**. (b) The electronic impacts of nitrogen atoms on π system.

To ascertain such impacts on electronic structure of BODIPY, DFT calculations (B3LYP/6-31G(d)) were conducted on the BODIPY, dipyrromethene, and dipyrromethane, respectively. As shown in Figure 4, the dipyrromethene consisted of pyrrole and azafulvene has the much lower-lying LUMO level by 3.32 eV than dipyrromethane. Upon formation of the B–N coordination bond in BODIPY, the LUMO level of dipyrromethene further decreases by 0.75 eV. On the other hand, the degree of decreasing the HOMO levels is rather small (0.18 and 0.50 eV, respectively) relative to that of the LUMO levels in these compounds. These results suggest that the contribution of azafulvene moiety and the formation of the B–N coordination bond induce the significant electron-accepting ability in the BODIPY skeleton, leading to the low-lying LUMO level and narrow HOMO–LUMO gap (Figure 4). On account of the effective π -conjugation in BODIPY skeleton, a variety of structural modifications in the BODIPY core skeleton significantly affect their electronic structures, which enables the BODIPY derivatives to exhibit more intriguing properties and novel functions.⁹ Several examples of structural modification of BODIPY skeleton are shown below.

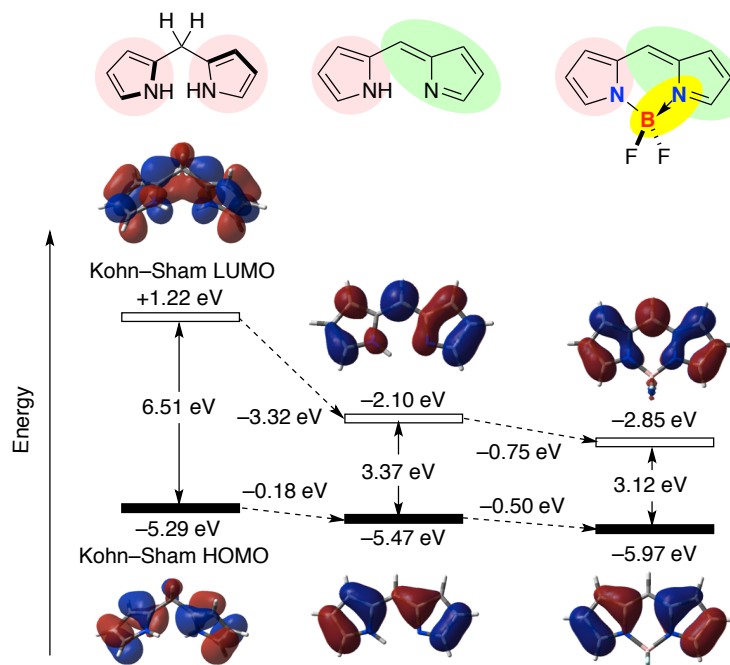


Figure 4. Effects of formation of intramolecular B–N coordination bond and pictorial presentation of a plot of the Kohn–Sham HOMO and LUMO levels (B3LYP/6-31G(d)).

1-1. π -Extended BODIPYs by Ring-Fusion

Introducing substituents, such as aryl groups and alkenes, at peripheral positions of BODIPY core can modify its electronic structure. However, the steric hindrance of substituents often limits the effective extension of the π -conjugation. In contrast, introducing ring-fused structure to BODIPY core extends π -conjugation effectively while maintaining high planarity and rigidity of π -skeleton. Suzuki et al. demonstrated fluorescence color tuning by introducing the furano-fused structure to the BODIPY skeleton (Figure 5).¹¹ Furano-fused BODIPYs **2–5** exhibit sharp absorption bands with high extinction coefficients and intense fluorescence peaks with high quantum yields. The significantly red-shifted absorption and fluorescence in **2–5** compared to non-fused BODIPY **1** are due to the effectively delocalized π - and π^* -orbitals over whole of π -skeleton. The high quantum efficiency in **2–5** is most likely due to the rigidity of furano-fused BODIPY core. In addition, their emission wavelength could be easily controlled by simple additional modifications at the fused-furan ring or *meso*-position of BODIPY skeleton, in keeping with their high fluorescence quantum yields. For example, furano-fused BODIPY **5** possessing *p*-anisyl groups at the terminal-position and a CF₃ group at the *meso*-position exhibits fluorescence peak (738 nm) with a high quantum yield (0.56) even in the NIR region (Figure 5).

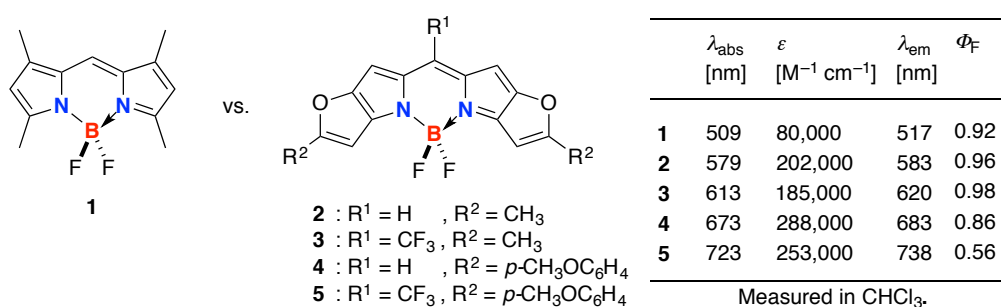


Figure 5. Furano-fused BODIPYs **2–5**.

1-2. Modification of the Substituents on Boron in BODIPYs

The modification of the substituents on the boron center also affects the electronic structure of BODIPY core. Ziessel et al. reported a series of BODIPY derivatives possessing aryl substituents on boron center, of which redox potentials are varied depending on the electronic property of substituents on boron center (Figure 6).¹² The substituents on boron in BODIPY skeleton can be introduced using aryl Grignard or

aryl lithium reagents toward the difluoro derivative. In the substitution using Grignard reagents, the monosubstituted derivatives are isolated, while the use of lithium reagents leads to exclusive formation of the disubstituted derivatives. Cyclic voltammetry reveals that the replacement of the fluorine by aryl fragments shifts the oxidation potential of the BODIPY core more positively by 0.10 V in monophenyl derivative **7**, 0.18 V in diphenyl derivative **8**, 0.21 V in di(*p*-anisyl) derivative **9**, and 0.16 V in di(1-pyrenyl) derivative **10**. Additionally, reduction potentials also shift more positively by a comparable amounts.

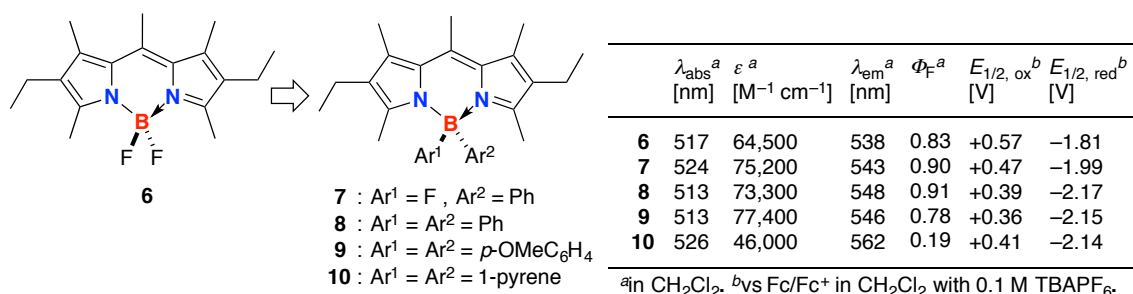
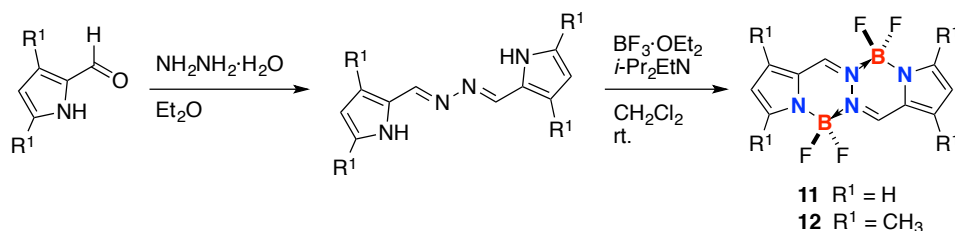


Figure 6. BODIPYs modified on boron atom; structures and properties of **6**–**10**.

1-5. Boron-Containing π Systems with N–B–N Bridge Similar to BODIPYs

Apart from the modification of substituents on BODIPY core, the modification of π system itself has also been reported as new building blocks for functional materials. For example, Ziegler et al. reported the new fluorescent chromophores **11** and **12**, which can be readily synthesized in two steps via the coupling of pyrrole-2-carboxaldehyde with hydrazine followed by reaction with BF₃ (Scheme 1). The resultant symmetric and dimeric tetracycle is composed of two BF₂ units in 6-membered chelate rings appended with pyrrole units on the periphery. The quantum yields of fluorescence for unmodified compound **11** and tetramethyl variant **12** are near unity, with values of 0.95 and 0.92, respectively, in CH₂Cl₂.¹⁹

Scheme 1.



Liu et al. developed doubly B–N-bridged bipyridyl **13** as a new class of electron-deficient building blocks for polymer electron acceptors. Formation of B–N intramolecular coordination bonds in **13** fixes bipyridine skeleton in a planar conformation and decreases both of the HOMO and LUMO levels. Polymer **14** containing this unit also has the low-lying HOMO and LUMO energy levels. The properties of **14** exhibiting high electron mobility and strong absorbance in the visible range enables the application to electron acceptors in all-polymer solar cell devices (Figure 7).²⁰

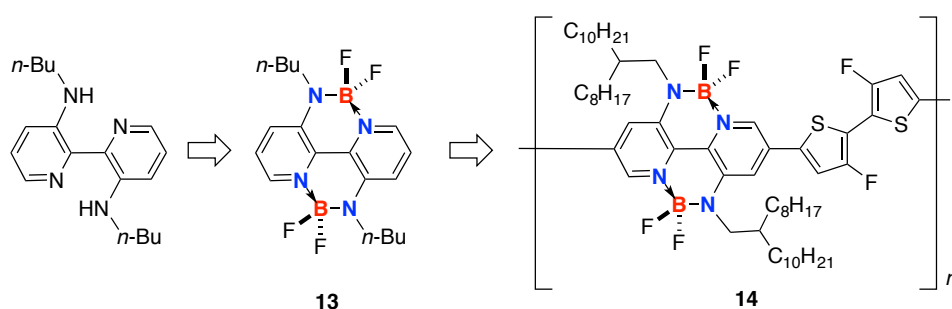
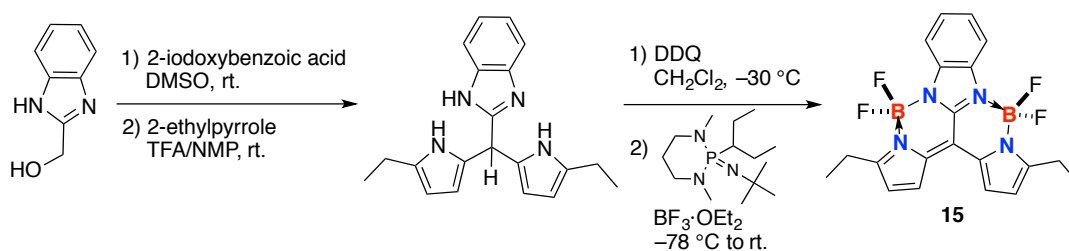


Figure 7. Doubly B–N bridged bipyridyl **13** and polymer **14**.

Recently, Werz et al. developed a new class of fused-BODIPY core, such as **15**, which shows high fluorescent property (Scheme 2). This skeleton is easily accessible by two-step reaction from 2-ethylpyrrole and a benzoimidazole derivative. The use of benzoimidazole as a bridging skeleton with two Lewis base sites enables the binding of two BF₂ units to provide sufficient rigidity and enhanced electron-accepting ability. Thus, absorption and emission bands are observed around 600 nm; the fluorescence quantum yields can reach unity (0.96) and show little dependence on solvent polarities.²¹

Scheme 2.



2. Boron β -Diketonates

Boron β -diketonates are also well-known tetracoordinated boron-containing π systems bearing an intramolecular B–O coordination bond, which were first reported in 1924.¹³ Despite the less diversity in structural modifications compared to the BODIPY core, this system has been widely used as an electron-accepting unit in the emissive materials.¹⁴

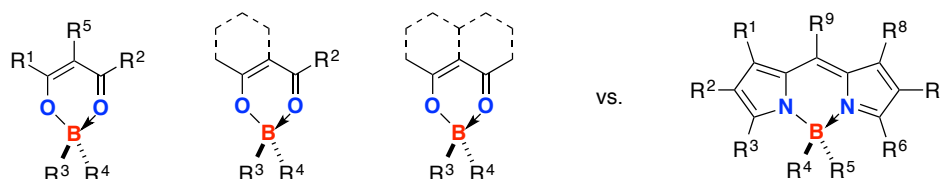


Figure 8. Boron β -diketonates and their structural modifications.

One of the most intriguing application of this kind of π system would be a functionalization of curcumin, which is a natural pigment possessing β -diketone unit.²² Moore et al. reported that BF_2 -bridged curcumin **16** and its derivatives can work as NIR biological imaging probes (Figure 9).¹⁵ Incorporation of a BF_2 group into curcumin affords the red-shifted emission by 80 nm at 640 nm relative to curcumin owing to the formation of the B–O coordination bond. Such a longer wavelength emission in the NIR region has a great advantage for biological imaging in terms of light penetration, i.e. the shorter wavelength emission is strongly absorbed by hemoglobin and other body tissues in blood. Since then, a variety of probes involving the BF_2 -bridged curcumin unit have been investigated for NIR biological imaging.¹⁶

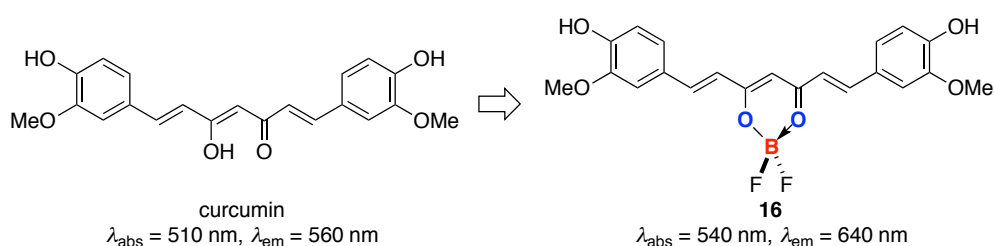


Figure 9. BF_2 -bridged curcumin **16**.

3. Boron-Containing π Systems with O–B–N Bridges

Boron-containing π systems with an O–B–N bridge have been studied as the emissive and the electron-transporting materials in OLEDs owing to their intense and sharp fluorescence profiles and their low-lying LUMO levels (~ -3.0 eV). Alq₃ (tris(8-hydroxyquinolino)aluminium)²³ is well-known as a standard material of electron-transporting and emissive materials in OLED devices. As alternative materials to Alq₃, several boron analogues, such as boron hydroxyquinolinato²⁴ and boron pyridylphenolate,¹⁷ have been pursued (Figure 10). The effects of the substituents of the boron center and π system on fluorescence properties were intensively investigated.^{17,24} As a whole, the substituents on the *para*-position of oxygen are found to affect the fluorescence wavelength significantly. In addition, phenyl groups as substituents on boron center efficiently prevented π -stacking in the solid state because they protrude out of plane with π system, which avoids fluorescence quenching.

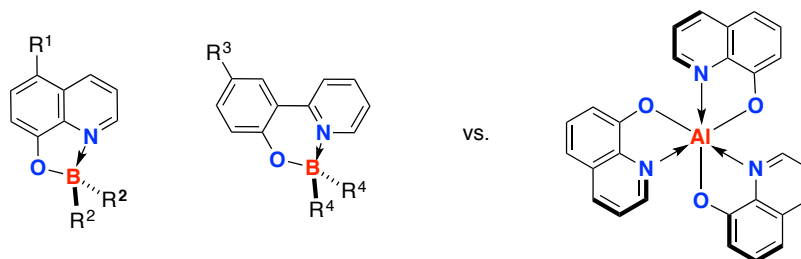


Figure 10. Typical boron-containing π systems with an O–B–N bridge; boron hydroxyquinolinato and boron pyridylphenolate as an alternative to Alq₃.

Zhang et al. investigated various ladder-type π -conjugated compounds **17–23** with two boryl groups (Figure 11).²⁵ Incorporating two B–N intramolecular coordination bonds into such π -conjugated π systems endows these materials with strong electron-accepting ability, leading to a substantially red-shifted emission compared to compounds with parent monoboron compound. In addition, four phenyl groups attached to boron atoms effectively prevent dense π -stacking in the solid state. As a result, these compounds show bright fluorescence even in the solid state. These compounds display good performance as electron-transporting and emitting materials in OLED devices.

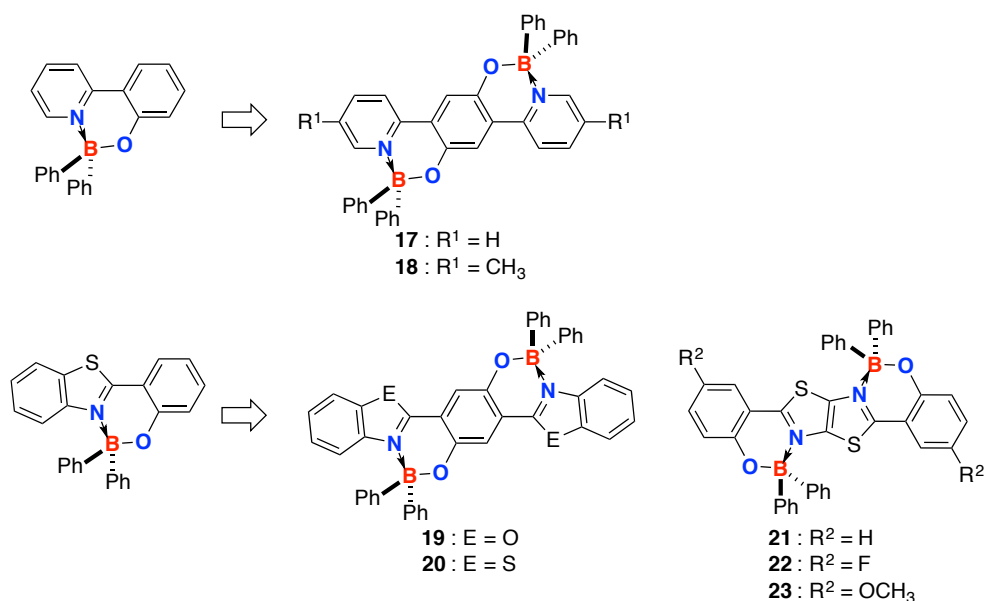


Figure 11. Structures of diboron compounds **17–23**.

4. Boron-Containing π Systems with C–B–N Bridges

Wakamiya and Yamaguchi et al. reported boryl-substituted thienylthiazole **24** as a building unit for electron-transporting materials (Figure 12).¹⁸ Incorporation of boryl groups into the thienylthiazole system fixes the π -conjugated framework in a planar fashion and substantially enhances the electron-accepting ability owing to the formation of the intramolecular B–N coordination. Its dimer **25** also has a highly planar structure and exhibits high electron-accepting ability. According to time of flight (TOF) carrier mobility measurement, the amorphous film of **25** exhibits good electron mobility ($\mu = 1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Since this methodology is simple and general, it has been applied to a variety of C=N-containing π -electron systems to modify their electronic structures.^{26–28}

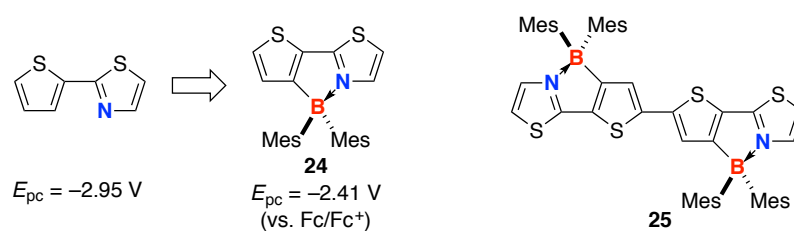
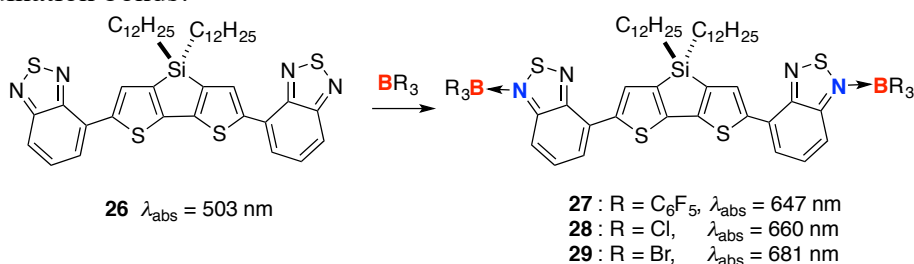


Figure 12. Mes₂B-substituted thienylthiazole **24** and its dimer **25**.

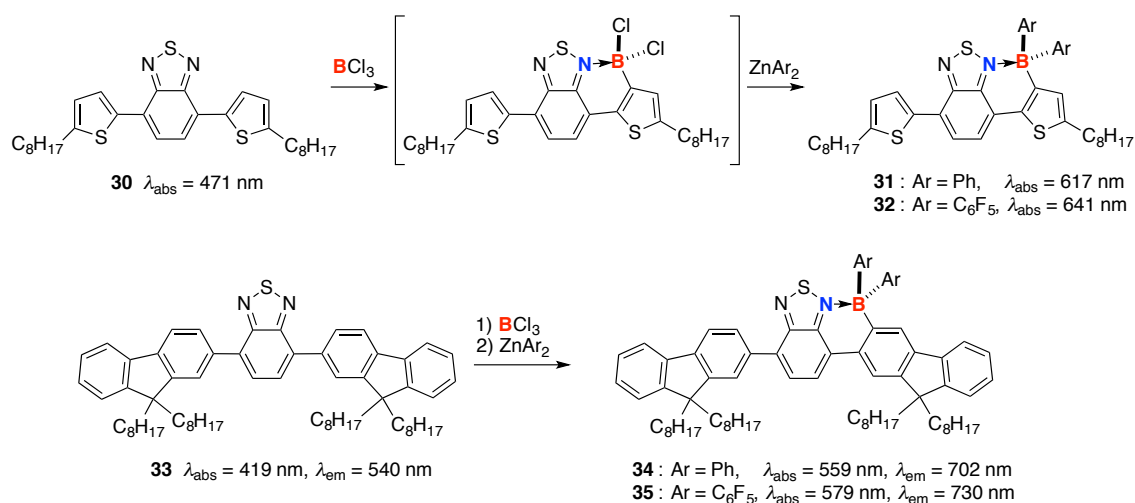
Bazan et al. demonstrated that a simple and effective strategy for control of an optical band gap using intermolecular B–N coordination bond formations. Upon adding stoichiometric quantities of Lewis acids, such as $B(C_6F_5)_3$, BCl_3 , and BBr_3 , the absorption peak of benzothiadiazole (BT) derivative **26** in solution were progressively red-shifted with increasing the Lewis acidity of additives. NMR spectroscopy and X-ray diffraction studies revealed that **26** binds 2 equiv of Lewis acid via the nitrogen at the 3-position of BT (Figure 15).²⁶

Scheme 3. Benzothiadiazole derivatives **27–29** with intermolecular B–N coordination bonds.



Ingleson and Turner et al. synthesized BT derivatives **31** and **32** with intramolecular B–N coordination bonds by the directed C–H borylation using BCl_3 to the thienyl unit and subsequent nucleophilic substitution reactions (Scheme 4).²⁷ Borylative fusion dramatically lowers the LUMO levels of these materials owing to the formation of the intramolecular B–N coordination bond, whilst the changes in the HOMO levels are minimal. Products **34** and **35** were found to act as far-red/NIR-emitting materials. Such directed C–H borylation reactions have been explored intensively,²⁹ which will accelerate the use of the electronic structural modification by the formation of the intramolecular B–N coordination bond in C=N-containing π systems.

Scheme 4.



Overview of This Thesis

As introduced above, an intramolecular coordination bond formation using boron as a key element is a powerful methodology to modify the electronic structures of π -conjugated compounds. Therefore, such an electronic structural modification has been applied to a large number of compounds.²

In this study, the author focused on the electronic structural modification of C=N-containing π systems by the formation of an intramolecular B–N coordination bond as a key approach in the molecular design and has devoted his effort to the development of sophisticated functional materials using this methodology. His approaches are based on the following three aspects of the molecular design. The first one is how to enhance the characteristic electronic structure of boron-containing π -electron systems induced by the formation of B–N bonds. Based on the elucidation of the structure-property relationship in pre-exist boron-containing π -electron systems, the author designed several novel π -electron systems by their modifications or ingenious molecular design utilizing the effects of the intramolecular B–N bond formation. The second one is the molecular design based on the elucidation of the properties of intramolecular B–N coordination bonds in the π -electronic systems. The author focused on the properties of the intramolecular B–N bond in the π -electronic systems with C=N bond and the bulky boryl-substituents. The third one is to apply the B–N-containing compounds for the practical device as a key functional material used therein. The author focused on the fact that electronic structure of B–N-containing π system can be tuned

by the selection of the substituents on the boron center depending on their electron-accepting ability. He developed a series of D- π -A dyes with a B-N bond in an electron-accepting group and applied these dyes to the dye-sensitized solar cells (DSSCs) as photosensitizers. The effect of the boryl substituents and the device performance were investigated in detail.

This thesis is composed of the following five chapters.

In Chapter 1, from the viewpoint of the utilization of characteristic electronic feature of BIDIPYs containing tetracoordinated boron, the author investigated the impacts of the structural modification of BODIPYs by introducing aromatic ring-fused structure, such as benzene or thiophene, at the *b,g*-bonds. A set of experiments and theoretical calculations revealed such a modification enhances the quinoid and azafulvene character in the BODIPY skeleton, which effectively increases the electron-accepting ability and affords the red-shifted absorption.

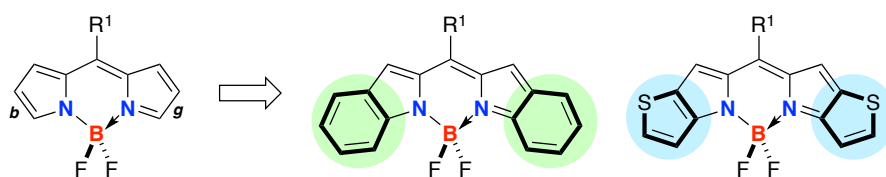


Figure 13. Dibenzo[*b, g*]- and dithieno[*b, g*]-fused BODIPY.

In Chapter 2, focusing on the high electron-accepting ability of azafulvene unit, the author designed and synthesized dipyrrolylethanedione bridged by two boryl groups as a new electron-accepting unit. The single-crystal X-ray diffraction analysis revealed that the formation of intramolecular B-N coordination bonds toward dipyrrolylethanedione endows the skeleton with π -conjugation mode as an azafulvene dimer. Cyclic voltammetry revealed that the compound exhibits extraordinary electron-accepting ability. In addition, D-A-D dye possessing this unit and triarylamine was also developed, which exhibits an intense NIR absorption, exceptional photostability, and high resistance towards oxidation by atmospheric oxygen, even in a dilute solution.

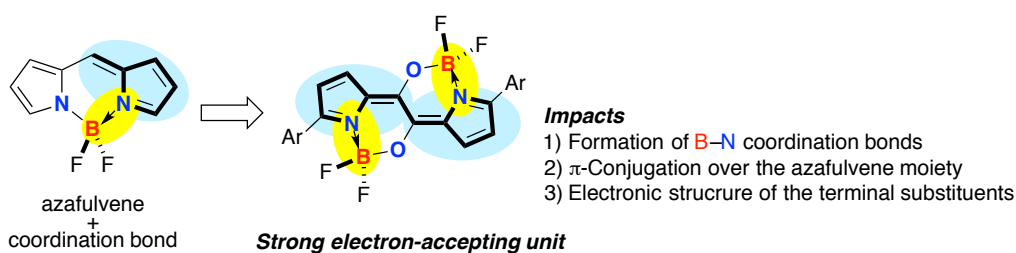


Figure 14. The BF_2 -bridged azafulvene dimer.

In most cases, the formation of an intramolecular B–N coordination bond fixes the π system in a planar fashion and substantially enhances the electron-accepting ability. However, its effects to the π system can differ according to the π -electronic skeletons with C=N bond and substituents on a boron center.

Chapter 3 describes the development of bis(Mes_2B)-substituted dithienylbenzothiadiazole which has bulky Mes groups on boron centers and the strain for B–N bond formation. Photophysical measurements, single-crystal X-ray diffraction analysis, and theoretical calculations revealed that an intramolecular B–N coordination bond of this compound forms reversibly. This equilibrium depends on the solid-state structure, solvent, temperature, and mechanical forces. Such a reversible bond formation leads to the significant color change of this molecule. The responsiveness toward external stimuli, resulting from the reversible formation of the B–N coordination bond, is achieved via weak intramolecular B–N coordination bonds induced by the steric bulk of the Mes groups on the boron centers.

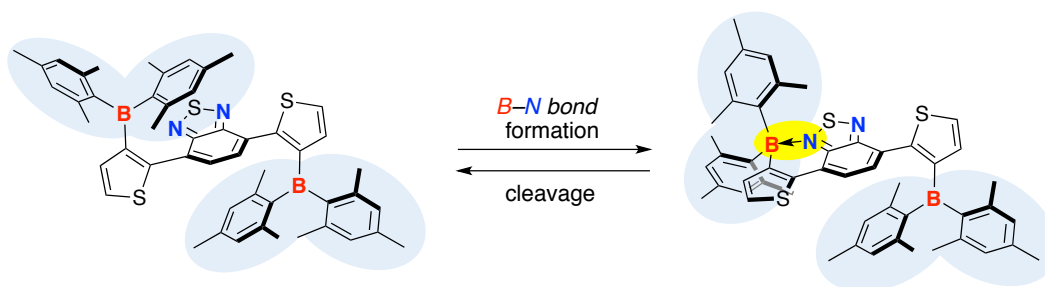


Figure 15. Bis(Mes_2B)-substituted dithienylbenzothiadiazole.

For application to DSSCs, which are one of the attractive photovoltaic devices, the author designed and synthesized a series of dyes possessing a B–N coordination bond. In order to achieve the excellent device performance, the development of bespoke

photosensitizers is required. In terms of an effective use of wide-ranging sunlight and effective electron injection into electrodes, the fine-tuning of the electronic structures of photosensitizer is highly required.

In Chapter 4, as photosensitizer for DSSCs, a series of D- π -A dyes possessing boryl-substituted thienylthiazole as a key electron-acceptor were designed and synthesized. The cyclic voltammetry indicated that the LUMO levels of these dyes can be fine-tuned with the aid of the formation of intramolecular B-N coordination bonds and the electronic effect of the substituents on the boron center as well as those on the anchor group. In addition, the relationship of the electronic structures of dyes and cell performance was investigated in detail. The DSSCs using these dyes exhibit good power conversion efficiencies of 5.1~6.1%, resulting from the red-shifted absorption owing to the formation of intramolecular B-N coordination bonds.

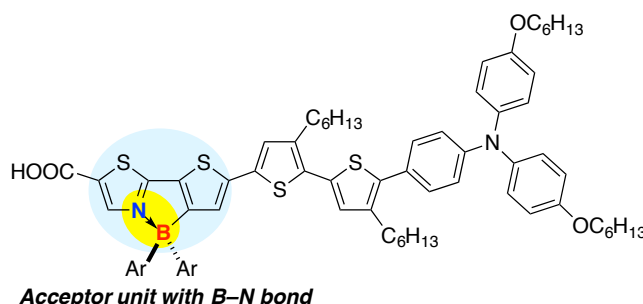


Figure 16. D- π -A dyes with boryl-substituted thienylthiazole group as an electron-accepting unit for DSSCs.

As continuous studies shown in Chapter 4, the photosensitizer with wide-ranging photoelectric conversion ability including the NIR region is required for further improvement of the DSSC performance.

In Chapter 5, focusing on a DPP unit as a narrow π - π^* -gap skeleton, the author designed and synthesized D- π -A dyes with a boryl-substituted thienylthiazole and a DPP unit as an electron-acceptor and a π -spacer, respectively. Incorporating a DPP unit into a D- π -A system leads to significantly red-shifted absorption relative to the parent dyes developed in Chapter 4. The DSSCs based on these dyes exhibited the photoelectric conversion in the NIR region and thus gave remarkably high short-circuit current density (J_{SC}) even compared to the organic sensitizers that have ever been reported.

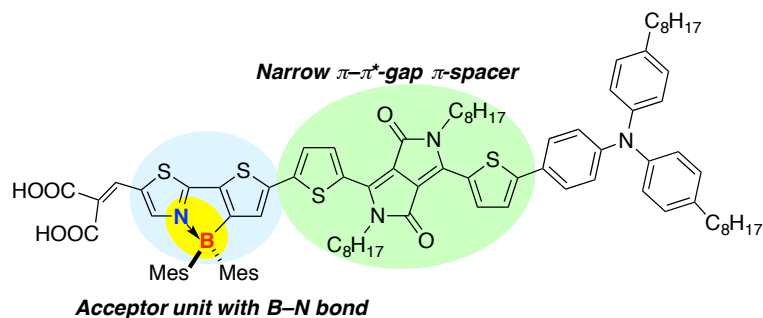


Figure 17. D- π -A dyes with diketopyrrolopyrrole (DPP) group as a narrow π - π^* -gap π -spacer for DSSCs.

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Chapter 1

Effects of Dibenzo- and Dithieno-Fused Structures at the *b*, *g* Bonds in the BODIPY Skeleton

Abstract: Dibenzo[*b,g*]-fused and dithieno[*b,g*]-fused BODIPY derivatives were synthesized, and the electronic impacts of the introducing dibenzo- and dithieno-fused structures at both of the *b* and *g* bonds in the BODIPY skeleton were investigated. Electrochemical and photophysical measurements demonstrated that these structural modifications effectively enhance the electron-accepting ability of the BODIPY skeleton leading to the red-shifted absorption.

Introduction

As mentioned in General Introduction, BODIPY (4,4-difluoro-4-bora-3*a*,4*a*-diazas-indacene) skeleton has unique electrochemical and optical properties, such as intense absorption profiles, high photostability, and high electron-accepting ability.¹ Various structural modifications on this skeleton have been extensively studied which demonstrates their significant utilities in a variety of applications, such as dye-sensitized solar cells (DSSCs),² organic photovoltaics (OPVs),³ organic light-emitting diodes (OLEDs),⁴ photodynamic therapy,⁵ etc. A simple structural modification to expand the π -conjugation would be the introducing ring-fused structure to the BODIPY skeleton. Whereas several derivatives having the ring-fused structures at the *a* bond have been reported,^{3b,6} the *b* bond-fused derivatives are still limited to a few examples,^{3c,7-8} such as difurano[*b,g*]-fused^{7b-c} and bisbiphenyl[*b,g*]-fused derivatives (Figure 1).^{3c}

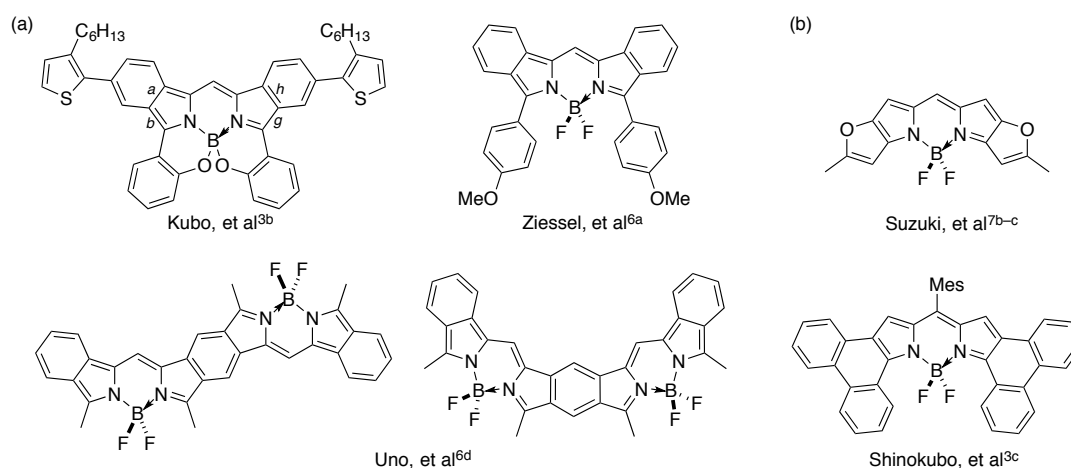


Figure 1. BODIPY derivatives having the ring-fused structures (a) at the *a* bond and (b) at the *b* bond.

Recently, Yamaguchi and Wakamiya reported monobenzo[*b*]-fused BODIPY **1** and demonstrated that the benzene-fusing at the *a* bond in the BODIPY skeleton increases the HOMO level, whereas the benzene-fusing at the *b* bond effectively decreases the LUMO level (Figure 2).⁸ The latter is important for the molecular design toward NIR dyes or electron-transporting materials with air-stability.⁹ Following this study, the author has been interested in dibenzo[*b,g*]- and dithieno[*b,g*]-fused BODIPYs. In this chapter, the author examines the synthesis and properties of dibenzo[*b,g*]- and

dithieno[*b,g*]-fused BODIPY derivatives **2** and **3**, in which the 3,5-bis(CF₃)phenyl group was introduced at *meso*-position for increment of the electron-accepting ability and solubility (Figure 2). The author discusses the impacts of aromatic ring-fusing at both of the *b* and *g* bonds in the BODIPY skeleton.

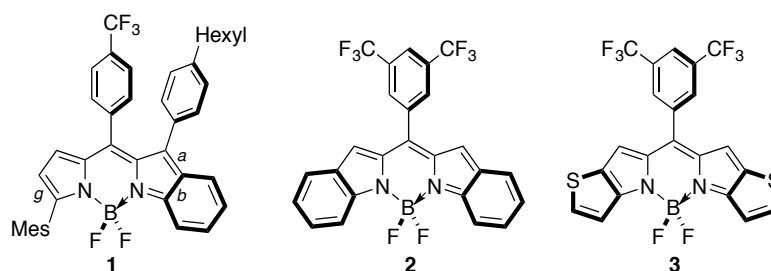


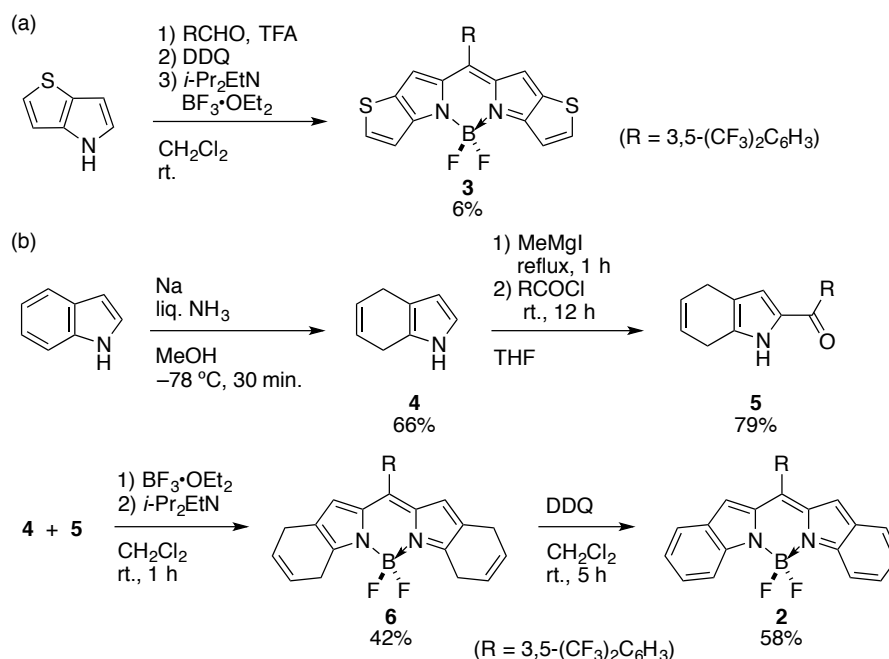
Figure 2. Ring-fused BODIPY derivatives **1**, **2**, and **3**.

Results and Discussion

Synthesis

Scheme 1 shows synthetic routes for BODIPYs **2** and **3**. By using thienylpyrrole as starting material, dithieno[*b,g*]-fused BODIPY **3** was obtained as dark purple solids with gold luster according to the conventional method (Scheme 1a).¹⁰ In the case of dibenzo[*b,g*]-fused BODIPY **2**, the similar synthetic route using 1*H*-indole as a starting material was not suitable due to the lower reactivity for an electrophilic substitution reaction at 2-position of indole compared to that of pyrrole.⁸ Therefore, the author synthesized **2** by another method using 4,7-dihydro-1*H*-indole **4** as a key intermediate (Scheme 1b). Thus, **4** was prepared by Birch reduction of 1*H*-indole,¹¹ followed by acylation to give **5**. Subsequently, addition of BF₃·OEt₂ as a Lewis acid into the mixture of **4** and **5** followed by treatment with *i*-Pr₂EtN directly produced tetrahydrodibenzo[*b,g*]-fused BODIPY **6** in 42% yield as dark purple solids. Finally, oxidation of **6** with DDQ afforded dibenzo[*b,g*]-fused BODIPY **2** in 58% yield as dark blue solids with gold luster. All compounds of **2**, **3** and **6** are stable toward air and water and could be purified by the silica gel column chromatography. BODIPY **6** was used as a reference compound in the following discussion.

Scheme 1. Synthesis of **2** and **3**



Electrochemical Properties

To evaluate the electronic impacts of introducing ring-fused structures at both of the *b* and *g* bonds in the BODIPY skeleton, cyclic voltammetry of **2**, **3** and **6** in CH_2Cl_2 was conducted and results are shown in Figure 3. While tetrahydrodibenzo derivative **6** exhibits a reversible reduction wave at $E_{1/2} = -1.33$ V (vs. Fc/Fc^+) and an irreversible reduction wave at $E_{\text{pc}} = -2.09$ V, dibenzo derivative **2** showed two reversible reduction waves at the significantly less negative potentials of $E_{1/2} = -0.67$ V and -1.62 V, respectively. The first reduction potential of **2** is much less negative even compared to that of monobenzo derivative **1** ($E_{1/2} = -1.05$ V),⁸ demonstrating the significant impact of introducing benzo-fused structures at both of the *b* and *g* bonds on increasing the electron accepting ability. In the case of dithieno derivative, **3** exhibits a reversible reduction wave at $E_{1/2} = -0.97$ V and an irreversible reduction wave at $E_{\text{pc}} = -1.85$ V. The first reduction potential of **3** is also less negative than that of **6**, but is negatively shifted by 0.30 V compared to that of **2**. This difference is likely due to the π -electron-donating ability of thiophene rings. In the oxidation process, dithieno derivative **3** as well as **6** show an irreversible oxidation wave at less positive potentials of $E_{\text{pa}} = +1.03$ V for **3** and $+0.92$ V for **6** compared to that of **2** ($E_{\text{pa}} = +1.20$ V), respectively.

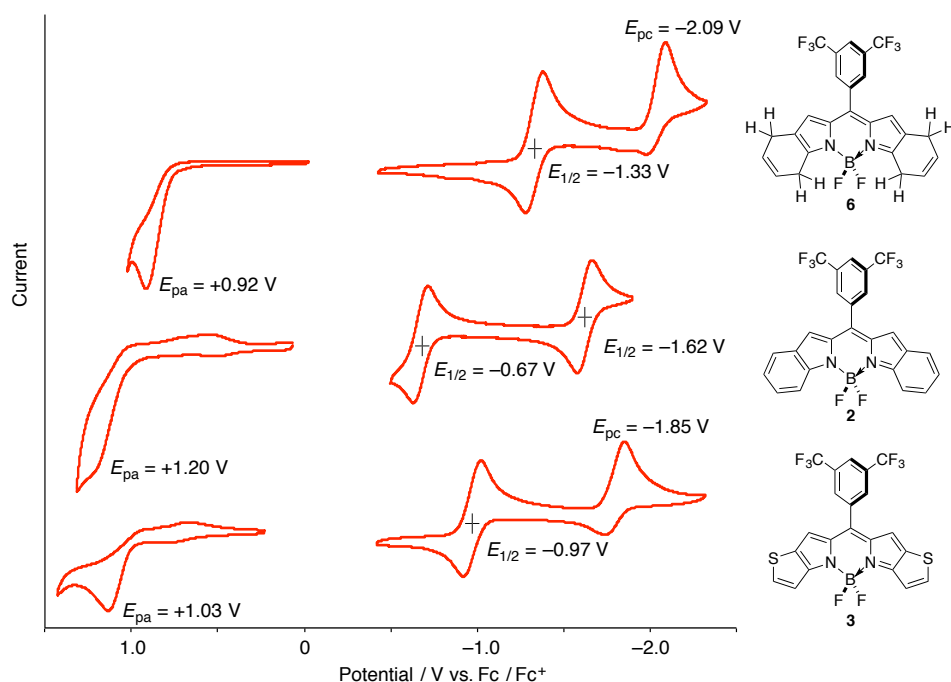


Figure 3. Cyclic voltammograms of **2**, **3** and **6** in CH_2Cl_2 (1 mM), measured with $(n\text{-Bu})_4\text{N}^+\text{PF}_6^-$ (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s^{-1} .

Photophysical Properties

In the absorption spectra in CH_2Cl_2 (Figure 4), tetrahydrodibenzo derivative **6** shows an absorption band (full width at half maximum (FWHM) = 1000 cm^{-1}) at $\lambda_{\text{abs}} = 556 \text{ nm}$ ($\log \varepsilon = 4.59$), whereas dibenzo derivative **2** shows a relatively broad band (FWHM = 2500 cm^{-1}) at $\lambda_{\text{abs}} = 581 \text{ nm}$ ($\log \varepsilon = 4.65$) with a tail up to 660 nm . The absorption band for **2** is red-shifted even compared to that of monobenzo derivative **1** ($\lambda_{\text{abs}} = 539 \text{ nm}$),⁸ indicating the significant impact of the dibenzo[*b,g*]-fused structure on the absorption profile. In the case of dithieno derivative **3**, an intense band (FWHM = 1100 cm^{-1}) was observed at $\lambda_{\text{abs}} = 582 \text{ nm}$ ($\log \varepsilon = 4.99$). In the fluorescence spectra in CH_2Cl_2 ,¹² **6** and **3** show an emission band at $\lambda_{\text{em}} = 579 \text{ nm}$ ($\Phi_{\text{F}} = 0.30$) and a weak emission band at $\lambda_{\text{em}} = 606 \text{ nm}$ with moderate quantum yield ($\Phi_{\text{F}} = 0.06$), respectively, whereas no emission band was observed for dibenzo derivative **2**.

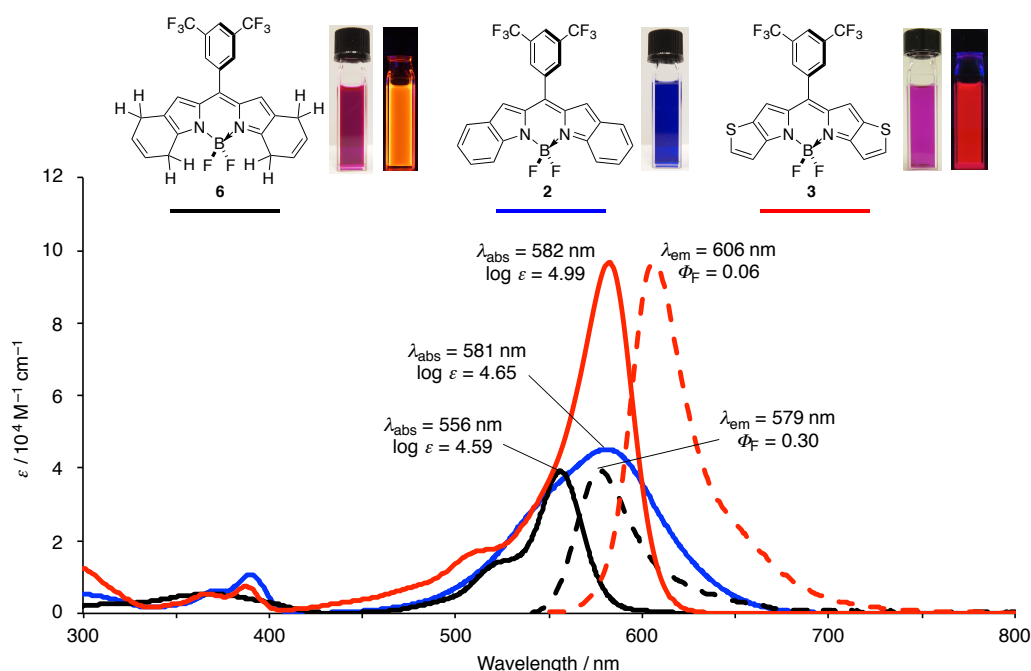


Figure 4. UV-vis absorption and fluorescent spectra of **2**, **3** and **6** in CH_2Cl_2 . The pictures of their CH_2Cl_2 solutions under ambient and UV light are included.

Theoretical Calculations

To gain deeper insights into the impacts of aromatic ring-fusing in the BODIPY skeleton, DFT calculations (B3LYP/6-31G(d)) were conducted on **2** and **3**, together with **1'**, in which one of the benzo-fused structure is removed from **2**, and **6** for comparison. The compounds **1'**, **2**, and **3** could be represented by the possible resonance structures as shown in Figure 5. In the optimized structures of unsymmetrical monobenzo derivative **1'**, the distances of the N1–C1 (1.335 Å) and C4–C5 (1.398 Å) bonds are shorter than those of the N2–C9 (1.364 Å) and C5–C6 (1.415 Å) bonds, respectively, indicating the more significant contribution of the canonical structure of the form **B** between two possible resonance structures. Dibenzo derivative **2** and dithieno derivative **3** were optimized with C_1 symmetry, but the π -conjugated skeletons are almost symmetric corresponding to the resonance structures in Figure 4. In the optimized structure of **2**, the C2–C3 and C7–C8 (1.399 Å) bonds are shortened and the C1–C2 and C8–C9 (1.442 Å) bonds are elongated compared to the C7–C8 (1.404 Å) and the C8–C9 (1.438 Å) bonds in **1'** respectively. This structural feature indicates that introducing of benzo-fused structures at both sides of the BODIPY skeleton coincidentally enhances the nonaromatic quinoidal character of the benzene rings and

the electron-accepting azafluvene character. These features are also supported by the results of NICS calculations at the HF/6-31+G(d,p) as shown in Figure 5; the NICS(0) values (ppm) for the benzene (−6.7) and pyrrole (−9.0) rings of the indole substructure in **2** are less negative compared to those of the benzene (−7.8) and pyrrole (−9.8) in **1'** as well as the benzene (−11.3) and pyrrole (−13.2) in the parent indole. A similar structural feature of enhancement of azafluvene character was also suggested in the optimized structure for dithieno derivative **3**. The N1–C1 and N2–C9 bonds (1.349 Å), and the C2–C3 and C7–C8 bonds (1.384 Å) are even shorter than those of **1'** and **2**. The NICS(0) values for the thiophene (−8.3) and pyrrole (−8.8) are also less negative than those of the thiophene (−11.9) and pyrrole (−14.2) rings in the parent thienopyrrole.

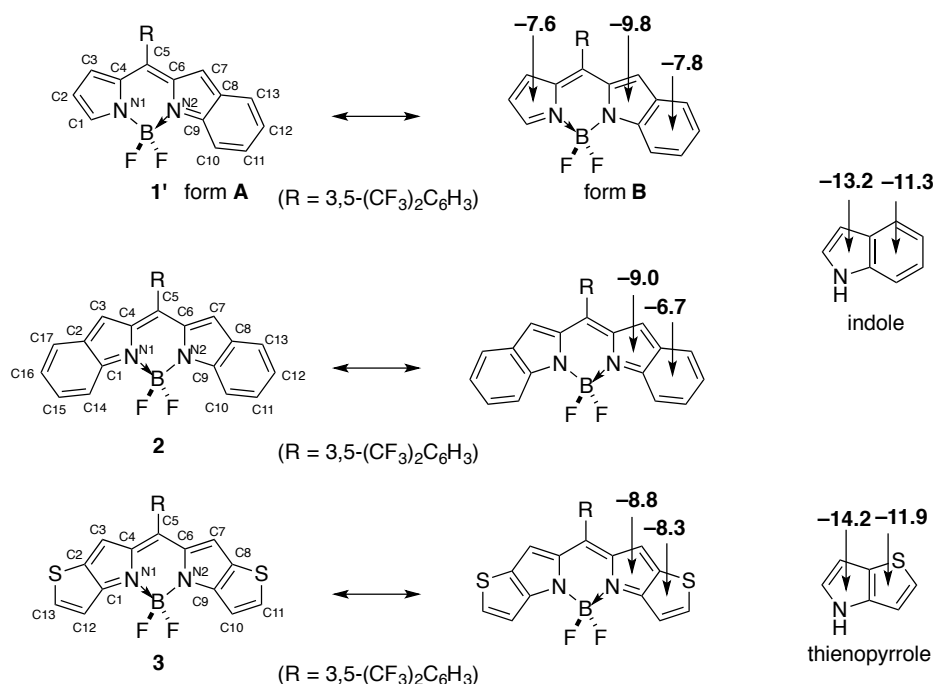


Figure 5. The NICS(0) values (ppm) calculated at the HF/6-31+G(d,p)//B3LYP/6-31G(d) level.

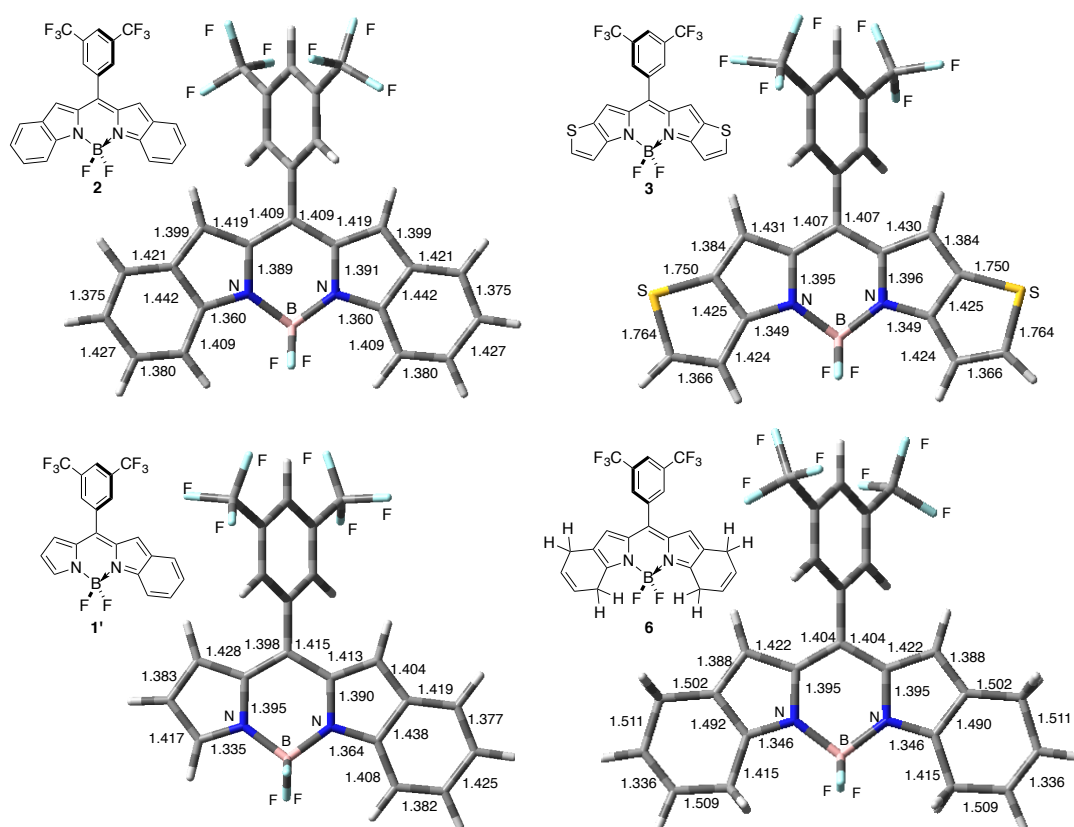


Figure 6. The bond lengths (Å) in the optimized structures of **1'**, **2**, **3**, and **6** calculated at the B3LYP/6-31G(d) level of theory.

These structural perturbations affect the frontier orbitals of **2** and **3**. Dibenzo derivative **2** and dithieno derivative **3** have the low-lying LUMO levels compared to that of **6**. The HOMO and LUMO levels in **3** are slightly elevated compared to those of **2**. These results are in quantitative agreement with the redox potentials in CV (Figure 3). It should be noted that the LUMO level of **2** (−3.58 eV) is lower than that of monobenzo derivative **1'** (−3.38 eV), indicating that the benzene-fusing at both side of the *b* and *g* bonds in the BODIPY skeleton is significantly effective to enhance the electron accepting ability. TD-DFT calculations (CAM-B3LYP/6-31G(d)) suggested that the longest absorption bands in **3** and **6** correspond to the HOMO→LUMO transition, whereas the broad absorption band in **2** is assignable to the multi-transitions mainly from the HOMO−1→LUMO (contribution: 31%) as well as the HOMO→LUMO transition (67%) (Figure 7). Surprisingly, the lowest energy transition of **2** has the larger contribution of the HOMO−1→LUMO transition (66%) than that of the HOMO→LUMO transition (33%) and has the smaller oscillator strength ($f = 0.055$)

than those for **3** ($f = 0.809$) and **6** ($f = 0.547$). As the radiative rate constant is known to be proportional to the oscillator strength,¹² this electronic structural feature as well as the rotation of aryl group at *meso*-position is probably responsible for no emission in **2**.

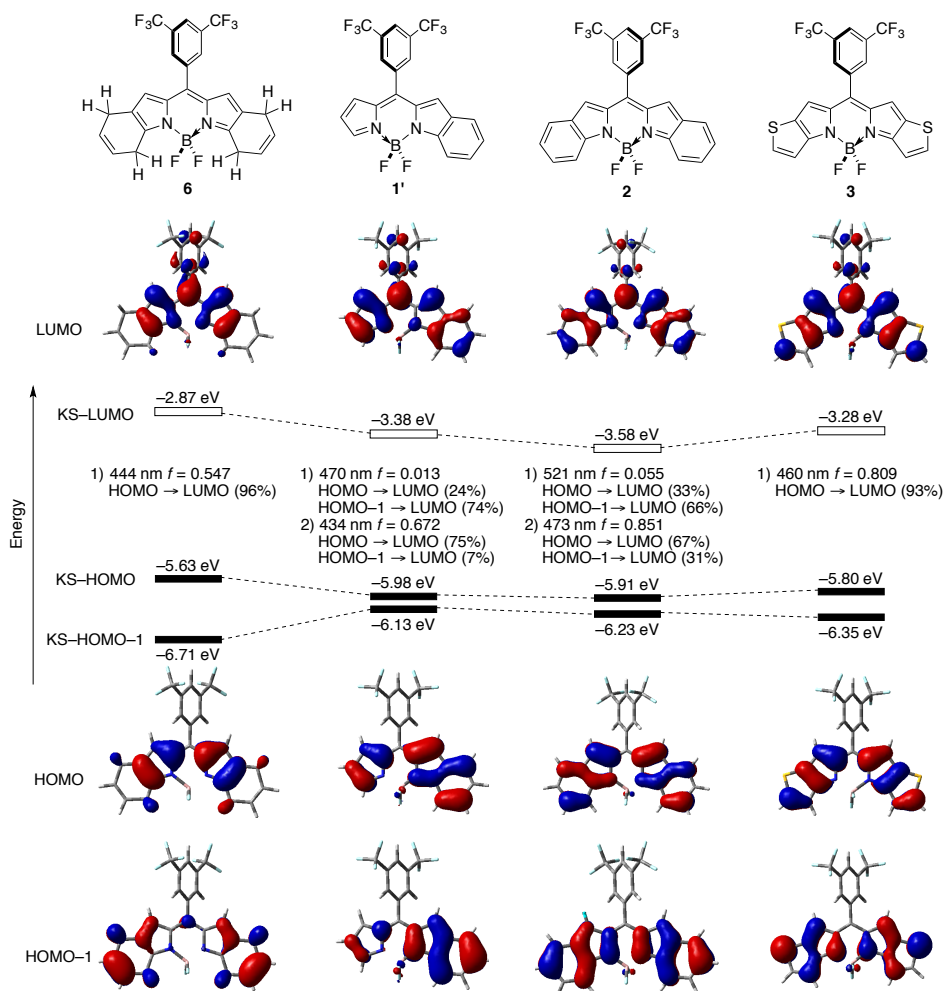


Figure 7. Pictorial presentation of the frontier orbitals, a plot of the Kohn–Sham (KS) HOMOs and LUMO levels (B3LYP/6-31G(d)) of **1'**, **2**, **3**, and **6**, and optical transitions with oscillator strength (CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d)) of **1'**, **2**, **3**, and **6**.

Conclusion

The author demonstrated that introducing aromatic ring-fused structures at the both of *b* and *g* bonds in the BODIPY skeleton perturbs the electronic structure to enhance the quinoid and azafluvene character in the indole or thienopyrrole subunits, which effectively increases the electron-accepting ability as confirmed by CV. The comparison of electrochemical and photophysical properties of **1–3** and **6** as well as DFT calculations revealed that the impacts of the dibenzo[*b,g*]-fusing are more significant compared to that of the monobenzo[*b*]-fusing.

Experimental Section

General

Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. ^1H , ^{13}C , ^{11}B , and ^{19}F NMR spectra were recorded with a Varian Mercury 300 instrument (300 MHz for ^1H and 75 MHz for ^{13}C) or a Bruker Avance III 600US instrument (192 MHz for ^{11}B and 564 MHz for ^{19}F). The chemical shifts in ^1H and ^{13}C NMR spectra were reported in ppm with reference to residual protons and carbons of CDCl_3 (δ 7.26 ppm in ^1H NMR and δ 77.0 ppm in ^{13}C NMR) as internal standards. The chemical shifts in ^{11}B and ^{19}F NMR spectra were reported in ppm with reference to $\text{BF}_3\cdot\text{OEt}_2$ in C_6D_6 (δ 0.00 ppm in ^{11}B NMR) and trifluoromethylbenzene in CDCl_3 (δ -64.0 ppm in ^{19}F NMR) as external standards, respectively. APCI mass spectra were measured with Bruker micrOTOF-QII. UV-vis absorption spectra and fluorescence spectra measurements were performed with a Shimadzu UV-3150 spectrometer and a HORIBA Fluoromax-4, respectively, in degassed spectral grade solvents. Quantum yields were determined with a Hamamatsu Quantaurs-QY(C11347-01). Cyclic voltammetry (CV) was performed on a BAS-ALS620C electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode. The measurements were carried out under an argon atmosphere using a CH_2Cl_2 solution of 1mM sample and 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{N}^+\text{PF}_6^-$) as the supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Separation by column chromatography was performed using PSQ 100B (Fuji Silysia). Separation by gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped

with JAIGEL 1H and 2H columns using CHCl₃ as an eluent at a flow rate of 3.8 mL/min. All reactions were carried out under an argon atmosphere unless stated.

Synthesis

8-((3,5-Bis(trifluoromethyl)phenyl)-dithieno[2,3-*b*]-[3,2-*g*]-4,4-difluoro-4-3*a*,4*a*-diaz-a-s-indacene (3).

4*H*-Thieno[3,2-*b*]pyrrole was prepared according to the literature.¹³ To a solution of 4*H*-thieno[3,2-*b*]pyrrole (353 mg, 2.86 mmol) and 3,5-bis(trifluoromethyl)benzaldehyde (0.225 mL, 1.38 mmol) in CH₂Cl₂ (5 mL) was added trifluoroacetic acid (10.3 μ L, 0.138 mmol). After stirring for 4 h at room temperature, to the reaction mixture was added DDQ (316 mg, 1.39 mmol) and stirred for 30 min at room temperature. Then, *i*-Pr₂EtN (1.45 mL, 8.28 mmol) and BF₃·OEt₂ (1.56 mL, 12.4 mmol) was added. After the reaction mixture was stirred for 2 h at room temperature, a saturated NaHCO₃ aqueous solution was added carefully. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (1:1 CH₂Cl₂/hexane, *R*_f = 0.25) and GPC (CHCl₃) to give 45.0 mg (87.2 μ mol) of **3** in 6% yield as dark purple solids with gold luster; mp 240.4–241.0 °C (sublimation); ¹H NMR (300 MHz, CDCl₃): δ 8.12 (s, 1H), 8.07 (s, 2H), 7.75 (d, *J*_{HH} = 5.4 Hz, 2H), 7.21 (d, *J*_{HH} = 6.0 Hz, 2H), 6.76 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 160.8, 143.2, 141.2, 140.6, 135.8, 132.2 (q, *J*_{CF} = 33.8 Hz), 130.4, 124.0 (m, *J*_{CF} = 4.1 Hz), 122.8 (q, *J*_{CF} = 271 Hz), 113.9; ¹¹B NMR (192 MHz, CDCl₃): δ 0.13 (t, *J*_{BF} = 28.8 Hz); ¹⁹F NMR (564 MHz, CDCl₃): δ –64.0 (s, CF₃), –150.2 (q, *J*_{BF} = 28.8 Hz, BF₂); HRMS (APCI-TOF) (*m/z*): [M]⁺ calcd for C₂₁H₉F₈N₂S₂, 516.0171; found, 516.0185; Elemental analysis calcd (%) for C₂₁H₉F₈N₂S₂: C 48.86, H 1.76, N 5.43; found: C 48.66, H 1.70, N 5.36.

4,7-Dihydro-1*H*-indole (4).

4,7-Dihydroindole **4** was prepared according to the literature.¹⁴ The apparatus is shown in Figure 8. To a solution of indole (5.85 g, 49.9 mmol) in MeOH (50 mL), liquid NH₃ (ca. 250 mL) was added dropwise at –78 °C. Na pieces (3.02 g 131 mmol) were added as large as possible. Stirring the mixture vigorously at –78 °C, the solution color turned to deep blue. After being stirred at –78 °C until the solution color returned

to pale yellow, the mixture was allowed to warm to room temperature gradually to remove liquid NH_3 as gaseous phase. After a gaseous NH_3 was removed, the mixture was poured into water and neutralized with an aqueous HCl solution. The aqueous layer was extracted with EtOAc . The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by GPC (CHCl_3) to give 3.89 g (32.7 mmol) of **4** in 66% yield as white solids.

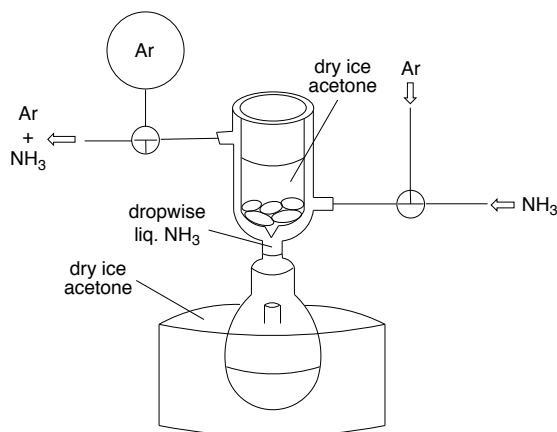


Figure 8. The apparatus for the Birch reduction.

(3,5-Bis(trifluoromethyl)phenyl)(4,7-dihydro-1*H*-indol-2-yl)methanone (5**).**

To a solution of **4** (472 mg, 3.96 mmol) in THF (40 mL), MeMgI (1.61 M in ether, 2.70 mL, 4.35 mmol) was added dropwise at room temperature. After the mixture was refluxed for 1 h and cooled to room temperature, 3,5-bis(trifluoromethyl)benzoylchloride (790 μL , 4.36 mmol) was added. After the mixture was stirred at room temperature for 12 h, a saturated aqueous NH_4Cl solution was added. The water layer was extracted with EtOAc . The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2 , $R_f = 0.45$) to give 1.12 g (3.12 mmol) of **5** in 79% yield as yellow solids: mp 169.7–171.0 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 9.38 (s, 1H), 8.31 (s, 2H), 8.04 (s, 1H), 6.62 (d, $J_{\text{HH}} = 2.4$ Hz, 1H), 5.95 (d, $J_{\text{HH}} = 9.9$ Hz, 1H), 5.87 (d, $J_{\text{HH}} = 10.2$ Hz, 1H), 3.39 (m, 2H), 3.26 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 180.5, 140.5, 135.7, 131.8 (q, $J_{\text{CF}} = 34$ Hz), 128.9 (d, $J_{\text{CF}} = 4.6$ Hz), 125.4, 124.8 (m, $J_{\text{CF}} = 4.6$ Hz), 123.0 (q, $J_{\text{CF}} = 271$ Hz), 119.0, 118.8; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_6\text{NO}$, 360.0818; found, 360.0813; Elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{11}\text{F}_6\text{NO}$: C 56.83, H

3.09, N 3.90; found: C 56.82, H 3.01, N 4.12.

8-((3,5-Bis(trifluoromethyl)phenyl)-bis(3,6-dihydrobenzo)[*b,g*]-4,4-difluoro-4-3a,4a-diaza-s-indacene (6).

To a solution of **4** (60.3 mg, 0.506 mmol) and **5** (180.2 mg, 0.502 mmol) in CH₂Cl₂ (5 mL), BF₃·OEt₂ (315 µL, 2.51 mmol) was added at room temperature. After the mixture was stirred for 5 min, *i*-Pr₂EtN (260 µL, 1.49 mmol) was added. After the mixture was stirred further for 1 h, water was added. The water layer was extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1:4 CH₂Cl₂/hexane, *R*_f = 0.08) to give 107 mg (0.210 mmol) of **6** in 42% yield as purple-red solids: mp 205.7 °C (dec); ¹H NMR (300 MHz, CDCl₃): δ 8.04 (s, 1H), 7.96 (s, 2H), 6.37 (s, 2H), 5.88 (dd, 4H), 3.74 (s, 4H), 3.22 (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 156.3, 137.4, 136.5, 133.8, 131.9 (q, *J*_{CF} = 34 Hz), 130.1, 127.4, 125.6, 123.8, 123.5 (m, *J*_{CF} = 4.0 Hz), 122.9 (q, *J*_{CF} = 272 Hz), 122.1, 25.2, 24.1; ¹¹B NMR (192 MHz, CDCl₃): δ 0.15 (t, *J*_{BF} = 30.7 Hz); ¹⁹F NMR (564 MHz, CDCl₃): δ -64.1 (s, CF₃), -151.2 (q, *J*_{BF} = 31.6 Hz, BF₂); HRMS (APCI-TOF) (*m/z*): [M+H]⁺ calcd. for C₂₅H₁₈BF₈N₂, 509.1434; found, 509.1425.

8-((3,5-Bis(trifluoromethyl)phenyl)-dibenzo[*b,g*]-4,4-difluoro-4-3a,4a-diaza-s-indacene (2).

A solution of **6** (204 mg, 0.402 mmol) and DDQ (200 mg, 0.881 mmol) in CH₂Cl₂ (20 mL) was stirred at room temperature for 2 h. An additional DDQ (72.8 mg, 0.321 mmol) was added. After the resulting solution was further stirred for 3 h, a saturated aqueous Na₂SO₃ solution was added. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1:1 CH₂Cl₂/hexane, *R*_f = 0.23) to give 117 mg (0.232 mmol) of **2** in 58% yield as dark-blue solids with gold luster: mp 243.1–244.0 °C (sublimation); ¹H NMR (300 MHz, CDCl₃): δ 8.18 (s, 1H), 8.11 (s, 2H), 7.83 (d, *J*_{HH} = 8.7 Hz, 2H), 7.50 (d, *J*_{HH} = 9.0 Hz, 2H), 7.45 (d, *J*_{HH} = 7.8 Hz, 2H), 7.12 (s, 2H), 7.04 (t, *J*_{HH} = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 152.2, 146.1, 139.4, 135.9, 132.7, 132.2 (q, *J*_{CF} = 34 Hz), 130.9, 127.3, 124.8, 124.4 (m, *J*_{CF} = 3.4 Hz), 123.9, 122.8 (q, *J*_{CF} = 272 Hz), 116.8;

^{11}B NMR (192 MHz, CDCl_3): δ 0.78 (t, $J_{\text{BF}} = 30.7$ Hz); ^{19}F NMR (564 MHz, CDCl_3): δ -64.0 (s, CF_3), -158.2 (q, $J_{\text{BF}} = 30.5$ Hz, BF_2); HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{25}\text{H}_{13}\text{BF}_8\text{N}_2$, 504.1043; found, 505.1036; Elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{13}\text{BF}_8\text{N}_2$: C 59.56, H 2.60, N 5.56; found: C 59.66, H 2.61, N 5.64.

Computation Method

All calculations were conducted using the Gaussian 09 program.¹⁵ The geometries for compounds **1'**, **2**, **3**, and **6** were optimized at the B3LYP/6-31G(d) level of theory and the fact that these geometries are at the energy minimum was confirmed by frequency calculations at the same level of theory.

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Chapter 2

NIR Dye Using BF₂-Bridged Azafulvene Dimer as an Electron-Accepting Unit

Abstract: BF₂-bridged azafulvene dimers were designed and synthesized as an electron-accepting unit. Single-crystal X-ray diffraction analyses revealed that the high electron-accepting ability in this skeleton stems from the contribution of the π -conjugation mode of the azafulvene dimer upon the formation of B–N coordination bonds. Due to the high electron-accepting properties, a corresponding D–A–D dye exhibits an intense NIR absorption band at 922 nm, which tails up to 1150 nm, while significant absorption bands in the visible region are absent. This NIR dye exhibits moreover exceptional photostability and resistance towards oxidation by atmospheric oxygen, even in a dilute solution.

Introduction

Dyes that absorb near infrared (NIR) light have been investigated intensively in the context of a variety of applications, including photovoltaics, photodetectors, heat absorbers, and medical applications.¹ Such NIR dyes¹ can be classified into donor–acceptor(D–A) small molecules² and polymers,³ rylenes,⁴ cyanines,⁵ as well as the corresponding heteroatom-bridged analogues.^{6–8} For various applications, the photostability and resistance towards oxidation of these NIR dyes are very important.¹ NIR dyes usually have narrow HOMO–LUMO gaps on account of the high-lying HOMO levels and thus easily oxidized by atmospheric oxygen (Figure 1). In order to develop air- and photo-stable NIR dyes, a key component should be low-lying LUMO levels. Such low-lying LUMO levels could be attained by strong electron-accepting properties of building blocks, which can generate narrow HOMO–LUMO gaps, while maintaining moderate HOMO levels.⁹

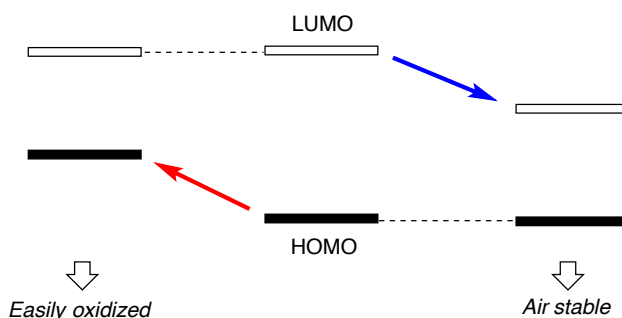


Figure 1. Strategy to diminish HOMO–LUMO gap.

As mentioned in General Introduction, the formation of intramolecular coordination bonds is an effective strategy to induce such strong electron-accepting properties. Recently, various boron-bridged skeletons have been developed as new building blocks for NIR dyes.^{6,10–13} For example, Ziegler reported BOPHYs, doubly BF_2 -bridged bis((2-pyrrolyl)methylene)hydrazine derivatives, as a new structural motif for highly fluorescent compounds.¹⁰ Liu reported a doubly B–N-bridged bipyridyl as an electron-deficient building block for n-type polymer, which exhibited good performance in all polymer solar cells.¹¹ Werz reported BOIMPYs, i.e., bis(borondifluoride)-8-imidazodipyrromethenes, which are easily accessible to red-emissive fluorophores and NIR dyes (Figure 2).¹²

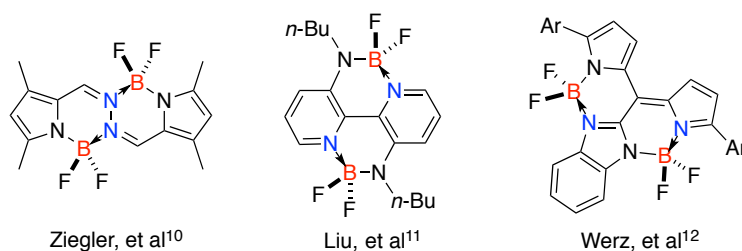


Figure 2. Examples of recently reported boron-bridged skeletons.

As mentioned in General Introduction, the author noticed that the origin of their strong electron-accepting ability of BODIPY skeleton stems from the electron-deficient azafulvene moiety, which is further enhanced by the formation of intramolecular B–N bonds involving BF_2 -bridges. Based on this notion, the author designed a twofold BF_2 -bridged azafulvene dimer as a strongly electron-accepting building block (Figure 3). As model compounds, the author designed and synthesized **1** and **2** having N–B–O bridging mode, as well as D–A–D dye **3** which contains triaryl amines as electron-donating units. In this chapter, the structural, electrochemical, and photophysical properties of **1–3** were examined in detail and discussed.

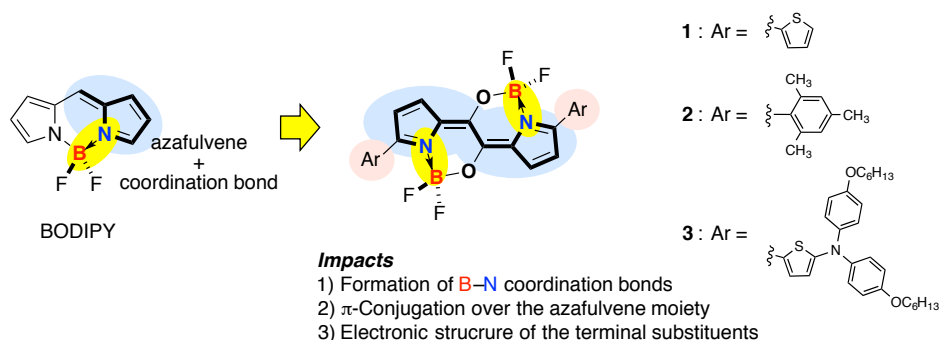


Figure 3. Molecular design concept for strongly electron-accepting BF_2 -bridged azafulvene dimer and structures of model compounds **1–3**.

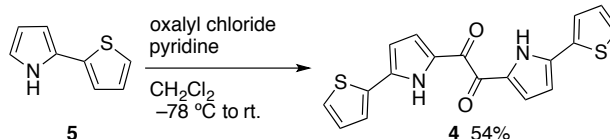
Results and Discussion

Synthesis

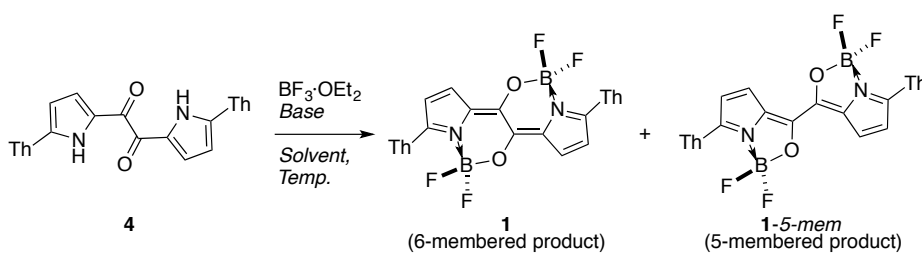
As shown in Schemes 1 and 2, dithienyl derivative **1** was synthesized by the reaction of dipyrrolylethanedione derivative **4**, which was prepared from oxalyl chloride and thienylpyrrole **5**, with $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of base. A typical protocol for the synthesis of BODIPY,^{8b} using *i*-Pr₂EtN in THF at room temperature, afforded **1** in 29% yield together with a large amount of a complex mixture of unidentified products. To improve the yield, screening of different bases was conducted. The use of organic bases,

such as DBU, Et₃N, or pyridine, furnished merely complex mixtures, whereas in the presence of inorganic bases, such as K₂CO₃ or K₃PO₄, no reaction was observed. Subsequently, the author focused on the bulky base 2,6-di-*tert*-butylpyridine, which led to a significant increment of the yield of **1**. Treatment of **4** with BF₃·OEt₂ in the presence of 2,6-di-*tert*-butylpyridine in THF at room temperature furnished **1** in 52%, together with 5-membered product **1-5-mem** in 26%; these structures were confirmed by single-crystal X-ray diffraction analysis (*vide infra*, Figures 5–6). Interestingly, when the reaction was performed in CH₂Cl₂ at room temperature, **1-5-mem** was obtained selectively in 71% yield. In wet CH₂Cl₂ or even in dry THF, **1-5-mem** was found to gradually deborylate. Conversely, 6-membered **1** was stable under such conditions. DFT calculations (B3LYP/6-31G(d)) suggested that **1-5-mem** is enthalpically less stable by +8.2 kcal/mol than **1**. These results indicate that **1** and **1-5-mem** represent the thermodynamically and kinetically controlled product, respectively (Figure 4). This was confirmed by the borylation of **4** in refluxing THF, which afforded **1** as the sole product in 74% yield.

Scheme 1. Synthesis of **4**



Scheme 2. Borylation of **4**



Base	Solvent	Temp.	1	1-5-mem
<i>i</i> -Pr ₂ EtN ^a	THF	r.t.	29%	–
2,6-di- <i>tert</i> -butylpyridine ^b	THF	r.t.	52% ^c	26% ^c
2,6-di- <i>tert</i> -butylpyridine ^b	CH ₂ Cl ₂	r.t.	–	71%
2,6-di- <i>tert</i> -butylpyridine ^b	THF	reflux	74%	–

Reaction condition and notes; ^aBase (4 eq), BF₃·OEt₂ (6 eq). ^bBase (46 eq), BF₃·OEt₂ (60 eq). ^cA mixture of **1** and **1-5-mem** was obtained: the ratio of the products were determined by ¹H NMR.

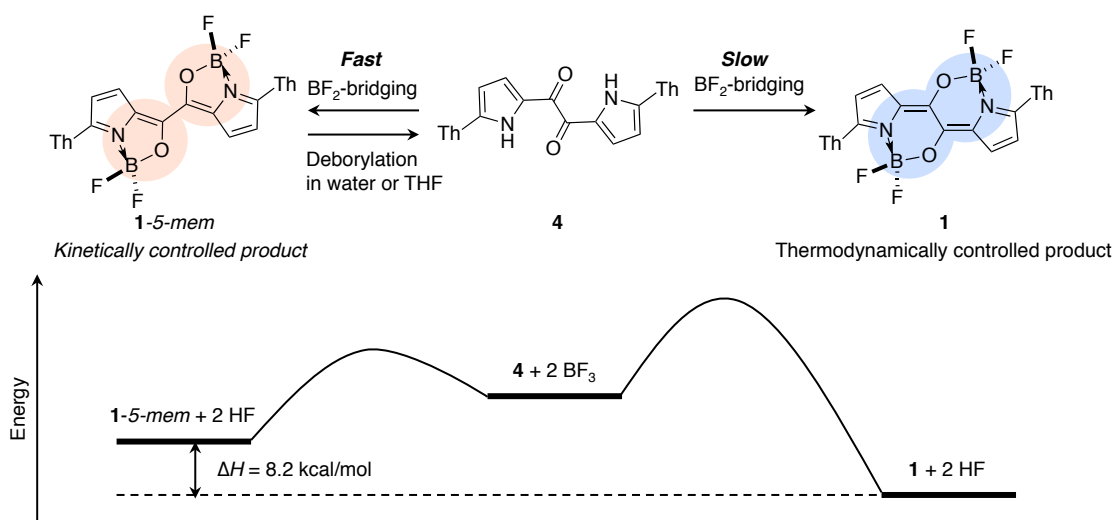
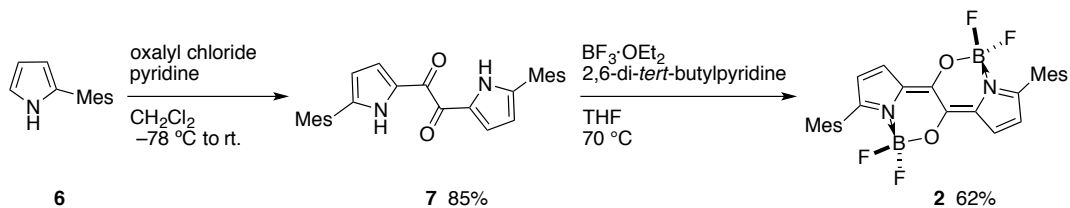


Figure 4. Isodesmic reaction for BF_2 -bridging formation: Comparison of 5-membered and 6-membered products.

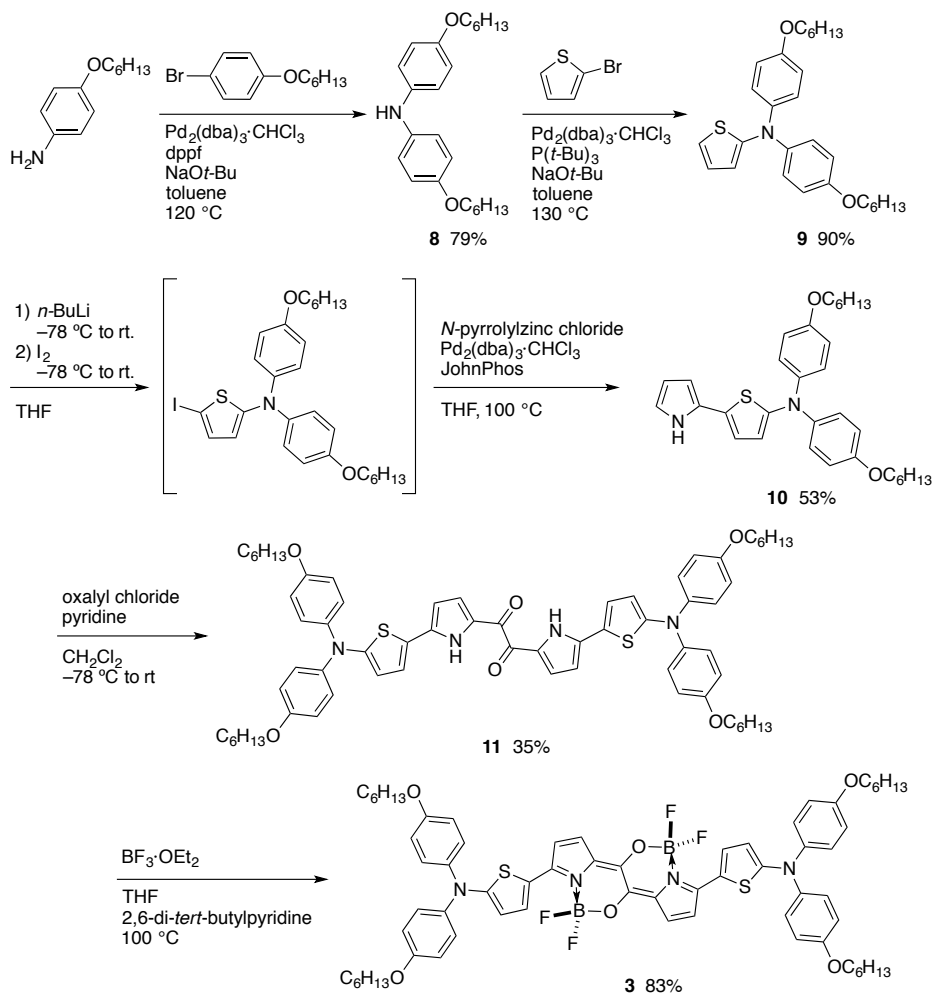
In a similar manner, dimesityl derivative **2** and D–A–D dye **3** with 6-membered rings were synthesized from the corresponding dipyrrolylethanedione derivatives **7** and **11**, respectively. The reaction of **7**, which was prepared from oxalyl chloride and mesitylpyrrole **6**, with $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of 2,6-di-*tert*-butylpyridine gave **2** in 62% yield (Scheme 3).

The outline for the synthesis of **3** is shown in Scheme 4. Pd^0 -catalyzed coupling reaction of *p*-hexyloxyaniline with *p*-hexyloxybromobenzene gave bis(4-hexyloxyphenyl)amine (**8**) in 79% yield. Subsequently, Pd^0 -catalyzed coupling reaction of **8** with 2-bromothiophene gave triarylamine **9** in 90% yield. After the lithiation of **9** with *n*-BuLi, followed by subsequent treatment with iodine, Pd^0 -catalyzed coupling reaction of iodo derivative of **9** with *N*-pyrrolylzinc chloride gave **10** in 53% yield. The reaction of oxalyl chloride and **10** gave **11** in 35% yield, and then the reaction of **11** with $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of 2,6-di-*tert*-butylpyridine gave **3** in 83% yield.

Scheme 3. Synthesis of **2**



Scheme 4. Synthesis of **3**



X-ray Crystal Structures

In order to gain a better understanding of the structural features of BF₂-bridged dipyrrolylethanedione, X-ray diffraction (XRD) analysis were conducted. A single-crystal XRD analysis revealed a highly planar structure for **1**, evident from a torsion angle of 0.0° between the pyrrole rings, and the fact that the terminal thienyl rings adopt torsion angles of 2.5° relative to the pyrrole rings (Figure 5a). For the BF₂-bridged dipyrrolylethanediones, two resonance structures are possible: **A** (B–O coordination) and **B** (B–N coordination) (Figure 5b). The central skeleton in **1** exhibited significant bond alternations (Table 1): C1–C2 [1.377(3) Å], C3–C4 [1.356(3) Å], and C5–N1 [1.351(3) Å] bonds are much shorter than C1–C1* [1.459(4) Å], C2–C3 [1.431(3) Å], C4–C5 [1.439(3) Å], and C2–N1 [1.396(3) Å] bonds. This alternation clearly indicates a significant contribution of the π -conjugation mode in the azafulvene dimer from the resonance structure **B** with B–N coordination bonds, rather than from the resonance structure **A** with B–O coordination bonds. High planarity and contributions from the π -conjugation mode of the azafulvene dimer with B–N coordination bonds were also observed in the crystal structures of **1-5-mem** and **2** (Figure 6). The N1–B1–O1 bond angle around the coordinated tetrahedral boron center in **1-5-mem** [100.0(2)°] is much smaller than a typical tetrahedral bond angle (109.5°) or that in **1** [109.79(16)°]. The lower degrees of distortion in the BF₂-bridged 6-membered ring of **1** should thus endow **1** with higher stability than **1-5-mem**.

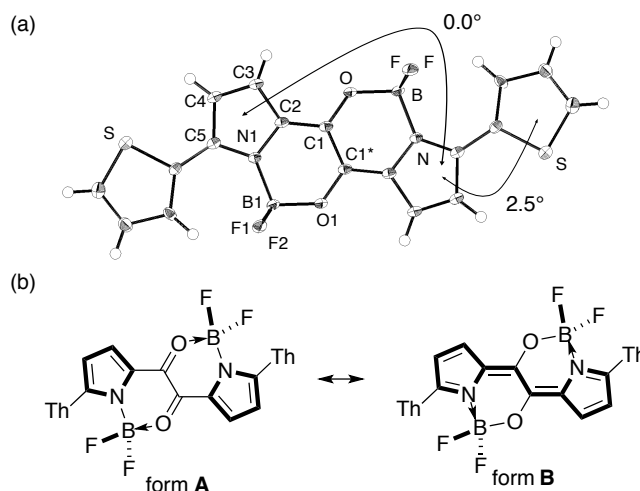


Figure 5. (a) *ORTEP* representation of the molecular structure of **1** (thermal ellipsoids set at 50% probability; only selected atoms are labeled), and (b) possible resonance structures **A** and **B**.

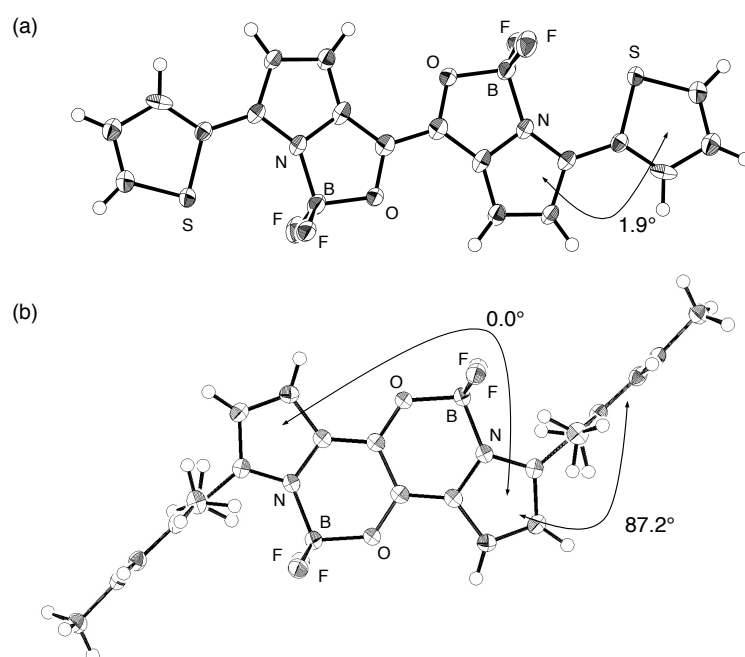


Figure 6. (a) *ORTEP* representation of the molecular structure of (a) **1-5-mem** and (b) **2** (thermal ellipsoids set at 50% probability; only selected atoms are labeled and dihedral angles are shown).

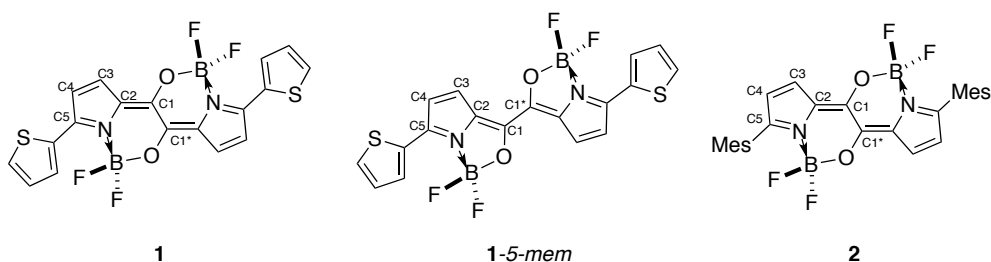


Table 1. Bond Lengths Obtained from Crystal Structures and Optimized Structures for **1**, **1-5-mem**, and **2**

	1	1	1-5-mem	1-5-mem	2	2
	(X-ray)	(calc. ^a)	(X-ray)	(calc. ^a)	(X-ray)	(calc. ^a)
C1–C1 [*]	1.459(4) Å	1.468 Å	1.420(5) Å	1.449 Å	1.475(3) Å	1.487 Å
C1–C2	1.377(3) Å	1.389 Å	1.385(3) Å	1.392 Å	1.373(2) Å	1.387 Å
C2–C3	1.431(3) Å	1.424 Å	1.423(3) Å	1.420 Å	1.422(2) Å	1.424 Å
C3–C4	1.356(3) Å	1.370 Å	1.363(3) Å	1.379 Å	1.363(2) Å	1.376 Å
C4–C5	1.439(3) Å	1.438 Å	1.433(4) Å	1.441 Å	1.432(2) Å	1.433 Å
C2–N	1.396(3) Å	1.395 Å	1.377(3) Å	1.385 Å	1.3984(18) Å	1.397 Å
C5–N	1.351(3) Å	1.354 Å	1.346(3) Å	1.346 Å	1.3395(18) Å	1.342 Å
C1–O	1.310(3) Å	1.298 Å	1.333(3) Å	1.310 Å	1.3030(17) Å	1.292 Å
N–B	1.567(3) Å	1.577 Å	1.576(3) Å	1.588 Å	1.563(2) Å	1.571 Å
O–B	1.483(3) Å	1.510 Å	1.512(3) Å	1.554 Å	1.5004(19) Å	1.524 Å
O–B–N	109.79(16)°	107.879°	100.0(2)°	97.948°	107.93(11)°	106.965°
B–N–C2	121.30(17)°	122.555°	108.68(18)°	109.211°	123.80(11)°	124.021°
B–N–C5	131.11(17)°	129.891°	144.0(2)°	142.295°	128.31(12)°	127.945°

^a Calculated at the B3LYP/6-31G(d) level of theory.

Evaluation of the Electronic Impacts of BF₂-Bridging Structure

In order to gain a better understanding of the effects of the BF₂-bridges on the electronic structure in the central skeleton, DFT calculations (B3LYP/6-31G(d)) were conducted on model compounds **1'** and dipyrrolylethanedione **4'**, in which the thienyl moieties were replaced with hydrogen atoms. Dipyrrolylethanedione **4'** consists of tautomers (Figure 7): one is well described as pyrrole and oxalyl groups in a keto form (**4'-keto**), while the other exhibits an azafulvene dimer skeleton with an enol form (**4'-enol**). While **4'-enol** is the energetically unfavorable tautomer, its electron-deficient azafulvene character lowers the LUMO level by 0.66 eV relative to that of **4'-keto**. In **1'**,

the formation of two B–N coordination bonds involving the BF₂-bridges induces a further decrease of the LUMO level by 0.93 eV, suggesting a high electron-accepting ability of the BF₂-bridged azafulvene dimer skeleton.

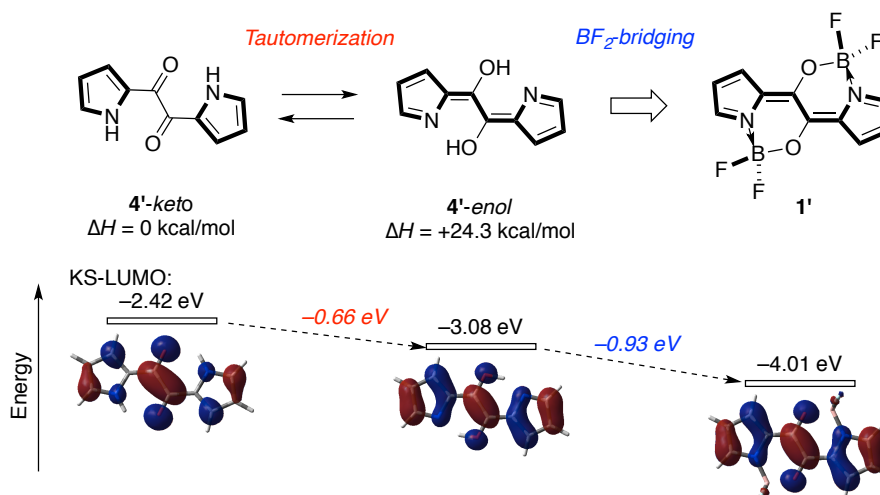


Figure 7. The energy diagram of isodesmic reaction (B3LYP/6-31G(d)) for BF₂-bridging reaction of **4'** to give 6-membered cyclized product **1'** (B3LYP/6-31G(d)).

Electrochemical Properties

The cyclic voltammogram of dithienyl derivative **1** in CH₂Cl₂ revealed two reversible reduction waves at $E_{1/2} = -0.48$ and -0.89 V (vs. Fc/Fc⁺), which appear at much less negative potential than that of **4** ($E_{pc} = -1.60$ V) (Figure 8). The first reduction potential of **1** appears at a considerably more positive potential than those of typical n-type materials such as fullerene C₆₀ ($E_{1/2} = -0.98$ V)^{14a} or perylene diimide ($E_{1/2} = -0.97$ V),^{14b} which demonstrates the high electron-accepting ability of **1**. Dimesityl derivative **2** shows two reversible reduction waves at $E_{1/2} = -0.50$ and -1.05 V. The difference between the first and second reduction potentials of **1** ($\Delta E_{1/2} = 0.41$ V) is smaller than that of **2** ($\Delta E_{1/2} = 0.55$ V), suggesting that the terminal thienyl groups effectively expand the π -conjugation to decrease the electron repulsion in the anionic species. Whereas **1** and **2** show no oxidation waves in the potential window of CH₂Cl₂, D–A–D dye **3** with diarylaminothienyl groups exhibits two reversible reduction waves ($E_{1/2} = -0.78$ and -0.98 V) and two reversible oxidation waves ($E_{1/2} = +0.21$ and $+0.54$ V). The HOMO and LUMO levels estimated from these potentials¹⁵ are summarized in Table 2. Owing to the significantly high electron-accepting ability of the BF₂-bridged

azafulvene dimer, **3** exhibits significantly narrow HOMO–LUMO gap (0.86 eV), while maintaining moderate HOMO level (−5.26 eV).

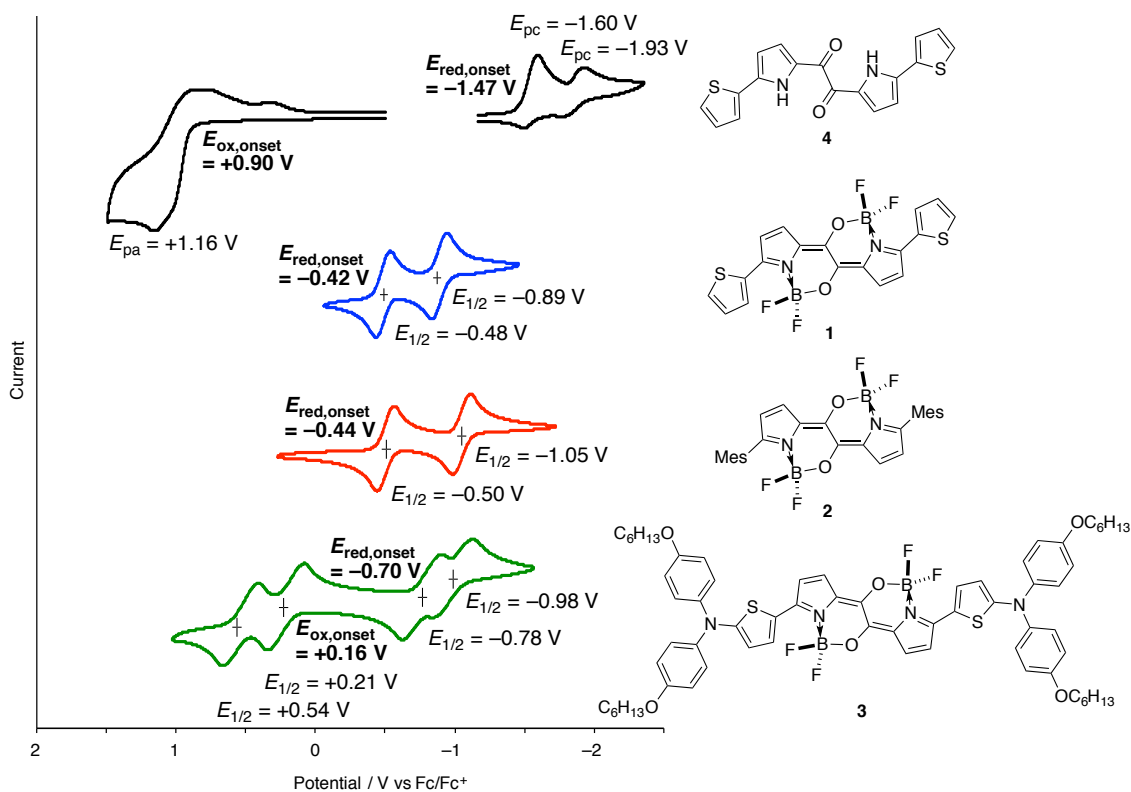


Figure 8. Cyclic voltammograms of **1–4** in CH₂Cl₂ (1 mM), measured with (n-Bu)₄N⁺PF₆[−] as a supporting electrolyte at a scan rate of 100 mV s^{−1}.

Table 2. Electrochemical Properties of **1–4**^a

Dye	E_{ox} [V] ^b	E_{red} [V] ^b	HOMO ^d	LUMO ^d
1	–	−0.48, −0.89	–	−4.68 eV
2	–	−0.50, −1.05	–	−4.66 eV
3	+0.21, +0.54	−0.78, −0.98	−5.26 eV	−4.40 eV
4	+1.16 ^c	−1.60 ^c	−6.00 eV	−3.63 eV

^aMeasured in CH₂Cl₂ (1 mM); supporting electrolyte: (n-Bu)₄N⁺PF₆[−] (0.1 M); scan rate: 100 mV s^{−1}. ^bHalf-wave potentials (vs. Fc/Fc⁺). ^cIrreversible wave; E_{pc} or E_{pa} are shown. ^dEstimated by: $-(E_{\text{onset}} + 5.1 \text{ eV})$.¹⁵

Photophysical Properties in Solution

In the UV/vis/NIR absorption spectra of **1–3** in CH_2Cl_2 , the longest absorption bands depend on the terminal substituents (Figure 9). The absorption band of **1** appears at $\lambda_{\text{abs}} = 625 \text{ nm}$ ($\log \varepsilon = 4.76$), which is red-shifted by 168 nm compared to that of **2** ($\lambda_{\text{abs}} = 457 \text{ nm}$; $\log \varepsilon = 4.57$) owing to the extension of π -conjugation by the terminal thienyl groups. Interestingly, D–A–D dye **3** exhibits an intense absorption band in the NIR region with a maximum at $\lambda_{\text{abs}} = 922 \text{ nm}$ ($\log \varepsilon = 5.06$), which tails up to $\lambda_{\text{edge}} = 1150 \text{ nm}$, while no significant absorption bands in the visible region were observed. Such substantial bathochromic shift to NIR region should reflect a narrow HOMO–LUMO gap in a relatively small molecular system, which results in the only absorption band in the visible and NIR range. In the fluorescence spectra, **1** and **2** show an emission in the visible region, while D–A–D dye **3** exhibits an emission in the NIR region ($\lambda_{\text{em}} = 1108 \text{ nm}$).

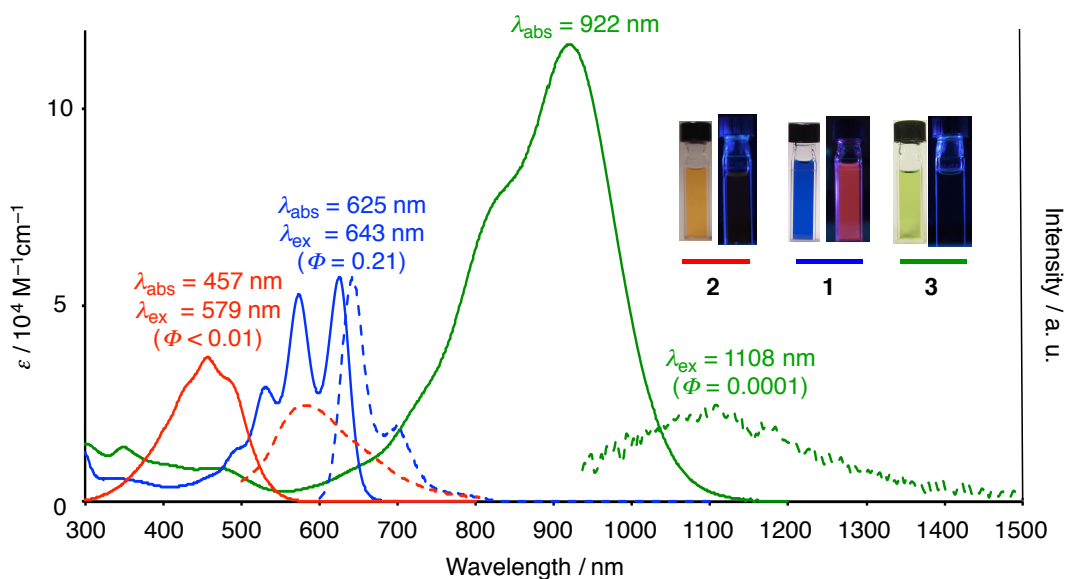


Figure 9. UV/vis absorption (solid line) and fluorescence spectra (dashed line) of **1–3** in CH_2Cl_2 . The pictures of their CH_2Cl_2 solutions are included (left: ambient light; right: UV light).

Photophysical Properties in Solid State

In order to examine the photophysical properties in the solid state, spin-coated thin films of **3** were prepared and their absorption spectra were recorded (Figure 10). Whereas the polymethylmethacrylate (PMMA) film doped with 1 wt% of **3** showed a similar spectrum ($\lambda_{\text{abs}} = 914$ nm) to that in solution, the neat film exhibited even more red-shifted absorptions ($\lambda_{\text{abs}} = 1066$ and 1174 nm), as well as a band at 930 nm, which is indicative of intermolecular interactions.

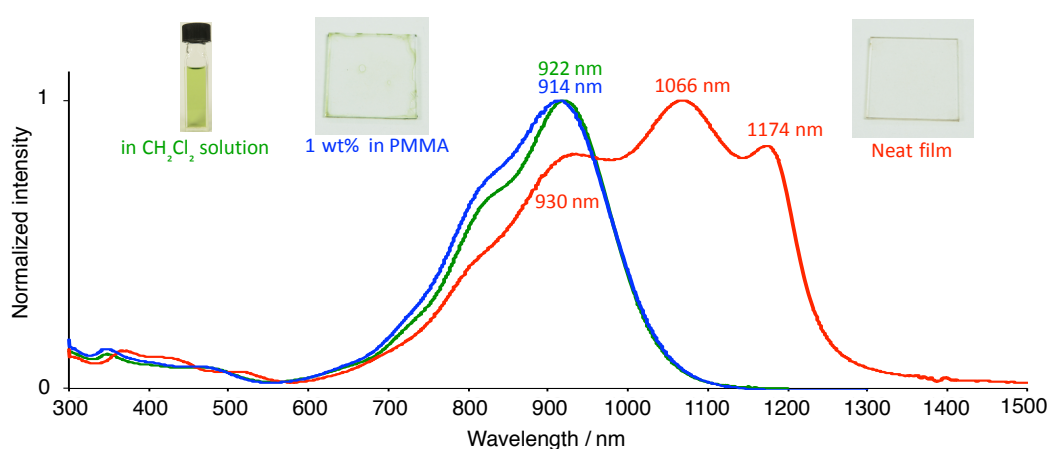


Figure 10. UV/vis/NIR absorption spectra of **3** in CH₂Cl₂ solution, and 1wt% doped film in PMMA, and neat film.

Theoretical Calculations

DFT calculations (B3LYP/6-31G(d)) on model compound **3'** confirmed that the HOMO and LUMO are delocalized over the entire π -conjugated skeleton (Figure 11). The results of TD-DFT calculations (CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d)) suggested that the longest absorption in **3** should be attributed to the HOMO→LUMO transition, which exhibits a large oscillator strength ($f = 2.313$).

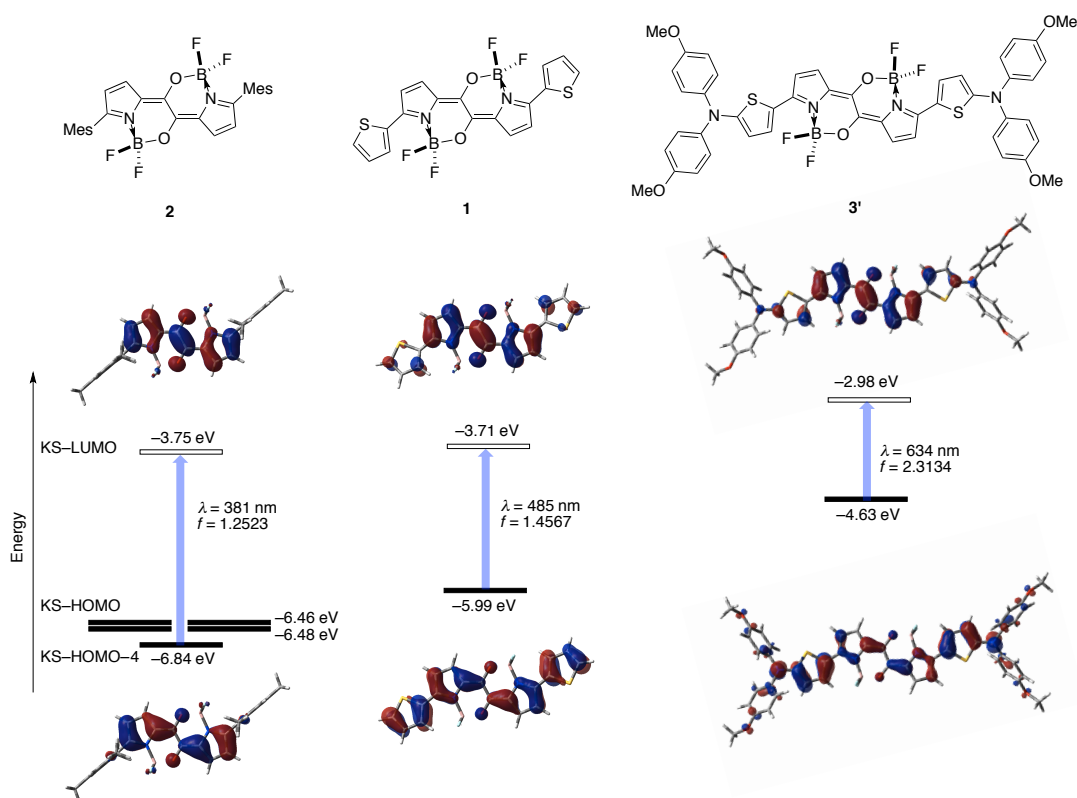


Figure 11. Comparison of the frontier orbital energy levels, the molecular orbitals, and the excitation energies among **1**, **2**, and **3'** based on the TD-DFT calculations at the CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

Photostability

The photostability of **3** was investigated under irradiation with NIR light (690–1100 nm, 1.3×10^4 lux) in degassed or non-degassed toluene (4×10^{-6} M), and compared to that of a commercially available naphthalocyanine (**Napht**) NIR dye^{5a}. After irradiation for 1 h, the absorbance of **Napht** ($\lambda_{\text{abs}} = 865$ nm) diminished to 27% in degassed toluene and to 6% in non-degassed toluene. In sharp contrast, the absorbance of **3** remained unchanged, even after irradiation for 50 h even in non-degassed toluene, clearly

demonstrating the high photostability of **3** and its resistance towards oxidation by atmospheric oxygen (Figure 12).

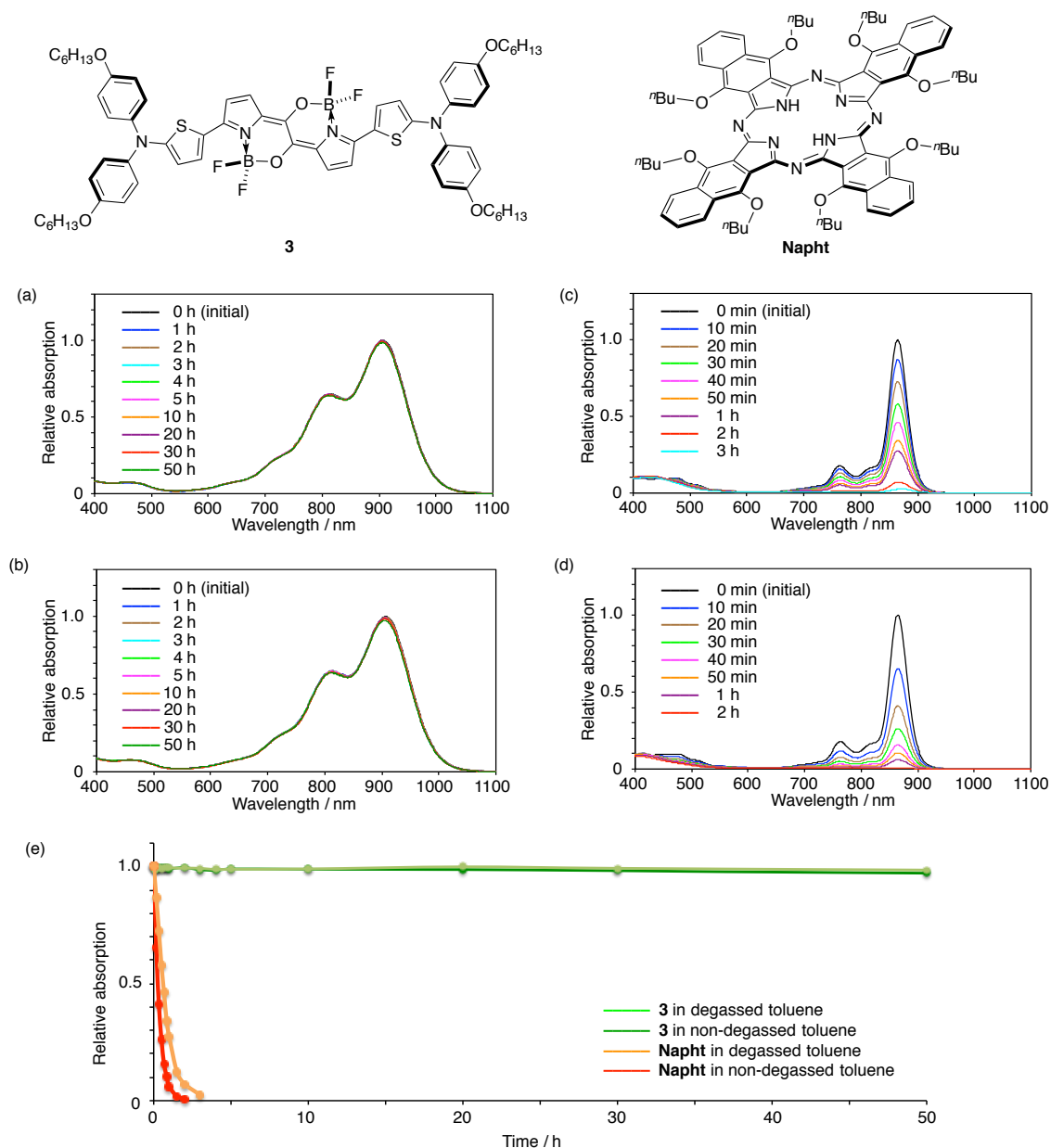


Figure 12. The time-dependence of UV/vis/NIR absorption spectra of **3** and naphthalocyanine (**Napht**) in toluene (4 μ M) under the NIR light irradiation at a range of 690–1100 nm with Xe lamp through optical filters: (a) **3** in degassed toluene, (b) **3** in non-degassed toluene, (c) **Napht** in degassed toluene, and (d) **Napht** in non-degassed toluene. (e) The temporal change of relative absorbance of the longest absorption band of **3** and **Napht**.

Thermal Stability

The thermal stability was investigated by thermogravimetric analysis (TGA). The decomposition temperatures (T_{d5}) of **1** ($T_{d5} = 264$ °C), **2** (282 °C), and **3** (282 °C) are higher than that of **1-5-mem** (212 °C).

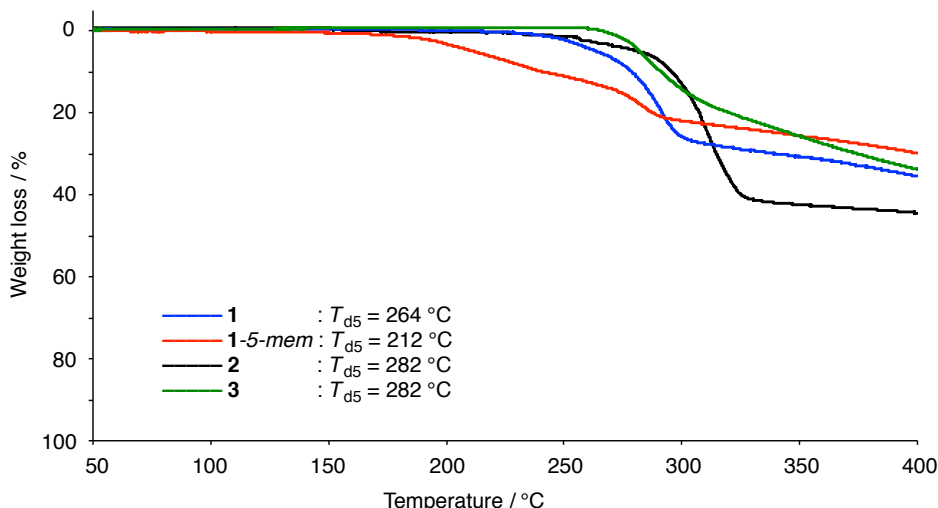


Figure 13. Thermogravimetric analysis of **1–3** and **1-5-mem** heating at 2 °C/min under N₂.

Conclusion

The author designed and developed a twofold BF₂-bridged azafulvene dimer. He demonstrated that the formation of intramolecular B–N coordination bonds toward dipyrrolylethanedione endows this skeleton with extraordinary electron-accepting properties. Based on this concept, D–A–D dye **3** was synthesized, which exhibits a narrow HOMO–LUMO gap while maintaining a moderate HOMO level. This is reflected in NIR absorption, high photostability, and resistance towards oxidation by atmospheric oxygen, while absorptions in the visible region are absent. In line with this new molecular design principle, the author believes that several more sophisticated NIR materials should be easily attainable.

Experimental Section

General

Melting points (mp) were measured on a Stanford Research System OptiMelt MPA100 instrument. The ^1H , ^{13}C , ^{11}B , and ^{19}F NMR spectra were recorded with a JEOL JNM ECA500 instrument (500 MHz for ^1H , 125 MHz for ^{13}C , 160 MHz for ^{11}B , and 470 MHz for ^{19}F), a Bruker Advance III 600US Plus (150 MHz for ^{13}C), and a Bruker Advance III 800US Plus (200 MHz for ^{13}C). Chemical shifts are reported in δ ppm using residual protonated solvent in the deuterated solvents for ^1H and deuterated solvent peak for ^{13}C NMR as an internal standard, whereas $\text{BF}_3\cdot\text{OEt}_2$ (0 ppm) for ^{11}B and CF_3Ph (−64.0 ppm) for ^{19}F NMR as an external standard. UV/vis/NIR absorption measurement was performed with a Shimadzu UV-3150 spectrometer, in spectral grade solvents. Fluorescence measurement was performed with a HORIBA FluoroMax 4P-NIR or a Hamamatsu Photonics Quantaaurus-QY Plus C13534. Quantum yields were determined with a Hamamatsu Photonics Quantaaurus-QY C11347 or C13534 with calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on an ALS/chi-620C electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode. The measurement was carried out under an argon atmosphere using CH_2Cl_2 solutions of samples (1.0 mM) with 0.1 M tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thermogravimetric analysis (TGA) was performed on a SHIMADZU TGA-50 apparatus. The values are given for a weight-loss of 5% (T_{d5}). Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia). The Gel Permeation Chromatography (GPC) was performed using JAI LC-918 apparatus with JAIGEL-1H and 2H columns using toluene as eluent at a flow rate of 3.8 mL/min, JAI LC-9130NEXT apparatus with JAIGEL-1H-40 and 2H-40 columns using CHCl_3 as eluent at a flow rate of 14.0 mL/min, or JAI LC-9130NEXT apparatus with JAIGEL-2HR and 2.5HR columns using toluene as eluent at a flow rate of 10.0 mL/min. All reactions were carried out under argon atmosphere unless otherwise noted. ZnCl_2 was dried at 300 °C under reduced pressure and stored in a glove box under Ar. Oxalyl chloride was purified by distillation before use. Pyridine and $\text{BF}_3\cdot\text{OEt}_2$ were purified by distillation over CaH_2 . The other chemicals were used without further purification.

Computation Methods

Geometry optimization and TD-DFT calculations were performed by using Gaussian 09 (revision A.02) program.¹⁶

Synthesis

2-(2-Thienyl)-1*H*-pyrrole (**5**).

N-Pyrrolylzinc chloride, prepared from *N*-pyrrolylsodium (17.0 g, 190 mmol)¹⁷ and dry ZnCl₂ (25.9 g, 190 mmol), were dissolved in dry THF (150 mL), and the mixture was stirred at room temperature for 30 min. Then, to the mixture was added Pd₂(dba)₃·CHCl₃ (104 mg, 0.100 mmol) and 2-(di-*tert*-butylphosphino)biphenyl (60.0 mg, 0.201 mmol, JohnPhos), and the mixture was stirred at room temperature for 10 min. Then, 2-bromothiophene (4.80 mL, 50.0 mmol) was added to the mixture, which was heated at 100 °C for 17 h. After cooling down, the reaction mixture was poured into NH₄Cl aq., filtered, and extracted with Et₂O. The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel short column chromatography (1:1 CH₂Cl₂/hexane) and GPC (JAIGEL-1H-40 and 2H-40 columns, 14.0 mL/min, CHCl₃, *R*_t = 86 min.) to give 5.27 g (35.3 mmol) of **5** in 71% yield as white solids; mp: 71.9–72.7 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ 8.41 (br, 1H), 7.17 (dd, *J*_{HH} = 5.0, 1.0 Hz, 1H), 7.05–7.01 (m, 2H), 6.82–6.81 (m, 1H), 6.39–6.38 (m, 1H), 6.23 (dd, *J*_{HH} = 6.0, 2.5 Hz, 1H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 136.63, 128.03, 126.84, 122.95, 121.09, 118.92, 110.24, 106.94; HRMS (EI) (*m/z*): [*M*]⁺, calcd. for C₈H₇NS, 149.0299; found, 149.0296.

1,2-Bis(5-(2-thienyl)-1*H*-pyrrol-2-yl)ethane-1,2-dione (**4**).

Oxalyl chloride (0.860 mL, 10.0 mmol) and pyridine (1.77 mL, 22.0 mmol) were added into dry CH₂Cl₂ (20 mL) at –78 °C. After stirred at –78 °C for 40 min, **5** (3.14 g, 21.0 mmol) in CH₂Cl₂ (20 mL) was added to the reaction mixture, and the mixture was slowly warmed up to room temperature and stirred for further 2 h. NH₄Cl aq. was added to the reaction mixture. The obtained mixture was extracted with CHCl₃. The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (CHCl₃, *R*_f = 0.12) to give 1.90 g (5.39 mmol) of **4** in 54% yield as orange solids; mp: 193.8–194.7

°C; ^1H NMR (500 MHz, acetone- d_6): δ 11.38 (br, 2H), 7.71 (dd, $J_{\text{HH}} = 4.0, 1.0$ Hz, 2H), 7.50 (dd, $J_{\text{HH}} = 5.0, 1.0$ Hz, 2H), 7.13 (dd, $J_{\text{HH}} = 5.0, 4.0$ Hz, 2H), 7.11 (dd, $J_{\text{HH}} = 4.0, 2.0$ Hz, 2H), 6.55 (dd, $J_{\text{HH}} = 4.0, 2.5$ Hz, 2H); ^{13}C NMR (125 MHz, acetone- d_6): δ 180.92, 136.25, 134.90, 130.95, 129.20, 127.06, 125.92, 123.45, 110.40; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2\text{S}_2$, 353.0413; found, 353.0400.

Dithienyl-substituted 6-membered product **1**.

4 (35.3 mg, 0.100 mmol) was dissolved in dry THF (2.0 mL) and 2,6-di-*tert*-butylpyridine (1.0 mL), and then the mixture was stirred at room temperature. After dropwise addition of $\text{BF}_3 \cdot \text{OEt}_2$ (0.740 mL, 6.00 mmol), the reaction mixture was heated at 70 °C for 29 h. After cooling down, the reaction mixture was diluted by CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude product was purified by reprecipitation of CH_2Cl_2 solution into MeOH to give 33.0 mg (73.7 μmol) of **1** in 74% yield as dark blue solids; mp: 264 °C (decomp.); ^1H NMR (500 MHz, CD_2Cl_2): δ 8.34 (dd, $J_{\text{HH}} = 4.0, 1.0$ Hz, 2H), 7.882 (d, $J_{\text{HH}} = 5.0$ Hz, 2H), 7.879 (d, $J_{\text{HH}} = 5.0$ Hz, 2H), 7.33 (dd, $J_{\text{HH}} = 5.0, 4.0$ Hz, 2H), 7.26 (d, $J_{\text{HH}} = 5.0$ Hz, 2H); ^{13}C NMR (200 MHz, CD_2Cl_2): δ 156.43, 150.28, 136.17, 135.29, 135.25 (t, $J_{\text{CF}} = 6.0$ Hz), 131.89, 130.40, 129.85; ^{11}B NMR (160 MHz, CD_2Cl_2): δ -0.45 (t, $J_{\text{BF}} = 13.8$ Hz); ^{19}F NMR (470 MHz, CD_2Cl_2): δ -143.42 (m); HRMS (APCI-TOF) (m/z): $[\text{M}]^-$, calcd. for $\text{C}_{18}\text{H}_{10}\text{B}_2\text{F}_4\text{N}_2\text{O}_2\text{S}_2$, 448.0313; found, 448.0314; Elemental analysis calcd. (%) for $\text{C}_{18}\text{H}_{10}\text{B}_2\text{F}_4\text{N}_2\text{O}_2\text{S}_2$: C 48.26, H 2.25, N 6.25; found: C 48.52, H 2.42, N 6.29.

Dithienyl-substituted 5-membered product **1-5-mem**.

4 (35.3 mg, 0.100 mmol) was dissolved in dry CH_2Cl_2 (2.0 mL) and 2,6-di-*tert*-butylpyridine (1.0 mL). After dropwise addition of $\text{BF}_3 \cdot \text{OEt}_2$ (0.740 mL, 6.00 mmol) at 0 °C, the reaction mixture was stirred at room temperature for 90 min. Then, the reaction mixture was pumped up to remove solvent. The obtained crude product was purified by silica gel short column chromatography (CH_2Cl_2), followed by reprecipitation of CH_2Cl_2 solution to hexane to give 31.8 mg (71.0 μmol) of **1-5-mem** in 71% yield as dark blue solids; mp: 212 °C (decomp.); ^1H NMR (500 MHz, CD_2Cl_2): δ 8.10 (dd, $J_{\text{HH}} = 4.0, 1.0$ Hz, 2H), 7.86 (d, $J_{\text{HH}} = 4.5$ Hz, 2H), 7.66 (d, $J_{\text{HH}} = 4.5$ Hz, 2H), 7.32 (dd, $J_{\text{HH}} = 5.0, 4.0$ Hz, 2H), 7.15 (d, $J_{\text{HH}} = 4.5$ Hz, 2H); ^{13}C NMR (150 MHz,

CD₂Cl₂): δ 156.69, 154.72, 141.76, 135.94, 134.46 (t, $J_{\text{CF}} = 3.0$ Hz), 132.76, 130.61, 129.20, 126.94; ¹¹B NMR (160 MHz, CD₂Cl₂): δ 3.11 (s); ¹⁹F NMR (470 MHz, CD₂Cl₂): δ -118.35 (m); HRMS (APCI-TOF) (m/z): [M]⁻, calcd. for C₁₈H₁₀B₂F₄N₂O₂S₂, 448.0313; found, 448.0307.

1,2-Bis(5-mesityl-1H-pyrrol-2-yl)ethane-1,2-dione (7).

2-Mesityl-1H-pyrrole (**6**) was prepared according to the literature.¹⁷ Oxalyl chloride (0.258 mL, 3.01 mmol) and pyridine (0.532 mL, 6.60 mmol) were added to dry CH₂Cl₂ (3.0 mL) at -78 °C. After stirred for 40 min, **6** (1.17 g, 6.32 mmol) in CH₂Cl₂ (6.0 mL) was added to the reaction mixture at -78 °C, and then the mixture was slowly warmed up to room temperature and further stirred for 1 h. To the reaction mixture was added NaHCO₃ aq., and the mixture was extracted with CH₂Cl₂. The organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (CH₂Cl₂, $R_f = 0.16$) to give 1.09 g (2.57 mmol) of **7** in 85% yield as yellow solids; mp: 254.8–255.2 °C; ¹H NMR (500 MHz, acetone-*d*₆): δ 11.07 (br, 2H), 7.22 (dd, $J_{\text{HH}} = 4.0$, 2.0 Hz, 2H), 6.95 (s, 2H), 6.22 (dd, $J_{\text{HH}} = 4.0$, 2.0 Hz, 2H), 2.30 (s, 6H), 2.12 (s, 12H); ¹³C NMR (125 MHz, acetone-*d*₆): δ 181.42, 140.79, 140.77, 138.51, 130.38, 130.19, 128.99, 122.39, 112.75, 21.20, 20.59; HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₂₈H₂₉N₂O₂, 425.2224; found, 425.2231; Elemental analysis calcd. (%) for C₂₈H₂₈N₂O₂: C 79.22, H 6.65, N 6.60; found: C 79.21, H 6.67, N 6.59.

Dimesityl-substituted 6-membered product 2.

7 (42.5 mg, 0.100 mmol) was dissolved in dry THF (2.0 mL) and 2,6-di-*tert*-butylpyridine (1.0 mL), and then the mixture was stirred at room temperature. After addition of BF₃·OEt₂ (0.740 mL, 6.00 mmol) dropwise, the reaction mixture was heated at 70 °C for 52 h. After cooling down, reaction mixture was diluted with CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by reprecipitation of CH₂Cl₂ solution to MeOH to give 32.1 mg (61.7 μ mol) of **2** in 62% yield as dark red solids; mp: 282 °C (decomp.); ¹H NMR (500 MHz, CD₂Cl₂): δ 7.99 (d, $J_{\text{HH}} = 5.0$ Hz, 2H), 6.99 (s, 1H), 6.80 (d, $J_{\text{HH}} = 5.0$ Hz, 2H), 2.36 (s, 6H), 2.09 (s, 12H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 168.88, 154.44, 140.60, 137.00, 134.96, 132.13,

128.29, 127.71, 127.49, 21.37, 19.96; ^{11}B NMR (160 MHz, CD_2Cl_2): δ -1.07 (s); ^{19}F NMR (470 MHz, CD_2Cl_2): δ -147.29 (m); HRMS (APCI-TOF) (m/z): $[\text{M}]^-$, calcd. for $\text{C}_{28}\text{H}_{26}\text{B}_2\text{F}_4\text{N}_2\text{O}_2$, 520.2126; found, 520.2127; Elemental analysis calcd. (%) for $\text{C}_{28}\text{H}_{26}\text{B}_2\text{F}_4\text{N}_2\text{O}_2$: C 64.66, H 5.04, N 5.39; found: C 64.57, H 5.14, N 5.39.

Bis(4-hexyloxyphenyl)amine (8).

4-Hexyloxyaniline (9.91 g, 51.3 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (266 mg, 0.257 mmol), 1,1'-bis(diphenylphosphino)ferrocene (290 mg, 0.523 mmol) and NaOt-Bu (5.20 g, 54.1 mmol) were mixed in dry toluene (50 mL). After addition of 4-hexyloxybromobenzene (12.0 mL, 56.6 mmol), the mixture was heated at 120 °C for 1.5 h. After cooling down, the reaction mixture was poured into water and extracted with Et_2O . The organic phase was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (1:2 CH_2Cl_2 /hexane, R_f = 0.18) to give 15.0 g (40.6 mmol) of **8** in 79% yield as pale yellow solids; mp: 78.4–78.9 °C; ^1H NMR (500 MHz, acetone- d_6): δ 6.95 (d, J_{HH} = 9.0 Hz, 4H), 6.81 (d, J_{HH} = 9.0 Hz, 4H), 6.72 (br, 1H), 3.92 (t, J_{HH} = 6.5 Hz, 4H), 1.75–1.71 (m, 4H), 1.48–1.45 (m, 4H), 1.37–1.30 (m, 8H), 0.90 (t, J_{HH} = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, acetone- d_6): δ 154.26, 139.39, 119.64, 116.19, 68.99, 32.46, 26.60, 23.39, 14.40 (one aliphatic signal overlaps with signals of acetone- d_6); HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{24}\text{H}_{36}\text{NO}_2$, 370.2746; found, 370.2750.

2-(Bis(4-hexyloxyphenyl)amino)thiophene (9).

8 (18.5 g, 50.1 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (260 mg, 0.251 mmol), $\text{P}(t\text{-Bu})_3$ (129 mg, 0.683 mmol) and NaOt-Bu (19.3 g, 201 mmol) were mixed in dry toluene (100 mL). After addition of 2-bromothiophene (14.5 mL, 150 mmol), the mixture was heated at 130 °C for 24 h. After cooling down, the reaction mixture was poured into NH_4Cl aq. and extracted with toluene. The organic phase was washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (1:4 CH_2Cl_2 /hexane, R_f = 0.29) to give 20.3 g (44.9 mmol) of **9** in 90% yield as yellow oil; ^1H NMR (500 MHz, CD_2Cl_2): δ 7.02 (d, J_{HH} = 9.0 Hz, 4H), 6.84–6.81 (m, 2H), 6.79 (d, J_{HH} = 9.0 Hz, 4H), 6.50 (dd, J_{HH} = 3.0, 2.0 Hz, 1H), 3.91 (d, J_{HH} = 6.5 Hz, 4H), 1.78–1.72 (m, 4H), 1.46–1.43 (m, 4H), 1.36–1.32 (m, 8H), 0.91 (t, J_{HH} = 7.0 Hz, 6H); ^{13}C NMR (125 MHz,

acetone- d_6): δ 156.42, 154.51, 142.72, 126.78, 125.07, 119.20, 118.52, 116.05, 68.88, 32.42, 30.14, 26.57, 23.37, 14.38; HRMS (APCI-TOF) (m/z): $[M+H]^+$, calcd. for $C_{28}H_{38}NO_2S$, 452.2618; found, 452.2601.

2-(5-(Bis(4-hexyloxyphenyl)amino)thiophen-2-yl)-1H-pyrrole (10).

n-BuLi (1.39 M in hexane, 21.1 mL, 29.3 mmol) was added to a solution of **9** (12.0 g, 26.6 mmol) in THF (150 mL) at -78°C . After the mixture was gradually warmed up to room temperature for 1 h, iodine (8.11 g, 32.0 mmol) was added to the reaction mixture at -78°C . The mixture was warmed up to room temperature and stirred for 1 h. After addition of $\text{Na}_2\text{S}_2\text{O}_3$ aq., the mixture was extracted with toluene. Organic phase was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude products of diarylaminothienyl iodide were used for next step without further purification. In another flask, pyrrolylzinc chloride in dry THF (200 mL) was prepared from pyrrolsodium (9.49 g, 107 mmol) and dry ZnCl_2 (14.5 g, 106 mmol) at room temperature. To the solution, $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (248 mg, 0.240 mmol) and 2-(di-*tert*-butylphosphino)biphenyl (152 mg, 0.509 mmol) were added and stirred at room temperature for 10 min. Then, the mixture was transferred into the solution of diarylaminothienyl iodide via cannula, and the mixture was heated at 100°C for 13 h. After cooling down, the reaction mixture was poured into water, filtered, and extracted with toluene. The organic phase was washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel short column chromatography (1:1 CH_2Cl_2 /hexane), followed by GPC (JAIGEL-1H and 2H columns, 10.0 mL/min, toluene, $R_t = 26$ min.) to give 7.27 g (14.1 mmol) of **10** in 53% yield as dark yellow oil; ^1H NMR (500 MHz, CD_2Cl_2): δ 8.32 (br, 1H), 7.06 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 6.81 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 6.76–6.75 (m, 1H), 6.74 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 6.40 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 6.24–6.22 (m, 1H), 6.17 (dd, $J_{\text{HH}} = 6.0$, 2.0 Hz, 1H), 3.92 (t, $J_{\text{HH}} = 6.5$ Hz, 4H), 1.78–1.72 (m, 4H), 1.48–1.42 (m, 4H), 1.37–1.32 (m, 8H), 0.91 (t, $J_{\text{HH}} = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 155.85, 151.41, 141.72, 128.43, 127.23, 124.63, 119.47, 118.49, 118.10, 115.41, 110.08, 106.02, 68.73, 31.98, 29.67, 26.08, 23.00, 14.17; HRMS (APCI-TOF) (m/z): $[M+H]^+$, calcd. for $\text{C}_{32}\text{H}_{41}\text{N}_2\text{O}_2\text{S}$, 517.2883; found, 517.2862.

1,2-bis(5-(5-(bis(4-hexyloxyphenyl)amino)thiophen-2-yl)-1*H*-pyrrol-2-yl)ethane-1,2-dione (11).

Oxalyl chloride (51.5 μ L, 0.600 mmol) and pyridine (0.102 mL, 1.27 mmol) were added to dry CH₂Cl₂ (12 mL) at -78 °C. After stirred for 40 min, **10** (681 mg, 1.32 mmol) in CH₂Cl₂ (5.0 mL) was added to the reaction mixture at -78 °C, and the mixture was slowly warmed up to room temperature and further stirred for 2 h. NaHCO₃ aq. was added to the mixture. After extracted with CH₂Cl₂, the organic phase was washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (CH₂Cl₂, R_f = 0.36) and GPC (JAIGEL-1H and 2H, 3.8 mL/min, toluene, R_t = 47 min.) to give 228 mg (0.209 mmol) of **11** in 35% yield as dark red solids; mp: 125.6–126.8 °C; ¹H NMR (500 MHz, acetone-*d*₆): δ 11.17 (s, 2H), 7.14 (d, J_{HH} = 9.0 Hz, 4H), 7.09 (d, J_{HH} = 4.0 Hz, 2H), 6.92 (d, J_{HH} = 9.0 Hz, 4H), 6.33 (d, J_{HH} = 4.0 Hz, 2H), 6.31 (d, J_{HH} = 4.0 Hz, 2H), 3.98 (t, J_{HH} = 6.5 Hz, 8H), 1.79–1.73 (m, 8H), 1.49–1.45 (m, 8H), 1.37–1.33 (m, 16H), 0.90 (t, J_{HH} = 7.0 Hz, 12H); ¹³C NMR (125 MHz, acetone-*d*₆): δ 180.16, 157.31, 156.27, 141.66, 136.97, 130.78, 126.46, 125.31, 123.75, 116.25, 115.31, 109.23, 68.93, 32.42, 30.12, 26.57, 23.38, 14.39; HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₆₆H₇₉N₄O₆S₂, 1087.5436; found, 1087.5403.

D–A–D type 6-membered product 3.

11 (109 mg, 0.101 mmol) was dissolved in dry THF (2.0 mL) and 2,6-di-*tert*-butylpyridine (1.0 mL). After dropwise addition of BF₃·OEt₂ (0.740 mL, 6.00 mmol), the reaction mixture was heated at 100 °C for 30 h. After cooling down, the reaction mixture was diluted with CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained crude product was purified by reprecipitation of CH₂Cl₂ solution to MeOH to give 98.0 mg (82.8 μ mol) of **3** in 83% yield as black solids; mp: 276.4–277.8 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ 8.08 (d, J_{HH} = 5.0 Hz, 2H), 7.53 (d, J_{HH} = 5.0 Hz, 2H), 7.27 (d, J_{HH} = 9.0 Hz, 4H), 6.933 (d, J_{HH} = 9.0 Hz, 4H), 6.930 (d, J_{HH} = 6.5 Hz, 2H), 6.39 (d, J_{HH} = 4.5 Hz, 2H), 3.98 (t, J_{HH} = 6.5 Hz, 8H), 1.80–1.76 (m, 8H), 1.50–1.44 (m, 8H), 1.37–1.34 (m, 16H), 0.92 (t, J_{HH} = 7.0 Hz, 12H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 167.37, 158.62, 152.69, 145.45, 138.60, 137.38, 127.81, 127.51, 125.30, 119.21, 115.98, 114.12, 68.83, 31.95, 29.55, 26.05, 22.99, 14.17 (one aromatic peak is not observed due to the

overlapping); ^{11}B NMR (160 MHz, CD_2Cl_2): δ -0.38 (s); ^{19}F NMR (470 MHz, CD_2Cl_2): δ -141.66 (s); HRMS (APCI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{66}\text{H}_{76}\text{B}_2\text{F}_4\text{N}_4\text{O}_6\text{S}_2$, 1182.5343; found, 1182.5297.

X-ray Crystal Structure Analysis

Compound 1: Single crystals suitable for X-ray analysis were obtained by recrystallization from slow diffusion of methanol to dichloromethane. Intensity data were collected at 100 K on a Bruker SMART APEX II with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator. A total of 3335 reflections were measured with a maximum 2θ angle of 51.0° , of which 1620 were independent reflections ($R_{\text{int}} = 0.0142$). The structure was solved by direct methods (SHELXS-97¹⁸) and refined by the full-matrix least-squares on F^2 (SHELXL-97¹⁸). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_{18}\text{H}_{10}\text{B}_2\text{F}_4\text{N}_2\text{O}_2\text{S}_2$; FW = 448.02, crystal size $0.05 \times 0.05 \times 0.02$ mm³, Triclinic, P -1, $a = 7.0325(13)$ Å, $b = 7.7449(14)$ Å, $c = 8.3621(15)$ Å, $\alpha = 80.907(2)^\circ$, $\beta = 77.913(2)^\circ$, $\gamma = 87.149(2)^\circ$, $V = 439.69(14)$ Å³, $Z = 1$, $D_c = 1.692$ g cm⁻³. The refinement converged to $R_1 = 0.0404$, $wR_2 = 0.1154$ ($I > 2\sigma(I)$), GOF = 1.062.

Compound 1-5-mem: Single crystals suitable for X-ray analysis were obtained by recrystallization from slow diffusion of hexane to dichloromethane. Intensity data were collected at 100 K on a Bruker SMART APEX II with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator. A total of 4119 reflections were measured with a maximum 2θ angle of 51.0° , of which 1622 were independent reflections ($R_{\text{int}} = 0.0237$). The structure was solved by direct methods (SHELXS-97¹⁸) and refined by the full-matrix least-squares on F^2 (SHELXL-97¹⁸). The terminal thiophene rings were disordered and were solved using an appropriate disordered model with the occupancies of C7A, S1A, H7A–H9A and C7B, S1B, H7B–H9B as 0.63 and 0.37, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_{18}\text{H}_{10}\text{B}_2\text{F}_4\text{N}_2\text{O}_2\text{S}_2$; FW = 448.02, crystal size $0.12 \times 0.08 \times 0.05$ mm³, Monoclinic, $P2_1/c$, $a = 8.582(2)$ Å, $b = 8.343(2)$ Å, $c = 13.167(3)$ Å, $\beta = 107.573(3)^\circ$, $V = 898.8(4)$ Å³, $Z = 2$, $D_c = 1.656$ g cm⁻³. The refinement converged to $R_1 = 0.0413$, $wR_2 = 0.0860$ ($I > 2\sigma(I)$), GOF = 1.100.

Compound 2: Single crystals suitable for X-ray analysis were obtained by recrystallization from slow diffusion of methanol to dichloromethane. Intensity data were collected at 100 K using a diffractometer equipped with an ADSC Quantun315 CCD detector with synchrotron radiation at a wavelength of 0.80 Å at the SPring-8 beamline BL38B1. A total of 24628 reflections were measured with a maximum 2θ angle of 55.0°, of which 1941 were independent reflections ($R_{\text{int}} = 0.0428$). The collected diffraction data were processed with the HKL2000 software program. The structure was solved by direct methods (SHELXS-97¹⁸) and refined by the full-matrix least-squares on F^2 (SHELXL-97¹⁸). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_{28}\text{H}_{26}\text{B}_2\text{F}_4\text{N}_2\text{O}_2$; FW = 520.13, crystal size $0.03 \times 0.02 \times 0.01 \text{ mm}^3$, Monoclinic, $P2_1/a$, $a = 7.32090(10) \text{ Å}$, $b = 22.8716(2) \text{ Å}$, $c = 7.46360(10) \text{ Å}$, $\beta = 91.1935(4)^\circ$, $V = 1249.44(3) \text{ Å}^3$, $Z = 2$, $D_c = 1.383 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0418$, $wR_2 = 0.1278$ ($I > 2\sigma(I)$), GOF = 1.034.

Photostability Test

Photostability was investigated as follows: Solution of compound **3** or naphthalocyanine NIR dye (**Napht**)^{5a} (Aldrich, CAS: 105528-25-4) in degassed and non-degassed toluene (4 μM) in 1.0 cm quartz cuvettes was illuminated with Xe lamp (USHIO, SX-UID501XAMQ) through optical filters (ASAHI SPECTRA, Longpass filter/vis 690 nm and Super Cold Filter/1100 nm), which correspond to irradiation at a range of 690–1100 nm ($1.3 \times 10^4 \text{ lux}$). Light irradiation and recording the absorption spectra were repeated alternately.

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Chapter 3

4,7-Bis[3-(dimesitylboryl)thien-2-yl]benzothiadiazole: Solvato-, Thermo-, and Mechanochromism Based on the Reversible Formations of an Intramolecular B–N Bond

Abstract: 4,7-Bis-[3-(dimesitylboryl)thien-2-yl]benzothiadiazole (**1**) was synthesized and its chromic behavior was investigated. Photophysical measurements, single-crystal X-ray diffraction analysis, and theoretical calculations revealed that an intramolecular B–N coordination bond forms reversibly. The equilibrium of this reversible bond formation depends on the solid-state structure, solvents, temperature, and mechanical forces, and leads to significant changes in the electronic structure and chromic behavior of this molecule. The responsiveness toward external stimuli, resulting from the reversible formation of open and closed forms of this system, is achieved via weak intramolecular B–N coordination bonds induced by the steric bulk of the mesityl groups on the boron centers.

Introduction

Chromic materials, i.e., materials that exhibit color changes in response to external stimuli such as light, temperature changes, redox reactions, solvents, and mechanical forces, have attracted much attention in the context of a variety of applications, including colorimetric chemosensors, memory devices, and light-control glass.^{1–15} Such chromic phenomena can be induced by structural isomerization,² phase transitions in liquid crystals,^{3,4} or changes in the intermolecular interactions, e.g. in hydrogen-bond networks,^{5,6} π -stacking alignments,^{4,7,8} metal–metal interactions,^{6,9} molecular aggregation,^{8,10} redox state,¹¹ or the reversible formation/cleavage of coordination bonds,^{12–16} etc.

As mentioned in General Introduction, boron-containing π -conjugated molecules are of interest as they can form coordination bonds between the vacant p-orbital of the Lewis-acidic boron center and the electron pair of a Lewis-basic species, which results in significant perturbation on the electronic structure of the π -conjugated system.^{12,17} Yamaguchi and Tamao et al. reported that trianthrylborane derivatives can be used as colorimetric sensors for fluoride ions based on the formation of B–F coordination bonds (Figure 1a).¹⁴ Kawashima et al. reported catecholborane-substituted azobenzene derivatives show the photoswitching of the coordination number of boron center by photoisomerization of azo group (Figure 1b).¹⁵ Wang et al. reported another type of boron-containing compounds that exhibits chromic behavior based on reversible structural changes via the formation/cleavage of intramolecular C–C and C–B bonds upon photo-irradiation and heating (Figure 1c).¹⁸ Recently, Wolf et al. reported an example of a “flexible” Lewis pair, bearing intramolecular B–O coordination bonds between boron atoms and phosphine oxides (Figure 1d).¹⁶ The equilibrium between the non-bonded and bonded forms was sensitive to temperature and solvents, and compounds with such flexible Lewis pairs exhibited thermo- and solvatochromism.

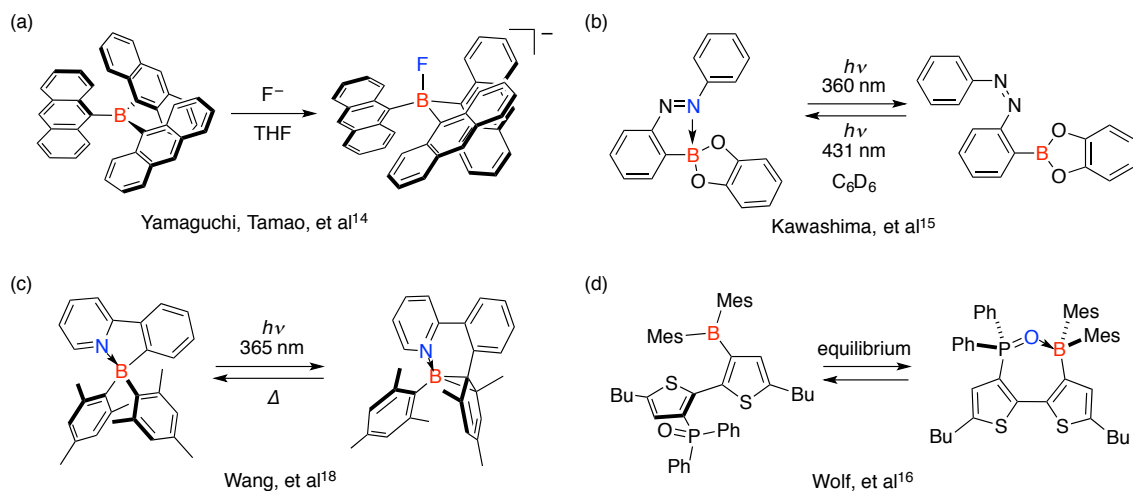


Figure 1. Examples of boron-containing chromic compounds.

It is also known that, the formation of B–N coordination bonds has a large impact on the electronic structure of C=N-containing π -system. For example, Bazan et al. demonstrated that the addition of triarylborane to a benzothiadiazole (BT) derivative allows tuning the band gap through the formation of intermolecular B–N coordination bonds (Figure 2a).¹⁹ Ingleson and Turner et al. reported BT derivatives with an intramolecular B–N coordination bond as far-red/NIR-emitting materials (Figure 2b).²⁰

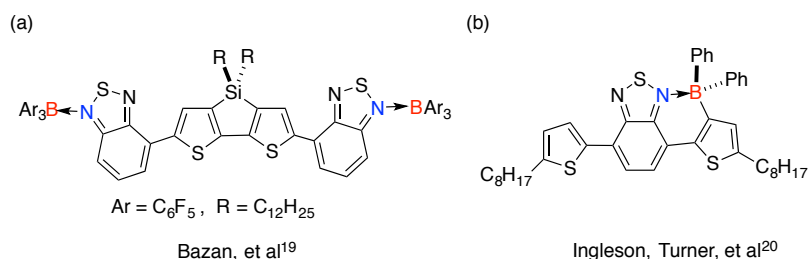


Figure 2. Examples of compounds with B–N coordination bond.

Following this idea, the author designed and synthesized Mes₂B-substituted BT derivative **1** as a new B–N functionalized building block (Figure 3a). During the investigation of the properties of **1**, he serendipitously observed the chromic behavior, which can be triggered by temperature, solvent polarity, and mechanical impact. A set of experiments and theoretical calculations revealed that these phenomena are caused by the reversible formation of an intramolecular B–N coordination bond (Figure 3b). Focused on the structures of boryl-substituted BT unit, it is found to have major strain for intramolecular B–N bond relative to that in quinoxaline derivatives (Figure 3c).²¹

The introduction of bulky boryl-substituents, e.g. Mes₂B group (Mes = 2,4,6-Me₃C₆H₂), in BT unit can be expected to induce the reversibility for the formation of B–N coordination bonds.

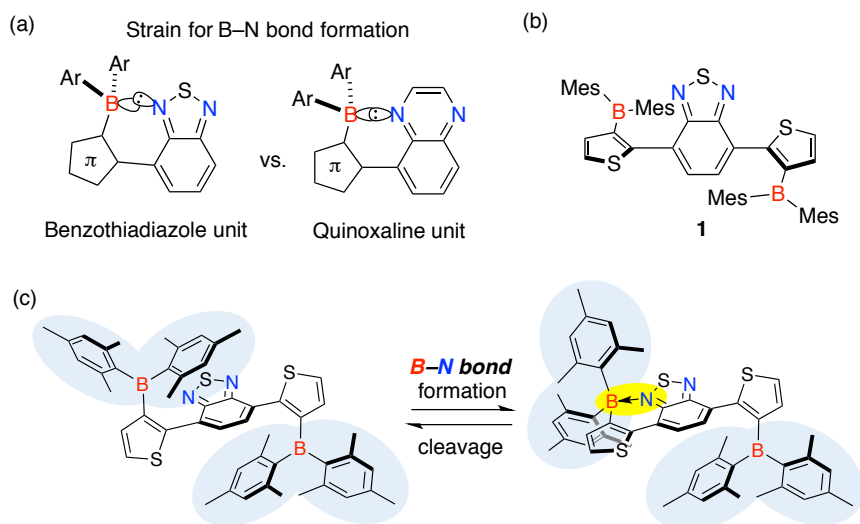


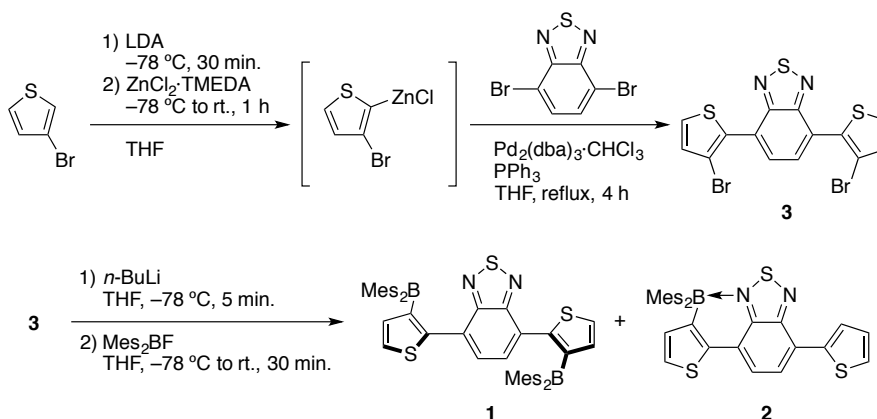
Figure 3. (a) Structural comparison between benzothiadiazole unit and quinoxaline unit regarding strain for intramolecular B–N bond formation. (b) Mes₂B-substituted bis(thienyl)benzothiadiazole derivative **1**. (c) Reversible formation of an intramolecular B–N coordination bond in **1**.

Results and Discussion

Synthesis of Compound 1

The outline for synthesis of **1** is shown in Scheme 1. Negishi coupling reaction of (3-bromothiophen-2-yl)zinc(II) chloride and 4,7-dibromobenzothiadiazole afforded bis(3-bromothiophen-2-yl)-1,7-benzothiadiazole **3** in 40% yield. Dilithiation of **3** with *n*-BuLi in THF, followed by subsequent treatment with Mes₂BF after 5 min at –78 °C gave diborylated product **1** in 10% yield and monoborylated product **2** in 6% yield as a side product together with large amounts of a complex mixture of unidentified products. The low yield of the borylated compounds is most likely due to instability of the lithiated compounds generated from **3**. This was confirmed by the fact that quenching of the reaction mixture with water after only a few minutes of the treatment of **3** with *n*-BuLi gave not only the corresponding protonated products but also some unidentified side products. The elongation period before addition of Mes₂BF unfortunately resulted in merely increasing complex mixture.

Scheme 1.



Crystal Structures of **1** and **2**

Both diborylated **1** and monoborylated **2** were obtained as crystalline solids; the former was yellow and the latter was dark blue. In order to ascertain the origin of the sharp contrast between the colors of these solids, X-ray diffraction analysis (XRD) was conducted on single crystals of **1** and **2**. The crystal structure of **1** is shown in Figure 4. The dithienyl BT moiety in **1** is disordered over two sites with relative occupancies of 0.55:0.45, and was solved using an adequate disorder model with flipping BT units. The B–N distances of 4.987(5) Å (B1–N1) and 3.270(5) Å (B2–N2) are much longer than those of typical intramolecular B–N coordination bonds (1.64(1)–1.667(3) Å),^{20,22} suggesting the absence of this type of bond in the yellow crystals of **1**. Considering that only the inner dithienyl BT moiety is disordered, the bulky Mes₂B groups should determine the packing structure and provide sufficient space for the flipping of the disordered dithienyl BT moiety. In sharp contrast, the XRD analysis on the blue crystals of **2** confirmed the formation of a B–N bond (1.66(2) Å) (Figure 5). These results are consistent with the solid-state ¹¹B NMR spectra of crystalline **1** and **2**. In the spectrum of **1**, only one signal was observed at δ_B 62.7 ppm, which is in the range of typical three-coordinated boron centers with three aryl groups (e.g. δ_B 77.4 ppm for BMe₃ in the solid state²³), indicating the absence of B–N coordination bonds. Conversely, the ¹¹B NMR signal for **2** appeared at δ_B 7.8 ppm, which corresponds to a four-coordinated boron center, and thus represents clear evidence for the presence of a B–N coordination bond (*vide infra*, Figure 15c). These results indicate that the color difference between the crystals of **1** and **2** can be explained by the absence or presence of an intramolecular B–N coordination bond.

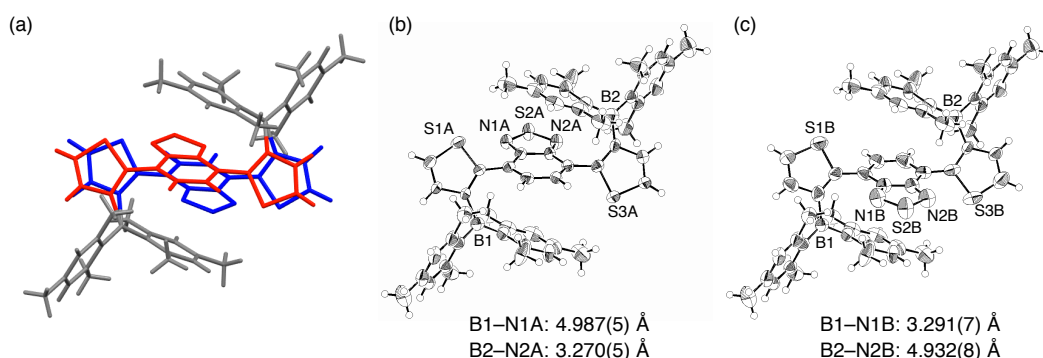


Figure 4. Molecular structure of **1**. (a) Capped sticks representation of **1**, whereby the BT moiety is disordered over two sites with relative occupancies of 0.55 (red) and 0.45 (blue). (b) ORTEP representation of the major occupancy and (c) the minor occupancy, whereby thermal ellipsoids are shown at 50% probability and only selected atoms are labeled. The distances between boron and nitrogen are also included.

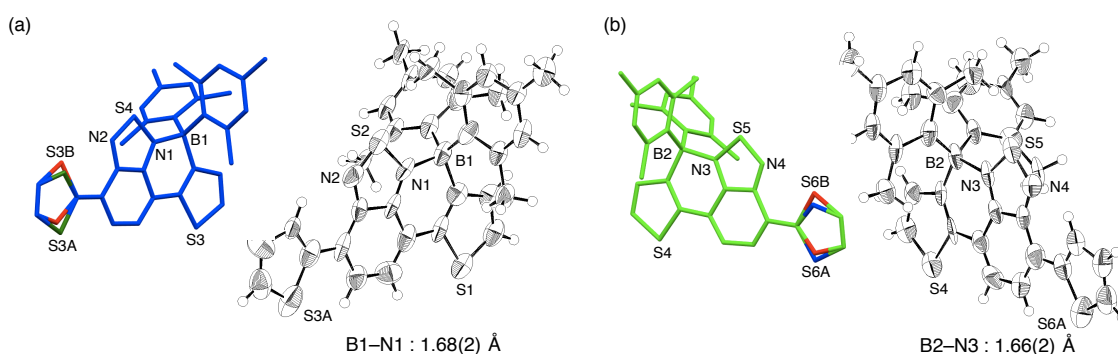


Figure 5. Molecular structure of **2**. The unit cell has two independent conformers shown as green and blue units. Clipped sticks representation of (a) blue and (b) green unit, whereby the thienyl moiety is disordered with relative occupancies of 0.67 (green) and 0.33 (red) for blue unit and 0.75 (blue) and 0.25 (red) for green unit, respectively. ORTEP drawings of the major occupancy are shown, whereby thermal ellipsoids are shown at 50% probability level and only selected atoms are labeled.

Photophysical Properties in Solution and in the Solid State of **1**

Interestingly, diborylated **1** exhibited a dramatic color change from yellow to dark blue upon dissolution in organic solvents, and the cast film prepared from a CHCl_3 solution of **1** maintained this dark blue color. After annealing at 150 °C for 10 min, the color of the film reverted to a shade of yellow similar to that of the crystalline solids (Figure 6a). The UV/vis spectra of the CHCl_3 solution and the cast film of **1** showed absorption maxima at $\lambda = 577$ nm and $\lambda = 591$ nm, respectively, while that of the annealed film exhibited a band at $\lambda = 430$ nm (Figure 6b).

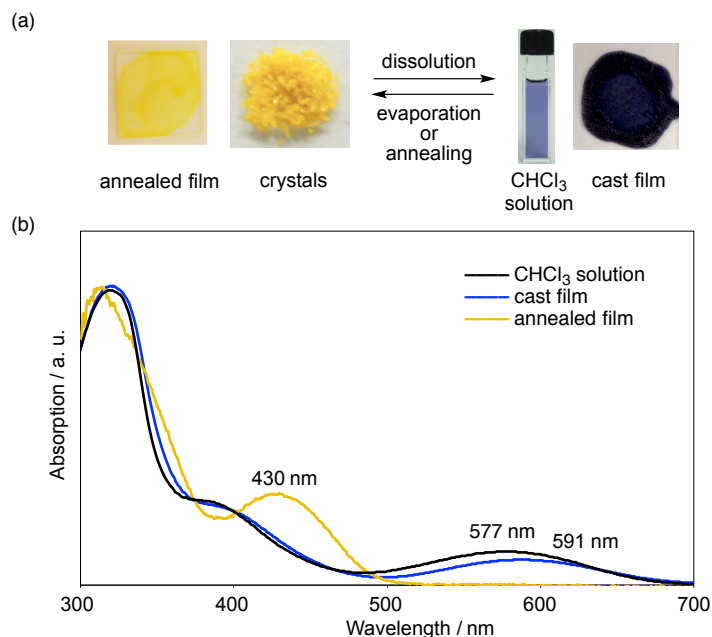


Figure 6. (a) Pictures of annealed film, yellow crystals, CHCl_3 solution, and cast film of **1**. (b) UV/vis spectra of cast film (blue), annealed film (yellow), and CHCl_3 solution (black) of **1**.

To gain further insight into the observed chromism, DFT calculations were conducted on **1** at the M06-2X/6-31G(d) level of theory. Optimizations were carried out on the structures with no B–N bonds (**1**-open), one B–N bond (**1**-mono-closed), and two B–N bonds (**1**-di-closed), and their minimum energies were confirmed by frequency calculations. While the Gibbs free energy (G) at 293 K for **1**-di-closed was much higher than that of **1**-open ($\Delta G = 9.49$ kcal/mol) due to steric hindrance and low nucleophilicity of the other nitrogen atom in the BT unit with one B–N bond (Figure 7),^{19–20} ΔG between **1**-open and **1**-mono-closed was found to be small (1.02 kcal/mol), supporting a possible formation of conformer and an easy transformation between them. As expected, the formation of a B–N bond significantly lowers the LUMO level of **1**-mono-closed (–2.29 eV) compared to that of **1**-open (–1.59 eV), while the HOMO level is slightly elevated (+0.18 eV) on account of the planarization of the π -skeleton, which results in the diminished HOMO–LUMO gap in **1**-mono-closed (Figure 7). TD-DFT calculations on **1**-open and **1**-mono-closed at the M06-2X/6-31G(d)/M06-2X/6-31G(d) level of theory suggested that the longest absorption bands in each conformation correspond to the HOMO→LUMO transition.

The obtained absorption wavelengths of **1**-open ($\lambda = 422$ nm) and **1**-mono-closed ($\lambda = 556$ nm) are in good agreement with those of the annealed film ($\lambda = 430$ nm), and the cast film ($\lambda = 591$ nm) as well as the solution ($\lambda = 577$ nm). These results support the hypothesis that the reversible formation of the B–N bond triggers the observed color change, indicating that the **1**-open form is favorable in the crystalline state of the annealed film, while the **1**-mono-closed form exists to some extent in solution and in the amorphous phase of the cast film.

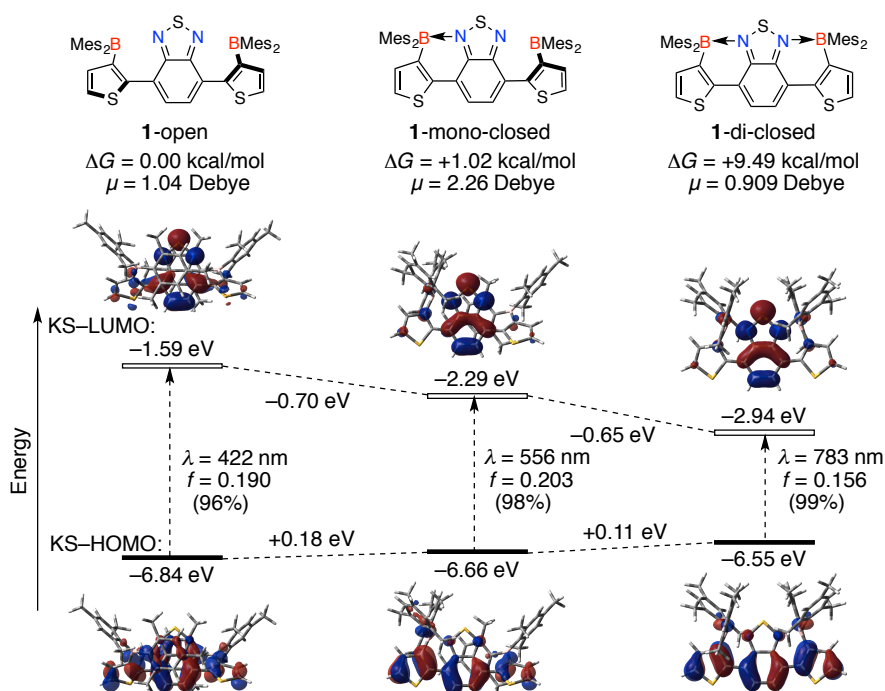


Figure 7. The calculated energy diagrams for **1**-open, **1**-mono-closed, and **1**-di-closed (M06-2X/6-31G(d)). The longest absorption profiles corresponding to HOMO→LUMO transition, the oscillator strengths, and the contribution (TD-M06-2X/6-31G(d))/M06-2X/6-31G(d)) are shown. Transition energies were calibrated using a factor of 0.90.

Solvatochromism and Thermochromism of **1**

The color of solution **1** shows solvent dependency. The UV/vis spectra of **1** in various organic solvents revealed that the longest absorption peak exhibits an increase in intensity upon increasing the solvent polarity, accompanied with a slight blue-shift from $\lambda = 580$ nm in cyclohexane to $\lambda = 568$ nm in DMF (Figure 8a). These results suggest that the concentration of the **1**-mono-closed form increases with the solvent polarity. This can be rationalized in terms of a stabilization of the polar B–N bond in

1-mono-closed in polar solvents, which is also supported by the results of the DFT calculations using polarizable continuum models (PCMs, Table 1). Moreover, a solution of **1** showed significant color changes in response to temperature changes. The reversibility of the color change was confirmed by variable-temperature (VT) UV/vis absorption measurements in toluene ($-40\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$), which showed spectral changes for the absorption maximum at $\lambda = 575\text{ nm}$ and several isosbestic points (Figure 8b). The color of the toluene solution of **1** is deep blue at $0\text{ }^{\circ}\text{C}$, whereas it adopts a pale shade of brown at $80\text{ }^{\circ}\text{C}$. Based on the analysis of absorbance using the oscillator strengths ($f = 0.190$ (**1**-open) and $f = 0.203$ (**1**-mono-closed)) obtained from TD-DFT calculations (Figure 7), the abundance ratio of **1**-open and **1**-mono-closed forms in toluene was estimated to be 85:15 at $100\text{ }^{\circ}\text{C}$, 47:53 at $20\text{ }^{\circ}\text{C}$, and 9:91 at $-40\text{ }^{\circ}\text{C}$, respectively, leading to ΔG in the range from $+1.26$ to -1.06 kcal/mol (for details, see Experimental section), which is in good agreement with the results of the DFT calculations (*vide supra*, Figure 7).

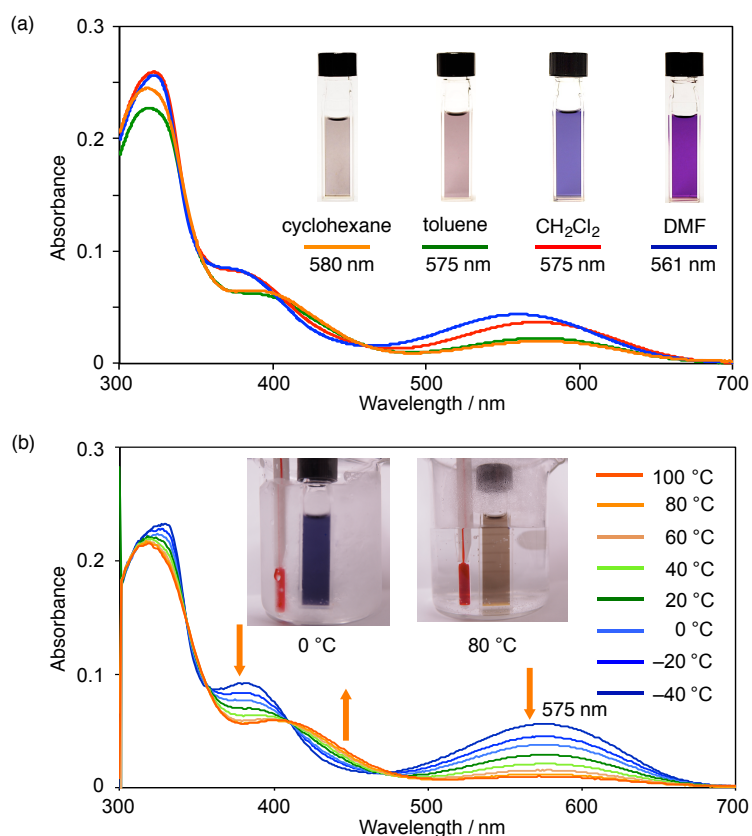


Figure 8. (a) Solvatochromism of **1** in different solvents at room temperature and (b) thermochromism of **1** in toluene. The wavelength of the longest absorption bands and the pictures of solutions are included.

Table 1. The Summary of the Solvent Effects on the Gibbs Free Energy of **1**-open/**1**-mono-closed (M06-2X/6-31G(d)) Using PCMs

Solvent	$\Delta G_{\text{closed-open}}$
DMF	+1.12 kcal/mol
CH ₂ Cl ₂	+1.13 kcal/mol
THF	+1.14 kcal/mol
CHCl ₃	+1.16 kcal/mol
toluene	+1.21 kcal/mol
cyclohexane	+1.22 kcal/mol

An increase of the abundance ratio of the **1**-mono-closed form at lower temperatures was also confirmed by VT-¹¹B NMR measurements in CD₂Cl₂ (Figure 6). The spectrum recorded at –80 °C revealed a resonance at δ_B 1.3 ppm and a broad signal at δ_B ~52 ppm, thus clearly indicating the presence of the **1**-mono-closed form. Upon increasing the temperature, the intensity of the signal corresponding to the B–N coordination bonds decreased, while the signal attributed to the three-coordinated boron species increased.

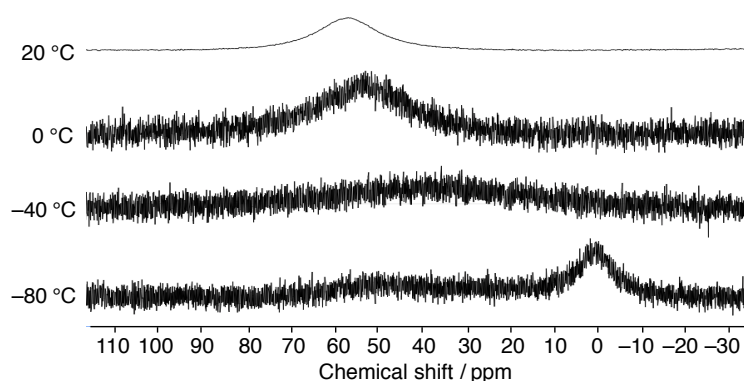


Figure 9. VT-¹¹B NMR spectra in CD₂Cl₂ of **1**.

Solvatochromism and Thermochromism of **2**

Similar to diborylated derivative **1**, monoborylated derivative **2** also shows solvatochromic and thermochromic behaviors despite the difference in the crystal structures regarding presence or absence of B–N coordination bond. Compound **2** in CH₂Cl₂ shows two absorption bands in visible region at 584 nm and 430 nm. UV/vis spectra of **2** in various organic solvents show that the intensity of the longest absorption increased accompanied with slightly blue-shifts from 599 nm (cyclohexane) to 583 nm (DMF) upon increasing the solvent polarity (Figure 10a). Moreover, thermochromic

behavior of **2** was also observed in VT-UV/vis absorption spectra in DMF from $-40\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$. Upon heating, the intensity of the peak around $\lambda = 593\text{ nm}$ (**2**-closed) decreased and that around $\lambda = 431\text{ nm}$ (**2**-open) increased (Figure 10b).

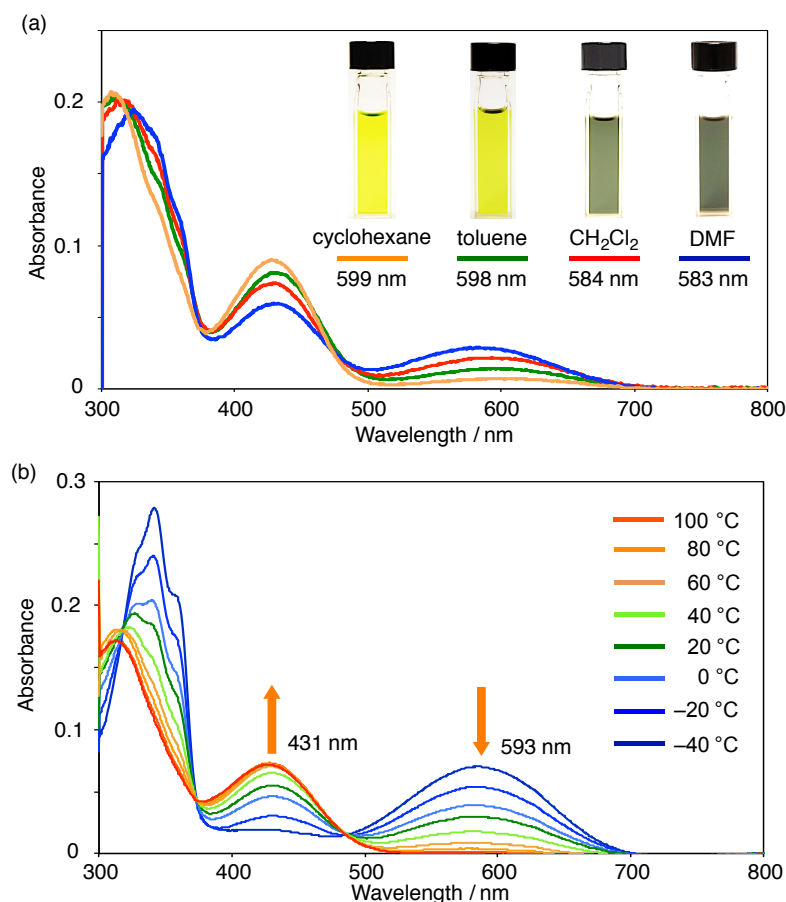


Figure 10. (a) Solvatochromism of **2** in different solvents at room temperature and (b) thermochromism of **2** in DMF. The wavelength of the longest absorption bands and the pictures of solutions are included.

Similarly, VT- ^{11}B NMR measurements of **2** in CD_2Cl_2 solution confirmed that the thermochromism is induced by the reversible formation of intramolecular coordination bonds (Figure 11). ^{11}B NMR spectrum recorded at $-80\text{ }^{\circ}\text{C}$ showed a signal around $\delta_{\text{B}} = -10\text{ ppm}$ assignable to four-coordinated boron atoms for the **2**-closed form. Upon increasing the temperature, this signal gradually shifted to low magnetic field. The observed signal around $\delta_{\text{B}} = \sim 50\text{ ppm}$ at room temperature is assignable to three-coordinated boron atoms and clearly indicates the presence of **2**-open form as the dominant conformation at higher temperature.

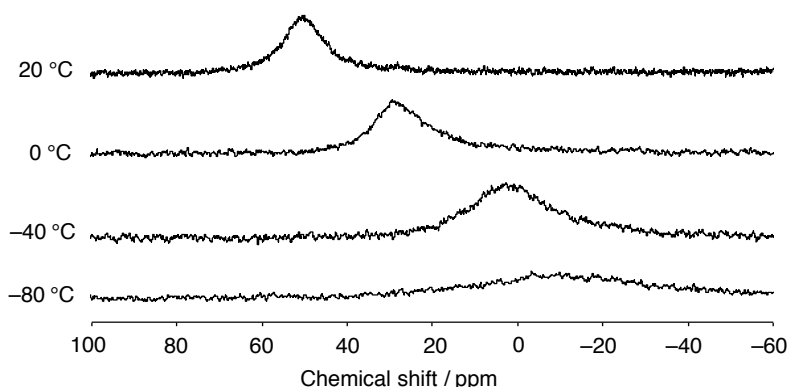


Figure 11. VT- ^{11}B NMR spectra in CD_2Cl_2 of **2**.

According to the results of DFT calculations (M06-2X/6-31G(d)), **2**-open form without B–N bond as well as **2**-closed were optimized as shown in Figure 12. The Gibbs free energy (G) for **2**-closed is higher by 3.80 kcal/mol than that of **2**-open form. In a similar manner to **1**, the HOMO-LUMO gap in **2**-closed form is diminished upon formation of B–N bond, compared to that in **2**-open form. TD-DFT calculations (M06-2X/6-31G(d)//M06-2X/6-31G(d)) on **2**-open and **2**-closed forms confirmed that the longest absorption wavelengths of $\lambda = 435$ nm (**2**-open) and $\lambda = 586$ nm (**2**-closed) are in good agreement with those for the observed peaks in solution (430 nm, 584 nm) (Figures 10a and 12).

Based on the analysis of absorbance using the oscillator strengths ($f = 0.238$ (**2**-open) and $f = 0.241$ (**2**-closed)), obtained from TD-DFT calculations (Figure 12), the abundance ratio of **2**-open and **2**-closed forms in DMF was estimated to be 95:5 at 100 °C, 65:35 at 20 °C, and 22:78 at -40 °C, respectively, leading to ΔG in the range from +2.93 to -0.588 kcal/mol (for details, Experimental section).

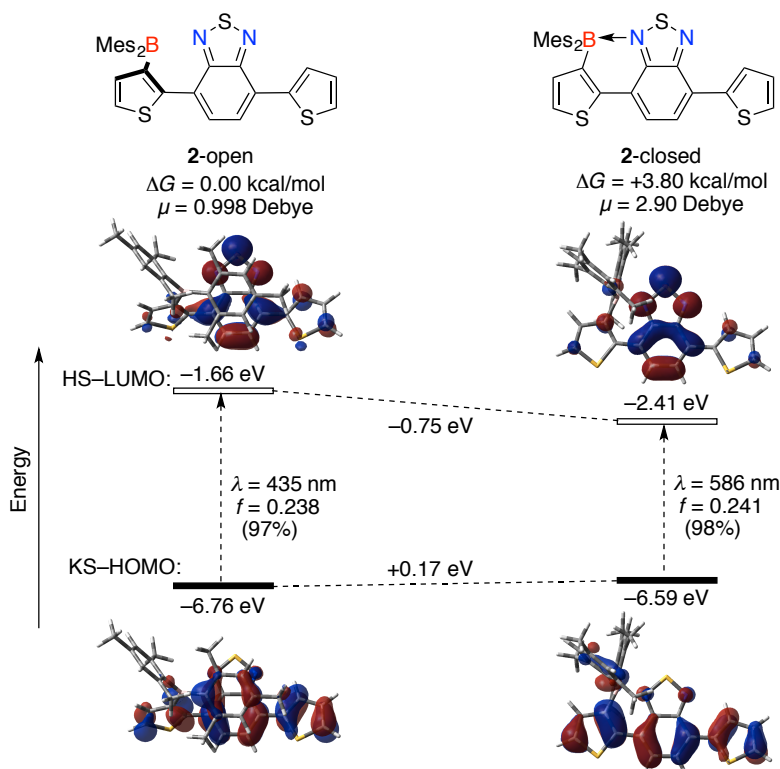


Figure 12. The calculated energy diagrams for **2**-open and **2**-closed (M06-2X/6-31G(d)). The longest absorption profiles corresponding to HOMO→LUMO transition, the oscillator strengths, and the contribution (TD-M06-2X/6-31G(d)/M06-2X/6-31G(d)) are shown. Transition energies were calibrated using a factor of 0.90.

Thermofluorochromism of **1** and **2**

The fluorescence spectrum of the toluene solution of **1** at room temperature shows two peaks at $\lambda_{\text{em}} = 568$ nm ($\Phi_{\text{em}} = 0.12$, $\lambda_{\text{ex}} = 470$ nm) and $\lambda_{\text{em}} = 718$ nm ($\Phi_{\text{em}} = 0.02$, $\lambda_{\text{ex}} = 590$ nm), corresponding to the **1**-open and **1**-mono-closed forms, respectively (Figure 9). The intensity of these two fluorescence peaks also shows temperature dependency corresponding to the varying abundance ratio of each form. Upon cooling, the orange-yellow fluorescence peak around $\lambda_{\text{em}} = 560$ nm gradually decreased and almost disappeared at -40 °C; in contrast, the intensity of the NIR fluorescence peak around $\lambda_{\text{em}} = 720$ nm simultaneously increased. (Figure 13). The observed properties are particularly interesting, considering that the fluorescence in the visible and NIR regions can be switched by the reversible formations of intramolecular B–N bonds.

Similar thermofluorochromic behavior was also observed in the solution of **2** (Figure 14). Upon cooling to -40 °C, orange-yellow fluorescence peak around 553 nm

decreases and, instead, the fluorescence peak around 740 nm in NIR region increases.

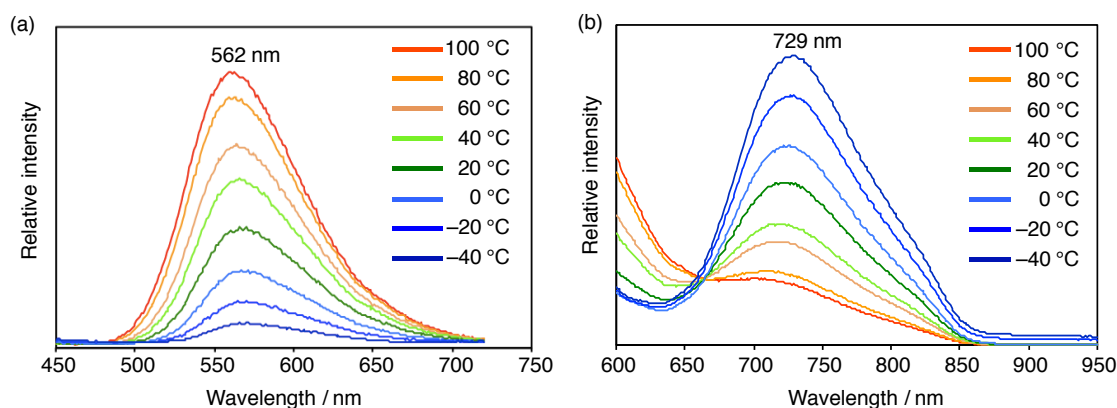


Figure 13. Temperature-dependent fluorescence spectra of **1** excited (a) at 370 nm and (b) at 540 nm in toluene.

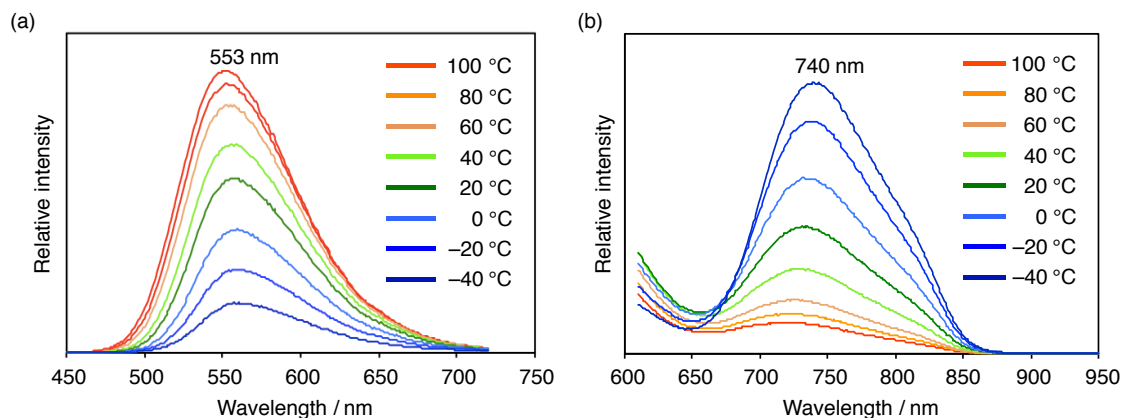


Figure 14. Temperature-dependent fluorescence spectra of **2** excited (a) at 370 nm and (b) at 570 nm in toluene.

Mechanochromism of **1**

Despite the similar behavior in solution, crystals of **1** and **2** present a different conformation with respect to absence or presence of a B–N coordination bond (*vide supra*; Figures 4 and 5). Accordingly, the conformation of **1** and **2** in the solid state must be highly affected by packing forces. In addition to the aforementioned relationship between the conformation and the packing structure, the author also found that crystals of **1** exhibit mechanochromism. The color of crystalline solids of **1** changed from yellow to dark green upon mechanical grinding (Figure 15a and b). The obtained green solids immediately reverted to yellow upon exposure to MeOH vapor or immersion in MeOH. The solid-state ^{11}B NMR measurements of the green solids obtained from grinding exhibited a new signal at δ_{B} 7.6 ppm, corresponding to a

four-coordinated boron center, in addition to a signal at δ_B 62.7 ppm (Figure 15b), suggesting that the mechanochromism should be due to the partial formation of **1**-mono-closed with an intramolecular B–N coordination bond.

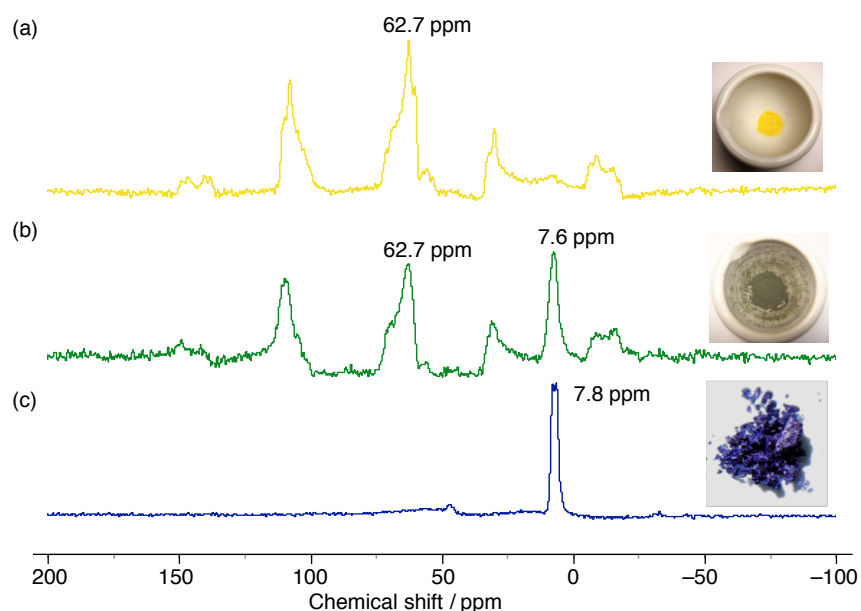


Figure 15. Solid-state MAS-¹¹B NMR spectra (257 MHz) of (a) yellow crystalline solids of **1**, (b) dark green solids of **1** obtained after grinding, and (c) dark blue crystalline solids of **2** with their photos. Spinning sidebands remained for (a) and (b) due to the low spinning speed.

The powder XRD patterns of the green solids exhibited some diffraction peaks at angles similar to those of the original yellow crystalline solids, corresponding to the (111), (200), (300), and ($3\bar{2}\bar{1}$) planes, although the peaks are slightly broadened. This result indicates that the green solids maintain the crystalline structure of **1**-open, despite the smaller particle size after grinding. A critical difference of the green solids is seen in the significantly decreased relative intensity of the diffraction peak at $2\theta = 16.8^\circ$, which corresponds to the ($2\bar{2}\bar{2}$) plane (Figure 16b). According to the single-crystal XRD analysis (*vide supra*, Figure 4), the ($1\bar{1}\bar{1}$) plane corresponds to the parallel direction of the arrangement of the Mes₂B groups in the packing structure of **1** (Figure 16c). Based on these results, the author concludes that the crystals of **1** are preferentially fractured along this plane upon mechanical grinding, which affords an amorphous phase on the surface of the crystals, wherein the **1**-mono-closed conformation is formed preferentially as a result of the reduced packing forces between the bulky Mes₂B groups

observed in the crystal structure of **1**-open. Most likely, the significantly different solubility of the amorphous and the crystalline phase in MeOH results in the instantaneous recovery of the yellow crystalline solids upon selectively washing out the surface containing **1**-mono-closed form with MeOH.

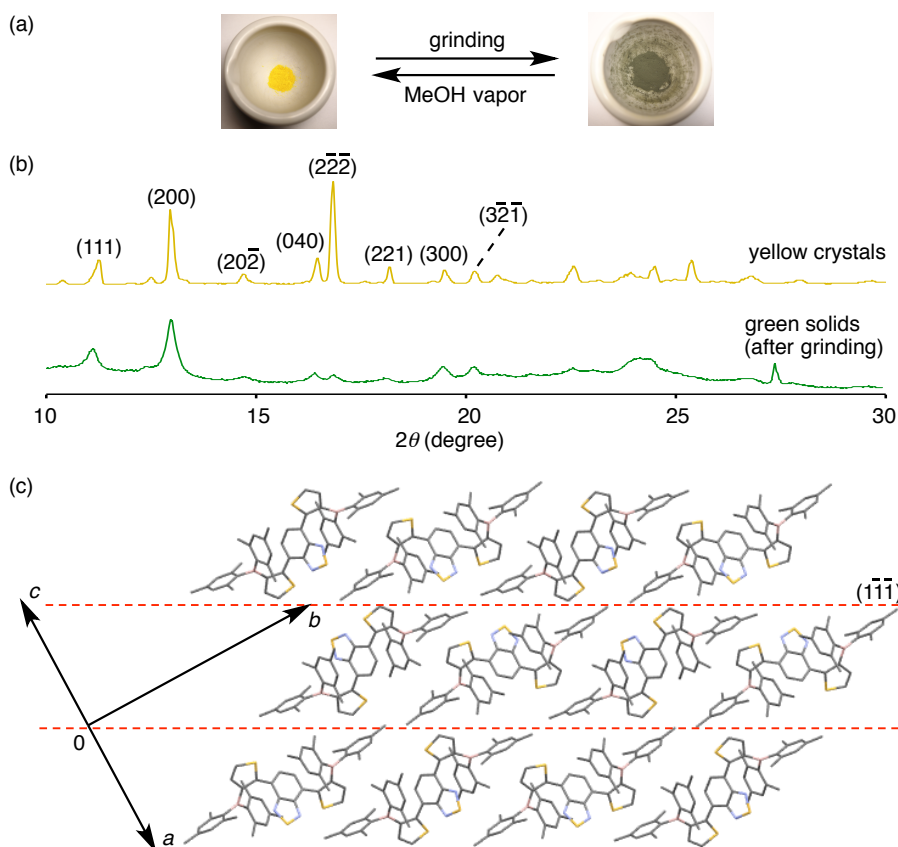


Figure 16. (a) Yellow crystals of **1** before and after grinding. (b) Powder XRD patterns ($\lambda = 1.54 \text{ \AA}$) of yellow crystals of **1** (yellow) and the dark green solids of **1** after grinding (green). (c) Packing structure of **1**, seen from a vertical angle with respect to the (111) plane.

Conclusion

In summary, boryl-substituted dithienylbenzothiadiazole derivative **1** with bulky Mes_2B groups were designed and synthesized. The author demonstrated that the combination of sterically demanding boryl groups, such as Mes_2B , with a benzothiadiazole unit induces the reversible formation of an intramolecular B–N bond, which can be controlled by external stimuli (solvent, temperature, and packing forces), leading to solvatochromism, thermochromism, and mechanochromism. The formation of these intramolecular B–N bonds has a significant impact on the present system, as it

lowers the HOMO–LUMO gap, which results in drastic color changes in the visible region, as well as in vis/NIR fluorescence switching. X-ray diffraction studies revealed that mechanical grinding fractures crystals of **1** along the (11 $\bar{1}$) plane, which alters the packing forces and represents a key factor for the mechanochromism. The present results thus demonstrate that the reversibility of intramolecular B–N bond formation induced by steric bulkiness can be used as the basis for novel chromic functional materials. Based on this new molecular design principle, the author believes that it should be possible to attain several other intriguing functional materials in the near future.

Experimental Section

General

Melting points (mp) were measured on a Stanford Research System OptiMelt. MPA100 instrument. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with a Varian Mercury 300 MHz (300 MHz for ^1H and 75.5 MHz for $^{13}\text{C}\{^1\text{H}\}$), VT- ^{11}B NMR spectra were recorded with a JEOL AL-500 spectrometer (160 MHz for ^{11}B), and solid state ^{11}B NMR spectra were recorded with a Bruker Advance III 800US Plus (257 MHz for ^{11}B). Chemical shifts are reported in δ ppm using residual protonated solvent in the deuterated solvents for ^1H and deuterated solvent peak for ^{13}C NMR as an internal standard, whereas $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) for ^{11}B as an external standard. UV/vis absorption spectra were recorded on a Shimadzu UV-3150 spectrometer, in degassed spectral grade solvents. Fluorescent spectra were recorded on a HORIBA FluoroMax 4. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia). The Gel Permeation Chromatography (GPC) was performed using JAI LC-908 apparatus with JAIGEL-1H and 2H columns using toluene as eluent at the flow rate of 3.8 mL/min. All reactions were carried out under argon atmosphere unless otherwise noted.

Synthesis

4,7-Bis(3-bromothieryl)benzo[2,1,3]thiadiazole (**3**).

A solution of LDA (1.07 M in THF, 50 mL) was added dropwise to a solution of 3-bromothiophene (8.07 mL, 85.1 mmol) in THF (30 mL) at $-78\text{ }^{\circ}\text{C}$. After the mixture was stirring for 30 minutes, $\text{ZnCl}_2\cdot\text{TMEDA}$ (14.7 g, 58.2 mmol) was added via a cannula at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and stirred for 1 h. The mixture was added into a mixture of 4,7-dibromobenzothiadiazole (8.53 g, 29.0 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (298.0 mg, 0.288 mmol), and PPh_3 (301 mg, 1.15 mmol) in THF (200 mL) by a syringe, and the mixture was stirring for 4 hours under reflux. After an addition of distilled water, the organic layer was separated. The obtained aqueous layer was extracted with chloroform (100 mL) three times. The combined organic layer was dried over Na_2SO_4 . After the removal of the solvent, the crude product was purified by silica gel column chromatography (1:1 hexane/ CH_2Cl_2 , $R_f = 0.25$) to give 5.34 g (11.7 mmol) of **3** in 40% yield as yellow crystalline solids.

Mp: $192.7\text{--}194.6\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 8.10 (s, 2H), 7.53 (d, $J = 5.5$ Hz, 2H), 7.19 (d, $J = 5.5$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3): 153.4, 132.9, 131.3, 129.9, 127.5, 125.9, 110.5; HRMS (APCI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{S}_3$, 455.8054; found, 455.8036; Elemental analysis calcd. (%) for $\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{S}_3$: C 36.70, H 1.32, N 6.11; found, C 36.50, H 1.36, N 6.08.

4,7-Bis[(3-dimesitylboryl)thien-2-yl]benzo[2,1,3]thiadiazole (**1**) and 4-[(3-dimesitylboryl)thien-2-yl]-7-thienylbenzo[2,1,3]thiadiazole (**2**).

A hexane solution of *n*-BuLi (2.41 M, 1.93 mL, 4.65 mmol) was added to a solution of 4,7-bis(3-bromothieryl)benzothiadiazole (850 mg, 1.86 mmol) in THF (150 mL) at $-78\text{ }^{\circ}\text{C}$. After the mixture was stirring for 5 min, a solution of Mes_2BF (2.50 g, 9.32 mmol) in THF (5 mL) was added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. The mixture was warmed in water bath and stirred for 30 min. To the reaction mixture, water (75 mL) and CHCl_3 (75 mL) was added. The obtained organic layer was washed with brine, and then dried over Na_2SO_4 . After the removal of the solvent under vacuum, the crude product was purified by silica gel column chromatography (1:3 hexane/ CH_2Cl_2 , **1**: $R_f = 0.36$, **2**: $R_f = 0.39$) and GPC with toluene as an eluent (retention time; **1**: 42 min, **2**: 53 min) to give 134 mg (0.177 mmol) of **1** in 10% yield as yellow crystalline solids and 50 mg (0.109 mmol) of **2** in 6% yield as blue solids.

1: Mp: 259.8–261.5 °C; ^1H NMR (500 MHz, CDCl_3 , room temperature): δ 7.37 (d, J = 5.2 Hz, 2H), 7.14 (s, 2H), 7.09 (d, J = 5.2 Hz, 2H), 6.51 (br, 8H), 2.12 (s, 12H), 1.94 (s, 24H); ^{13}C NMR (151 MHz, CDCl_3 , room temperature): δ 152.1 (br)*, 151.6, 144.8 (br)*, 143.8, 140.1, 137.6, 135.1, 128.3 (Two CH carbons overlapped.),** 126.6, 126.0, 23.7, 21.0. *Due to the broadening caused by the coupling with quadrupolar ^{11}B and ^{10}B nuclei. **In HMQC spectrum, the signal at 128.3 ppm has correlations with two ^1H signals at 7.14 and 6.51 ppm which are assignable to β -position of thiophene and Mes groups, respectively. Furthermore, only three CH carbons are observed in DEPT 90 spectrum, although **1** has four CH carbons. These observations suggest that the signal of β -carbon of thiophene and CH carbon of Mes groups overlapped in ^{13}C NMR spectrum. HRMS (APCI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{50}\text{H}_{50}\text{B}_2\text{N}_2\text{S}_3$, 796.3333; found, 796.3355.

2: Mp: 150.5–152.5 °C, ^1H NMR (500 MHz, CDCl_3 , room temperature): δ = 8.00 (dd, J = 3.7 Hz, 1.1 Hz, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.45 (dd, J = 5.2 Hz, 1.1 Hz, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.37 (d, J = 4.9 Hz, 1H), 7.19 (dd, J = 5.2, 3.7 Hz, 1H), 7.13 (d, J_{HH} = 4.9 Hz, 1H), 6.48 (br, 4H), 2.05 (s, 6H), 2.00 (s, 12H); ^{13}C NMR (76 MHz, CDCl_3 , room temperature): δ 153.1 (br), 151.4, 145.6 (br), 143.7, 140.1, 139.0, 137.7, 135.4 (CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 127.2, 126.7 (CH), 125.8, 125.7 (CH), 125.6 (CH), 23.6, 20.9. One aromatic quaternary carbon misses due to the overlaps. The missing is not probably due to the coupling with ^{11}B and ^{10}B nuclei, because the chemical shift of two broad signals observed at 153.1 and 145.6 are very close to those of broad signals of **1** (See above); HRMS (APCI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{32}\text{H}_{29}\text{BN}_2\text{S}_3$, 548.1586; found, 548.1602.

Single Crystal X-Ray Structural Analysis of **1** and **2**

Compound 1: The single crystals suitable for X-ray analysis were obtained by diffusion of MeOH into a solution of compound **1** in CH_2Cl_2 . Intensity data were collected at 103 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo $\text{K}\alpha$ radiation (λ = 0.71075 Å) and graphite monochromator. The collected diffraction data were processed with the HKL2000 software program. A total of 35646 reflections were measured with a maximum 2θ angle of 50.1°, of which 7556 were independent reflections (R_{int} = 0.0511). The structure was solved by direct methods (SHELXS-97²⁴) and refined by the full-matrix least-squares on F^2 (SHELXL-97²⁴). The molecule sits on symmetric axis. The

dithienylbenzothiadiazole moieties were disordered and were solved using an appropriate disordered model with the occupancies of S1A–S3A, N1A–N2A, C1A–C14A, H1A–H14A and S1B–S3B, N1B–N2B, C1B–C14B, H1B–H14B as 0.55 and 0.45, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{50}H_{50}B_2N_2S_3$; FW = 796.72, crystal size $0.15 \times 0.10 \times 0.10 \text{ mm}^3$, Monoclinic, $P2_1/c$, $a = 14.2558(3) \text{ \AA}$, $b = 21.4828(6) \text{ \AA}$, $c = 14.8835(3) \text{ \AA}$, $\beta = 109.3926(11)^\circ$, $V = 4299.53(17) \text{ \AA}^3$, $Z = 4$, $D_c = 1.231 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0783$, $wR_2 = 0.2223$ ($I > 2\sigma(I)$), GOF = 1.051.

Compound 2: The single crystals were obtained by diffusion of MeOH into a solution of compound **2** in $CHCl_3$. Intensity data were collected at 93 K using a diffractometer equipped with an ADSC Quantun315 CCD detector with synchrotron radiation at a wavelength of $0.75 \text{ \AA}$ at the SPring-8 beamline BL38B1. A total of 11364 reflections were measured with a maximum 2θ angle of 44.2° , of which 5115 were independent reflections ($R_{int} = 0.0583$). The structure was solved by direct methods (SHELXS-97²⁴) and refined by the full-matrix least-squares on F^2 (SHELXL-97²⁴). The molecule sits on symmetric axis. The thienyl moieties were disordered and were solved using an appropriate disordered model with the occupancies of S3A, C12A, H12A–H14A, and S3B, C12B, H12B–H14B as 0.67 and 0.33, and S6A, C44A, H44A–H46A, and S6B, C44B, H44B–H46B as 0.75 and 0.25, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{64}H_{58}B_2N_4S_6$; FW = 1097.12, crystal size $0.10 \times 0.05 \times 0.02 \text{ mm}^3$, Triclinic, $P-1$, $a = 7.4345(2) \text{ \AA}$, $b = 16.7184(4) \text{ \AA}$, $c = 22.1296(8) \text{ \AA}$, $\alpha = 102.6967(9)^\circ$, $\beta = 93.4997(12)^\circ$, $\gamma = 90.096(3)^\circ$, $V = 2677.97(14) \text{ \AA}^3$, $Z = 2$, $D_c = 1.361 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.1680$, $wR_2 = 0.4518$ ($I > 2\sigma(I)$), GOF = 1.284.

Our many efforts to obtain the suitable size of single crystal for X-ray structural analysis resulted in only obtaining tiny needle crystals, which may be due to the structural flexibility of **2** in solution. The structural analysis was conducted on such a tiny crystal using synchrotron. However, the sufficient number of independent reflections could not be obtained due to the essential problem of apparatus which can collect the reflections using only a single rotation of ϕ axis. In addition, significant numbers of reflections were missing at higher θ region due to tininess of the crystal. As

a result, the value of $\theta_{\max}$ is low and that of wR_2 is large as pointed out with Alart A in check CIF. Although the details of the structure could not be discussed, the obtained molecular structure would be reliable with respect to the presence of an intramolecular B–N bond, which is also clearly confirmed by the result of solid state ^{11}B NMR of **2** (Figure 15c).

Powder X-Ray Diffraction Analysis of **1**

Powder X-ray diffraction data were collected at room temperature with a Bruker D8 ADVANCE diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and analyzed by the Le Bail method using the RIETAN-FP program.²⁵

Theoretical Calculations

Geometry optimization and time-dependent (TD)-DFT calculations for **1**-open/**1**-mono-closed/**1**-di-closed and **2**-open/**2**-closed were performed by using Gaussian 09 (revision A.02) program by M06-2X method with 6-31G(d) basis sets.²⁶

Optimizations for **1** were carried out for structures with no B–N bonds (**1**-open), one B–N bond (**1**-mono-closed), and two B–N bonds (**1**-di-closed), and their minimum energies were confirmed by frequency calculations.

The Abundance Ratio of Open and Closed Forms in Solution

The abundance ratio of **1**-open and **1**-mono-closed in toluene was estimated by using absorbance at $\lambda = 410 \text{ nm}$ and 575 nm (Figure 8b) and calculated oscillator strengths obtained by DFT calculations (Figure 7) with the following two hypotheses. First, based on the calculated oscillator strengths ($f = 0.190$ (**1**-open) and $f = 0.203$ (**1**-mono-closed)), the author assume that the ratio of extinction coefficients for the longest absorption between **1**-open and **1**-mono-closed is the same as that of oscillator strengths as following equation (Equation 1),

$$\varepsilon_o = (0.190/0.203) \times \varepsilon_c \quad 1$$

where ε_o and ε_c are the extinction coefficient at the peak top of the longest absorption band of **1**-open and **1**-mono-closed forms, respectively. Second, since the isosbestic point ($\lambda = 410 \text{ nm}$, where $\varepsilon_o = \varepsilon_c$ (ε_c : the extinction coefficient for the second longest absorption of **1**-mono-closed)) is close to the peak top of the longest absorption band ($\lambda = 402 \text{ nm}$) of **1**-open form, the absorption (A_{410}) at $\lambda = 410 \text{ nm}$ (isosbestic point) can be

represented as following equation (Equation 2),

$$A_{410} = \varepsilon_o (c_c + c_o) L \quad 2$$

where A_{410} is the absorbance at $\lambda = 410$ nm, c_c and c_o are the molar concentration of **1**-mono-closed and **1**-open, and L is the path length (cm), respectively. The absorption at $\lambda = 575$ nm for **1**-mono-closed is described as the following equation (Equation 3),

$$A_{575} = \varepsilon_c c_c L \quad 3$$

where A_{575} is the absorbance at $\lambda = 575$ nm, ε_c and c_c are the extinction coefficient and the molar concentration of **1**-mono-closed, and L is the path length (cm), respectively. The following equation (Equation 4) is developed from above equations (Equations 1–3),

$$c_c/(c_c + c_o) = (A_{575}/A_{410}) (0.190/0.203) \quad 4$$

where $c_c/(c_c + c_o)$ means the abundance ratio of **1**-mono-closed form. Based on the ratio of $c_c : c_o$, the Gibbs free energy (G) can be estimated using the following equations (Equations 5 and 6),

$$\Delta G = -RT \ln K_{eq} \quad 5$$

$$K_{eq} = c_c/c_o \quad 6$$

where R is the gas constant ($R = 1.987$ cal K⁻¹ mol⁻¹), T is the absolute temperature, K_{eq} is the equilibrium constant, respectively. The obtained values are summarized in Table 2 and Figure 17.

According to the following equation (Equation 7),

$$\Delta G = \Delta H - T\Delta S \quad 7$$

where H is the enthalpy, T is the temperature (K), and S is the entropy, respectively., the following values are determined as $\Delta H_{\text{closed-open}} = -4.67$ kcal mol⁻¹ and $\Delta S_{\text{closed-open}} = -16.1$ cal K⁻¹ mol⁻¹. Thus, the ΔG value at 25 °C in toluene is estimated as $\Delta G_{\text{closed-open}} = +0.130$ kcal mol⁻¹, which is in good agreement with the calculated value ($\Delta G_{\text{closed-open}} = +1.02$ kcal mol⁻¹) obtained from DFT calculations (Figure 7).

Table 2. The Abundance Ratio of **1**-open and **1**-mono-closed Depending on Temperature in Toluene

	A_{575}/A_{410}	$c_c : c_o$	$K_{eq} (= c_c/c_o)$	$\Delta G_{closed-open}$
−40 °C	0.969	91 : 9	9.80	−1.06 kcal/mol
−20 °C	0.775	78 : 22	2.65	−0.489 kcal/mol
0 °C	0.663	62 : 38	1.64	−0.267 kcal/mol
20 °C	0.502	47 : 53	0.885	+0.0708 kcal/mol
40 °C	0.367	34 : 66	0.523	+0.403 kcal/mol
60 °C	0.269	25 : 75	0.336	+0.721 kcal/mol
80 °C	0.205	19 : 81	0.237	+1.01 kcal/mol
100 °C	0.165	15 : 85	0.183	+1.26 kcal/mol

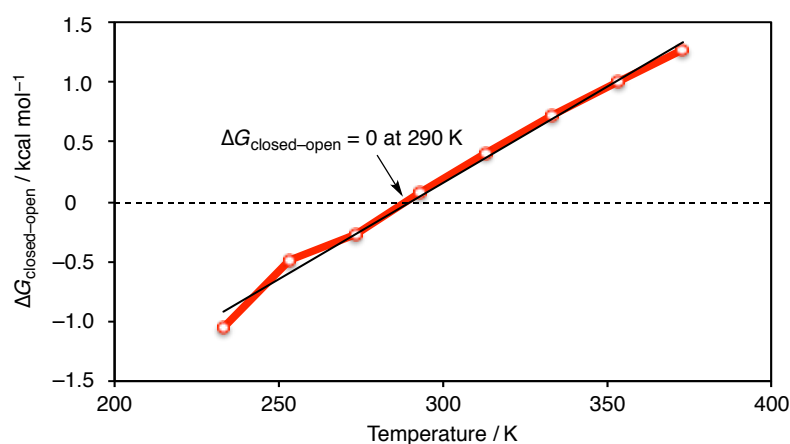


Figure 17. The difference of the Gibbs free energy ($\Delta G_{closed-open}$) between **1**-mono-closed and **1**-open depending on temperature in toluene.

The abundance ratio of **2**-open and **2**-closed was also estimated by using absorbance at $\lambda = 428$ nm and 587 nm in DMF (Figure 10b) and calculated oscillator strengths obtained by DFT calculations (Figure 12) with the following two hypotheses. First, the author regards the absorptions at $\lambda = 428$ nm and 587 nm correspond to only **2**-open and **2**-closed form, respectively. Second, he assume that the extinction coefficients for the longest absorption of **2**-open and **2**-closed are in the same ratio of the calculated oscillator strengths ($f = 0.238$ (**2**-open) and $f = 0.241$ (**2**-closed)). Based on above two hypotheses, the following equations (Equations 8–10) are described,

$$\varepsilon_o = (0.238/0.241) \times \varepsilon_c \quad 8$$

$$A_{428} = \varepsilon_o c_o L \quad 9$$

$$A_{587} = \varepsilon_c c_c L \quad 10$$

where ε_o and ε_c are the extinction coefficient of **2**-open ($\lambda = 428$ nm) and **2**-closed ($\lambda = 587$ nm), A_{428} and A_{587} are the absorbance at $\lambda = 428$ nm and $\lambda = 587$ nm, c_o and c_c are the molar concentration of **2**-open and **2**-closed, and L is the path length (cm), respectively. Then, the above equations (Equations 8–10) develop the following equation (Equation 11),

$$c_c/c_o = (A_{587}/A_{428}) (0.238/0.241) \quad 11$$

where c_c and c_o are the molar concentration of **2**-closed and **2**-open, and A_{587} and A_{428} are the absorbance at $\lambda = 587$ nm and $\lambda = 428$ nm, respectively. The estimated abundance ratios of $c_c : c_o$ at each temperature are summarized in Table 3. Based on these ratio, the ΔG were also estimated using Equations 5–6 and obtained values are given in Table 3 and Figure 18.

According to Equation 7, the following values are determined as $\Delta H_{\text{closed-open}} = -6.52$ kcal mol⁻¹ and $\Delta S_{\text{closed-open}} = -24.3$ cal K⁻¹ mol⁻¹. Moreover, according to Equation 7 and these values, the $\Delta G_{\text{closed-open}}$ at 25 °C in DMF is estimated to be +0.731 kcal mol⁻¹.

Table 3. The Abundance Ratio of **2**-open and **2**-closed Depending on Temperature in DMF

	A_{587}/A_{428}	$c_c : c_o$	$K_{\text{eq}} (= c_c/c_o)$	$\Delta G_{\text{closed-open}}$
−40 °C	3.60	78 : 22	3.56	−0.588 kcal/mol
−20 °C	1.78	64 : 36	1.75	−0.283 kcal/mol
0 °C	0.843	45 : 55	0.832	+0.0996 kcal/mol
20 °C	0.541	35 : 65	0.534	+0.365 kcal/mol
40 °C	0.271	21 : 79	0.267	+0.821 kcal/mol
60 °C	0.123	11 : 89	0.121	+1.40 kcal/mol
80 °C	0.0531	5 : 95	0.0515	+2.08 kcal/mol
100 °C	0.0194	2 : 98	0.0191	+2.93 kcal/mol

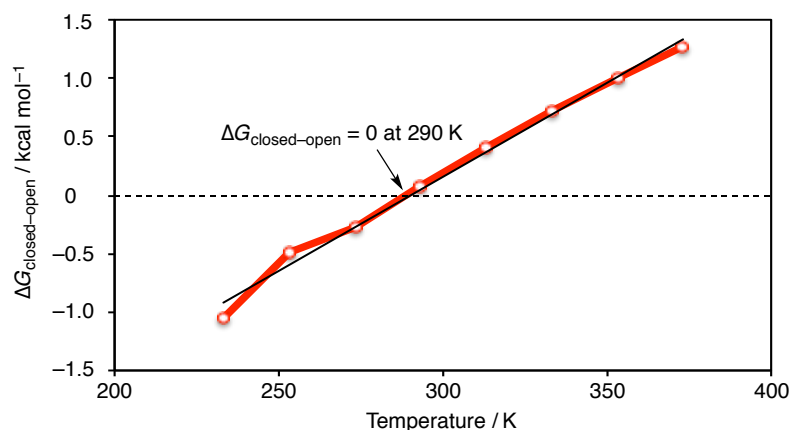


Figure 18. The difference of the Gibbs free energy ($\Delta G_{\text{closed-open}}$) between **2**-closed and **2**-open depending on temperature in DMF.

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Chapter 4

D- π -A Dyes Using an Intramolecular B-N Coordination Bond as a Key Scaffold for Electronic Structural Tuning and Their Application in Dye-Sensitized Solar Cells

Abstract: A series of D- π -A dyes (**AK1-5**) was designed and synthesized for applications in dye-sensitized solar cells (DSSCs). **AK1-5** contain triphenylamines as electron donors (D), bithiophene π -spacers, boryl-substituted thienylthiazole as electron acceptors (A), and carboxylic acid derivatives as anchor groups. Electrochemical and photophysical measurements on **AK1-5** revealed that the use of boryl-substituted thienylthiazole moieties with intramolecular B-N coordination bonds effectively increases the electron-accepting ability of such dyes. The electronic effects of the substituents on the boron center, as well as those of the anchor group, enable fine-tuning of the LUMO level, which leads to red-shift of the absorption of these dyes. Subsequently, DSSCs based on **AK1-5** were fabricated, and their performance was examined regarding to the relationship between their electronic structure and the absorption range for photon-to-current conversion.

Introduction

The increasing global demands for energy coupled with the concerns regarding increased greenhouse gas emissions from the combustion of fossil fuels have promoted the quest for renewable and more sustainable sources of energy. Solar energy has emerged as the most promising alternative energy source. Solar cells can effectively convert sunlight energy into electricity, and have thus been studied intensively.¹ Conventional crystalline silicon-based solar cells exhibit high power conversion efficiencies beyond 25%,¹ and thus currently dominate the commercial market. The next generation of photovoltaics, i.e., organic photovoltaics (OPVs)^{2,3} and dye-sensitized solar cells (DSSCs)^{2,4} have also been studied intensively, and remarkable progress has been accomplished in the last decade. Perovskite-based solar cells represent a relatively young family of printable solar cells,^{2,5} which have emerged recently and rapidly increased their power conversion efficiencies.^{1,5} DSSCs represent highly promising photovoltaic devices, mostly on account of their ease and low cost of fabrication, their expected short energy-pay-back time (< 1 year), operation even under indoor conditions or diffuse-light, and tunable design with respect to color and transparency.⁴ While the conversion efficiency of DSSCs has increased to 13%, further improvements are required for practical applications on a commercial stage. To this end, the development of high-performance photosensitizers is one of the most crucial issues. DSSC photosensitizers are traditionally based on complexes of transition metals, such as ruthenium (Ru), which exhibit broad absorption spectra that arise from metal to ligand charge transfer (MLCT).⁶⁻¹² While some conventional Ru complexes, such as **N3**,⁷ **N-719**,⁸ **Z907**,⁹ and **N-749** (black dye),¹⁰ are used as standard DSSC sensitizers, Segawa et al. has developed a phosphine-coordinated Ru(II) sensitizer (**DX1**) that enables wide-ranging light-to-current conversion in the NIR region (~1000 nm) by exploiting direct spin-forbidden singlet-to-triplet transitions.¹¹ Apart from modifications of Ru complexes, the development of new sensitizers based on organic dyes such as porphyrin derivatives^{13,14} and π -conjugated systems of the D- π -A type^{15,16} have been pursued, mostly due to the diversity of the molecular design, as well as on account of the high extinction coefficients that arise from π - π^* transitions. For the generation of photosensitizers with efficient light-to-current conversion, the systematic development of dyes according to a novel molecular design principle should be crucial, in which the key aspect is the fine-tuning of the electronic structure in relation to the working

principle of DSSCs.

The working principle of DSSCs (Figure 1) relies on photoexcitation, which promotes dyes adsorbed on a semiconducting metal oxide surface (usually TiO_2) into their excited state, from which an electron is injected into the conduction band of the semiconductor. Subsequently, the resulting oxidized dye is reduced by the redox couple (usually I^-/I_3^-), which transfers electrons from the counter electrode. Based on this working principle, the electronic structure of dyes is subject to several requirements toward its molecular design: i) the LUMO level of the dye should be higher than the conduction band of the semiconductor (TiO_2 : -4.0 eV)^{17,18} for effective electron injection; ii) the HOMO level should be lower than the energy level of the redox couple of the electrolyte (I^-/I_3^- : -4.9 eV)^{18,19} for immediate regeneration of dyes. The estimated required potential differences as driving forces for efficient charge transfer from the dye to the semiconductor and the redox couple of the electrolyte are at least 0.2 eV ¹⁷ and 0.15 eV ,²⁰ respectively. In order to develop dyes that enable a wide-ranging light-to-current conversion including the NIR region, the control of the HOMO-LUMO gaps should be critical, which should be as narrow as possible while fulfilling the aforementioned requirements. Therefore, the fine-tuning of the electronic structures of organic dyes, especially the energy levels of their frontier orbitals, is of paramount importance to develop high-performance sensitizers for DSSC applications.

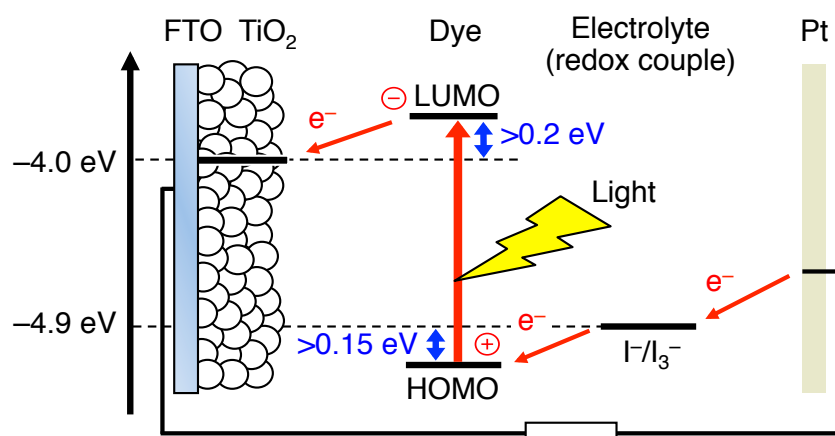


Figure 1. Energy diagram for DSSCs, including the conduction band edge of TiO_2 and the redox potential of I^-/I_3^- .

In order to control the energy levels of the frontier orbitals, the author focused on the boryl-substituted thienylthiazole unit in which B–N coordination bond enhances its

electron-accepting ability compared to the parent skeleton without boryl group (Figure 2).^{21–23} This unit has the following advantages: i) the LUMO level can be decreased without changing its distribution. The formation of B–N coordination bonds stands thus in contrast to other general modifications that rely on introducing electron-withdrawing substituents such as CN, NO₂, C=O, F, or alkyl fluorides, which leads to a deflection of the LUMO; ii) the selection of the substituents on the boron center enables fine-tuning of the LUMO level that depends on their electron-accepting ability. For example, DFT calculations at the B3LYP/6-31G(d) level of theory suggested that the replacement of the Mes groups in boryl-substituted thienylthiazole with (4-CF₃C₆H₄)₂B or (3,5-(CF₃)₂C₆H₃)₂B group decreases the Kohn–Sham (KS) LUMO level by –0.44 and –0.65 eV, respectively (Figure 2), based on the stronger electron-withdrawing ability of these substituents.

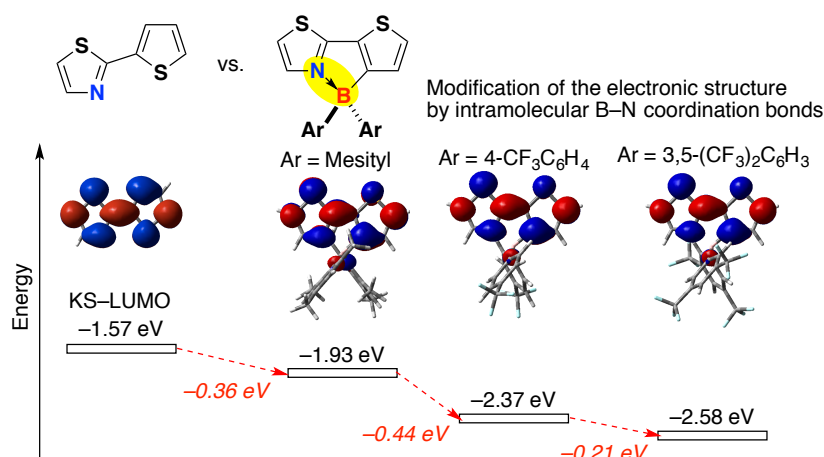


Figure 2. The effects of the formation of intramolecular B–N bonds and of the substituents on the boron center in the thienylthiazole unit; pictorial illustration and energy diagram of the Kohn–Sham (KS)-LUMOs calculated at the B3LYP/6-31G(d) level of theory.

Using this skeleton as the key electron-accepting unit that is susceptible to tuning of its electronic structure, the author designed a series of D– π –A dyes (**AK1–5**) as DSSC sensitizers (Figure 3). In addition to this acceptor unit, these D– π –A dyes contain a triphenylamine as an electron-donor unit, bithiophene as a π -spacer unit, and a carboxyl group to anchor onto TiO₂. In this chapter, the author synthesized **AK1–3**, which contain a variety of substituents on the boron center, while reference compound **AK0** does not contain a boryl group. By comparison of the properties and DSSC performance of these dyes, the impact of the formation of intramolecular B–N bonds and that of the

substituents on the boron center were examined in detail. Moreover, in order to examine the effect of the anchor unit, **AK4** and **AK5**, which contain methylenemalonic and cyanoacrylic acid anchors, respectively, were also synthesized. Herein, the author discusses the details of the electrochemical and photophysical properties of **AK0–5**, as well as the correlation between their properties in solution and their performance in DSSC devices.

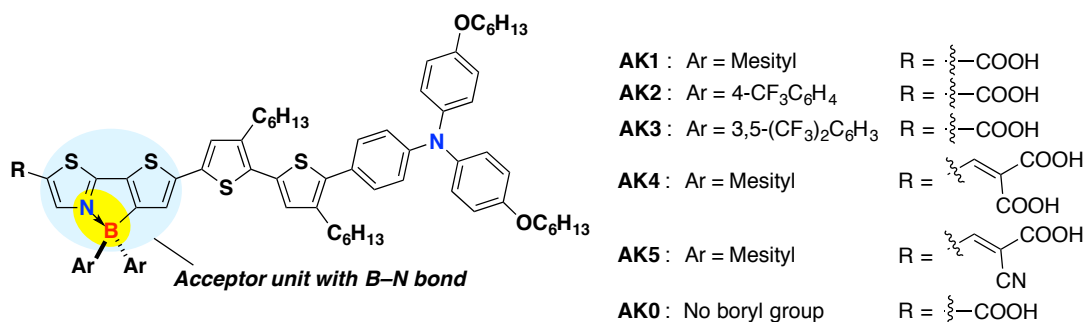


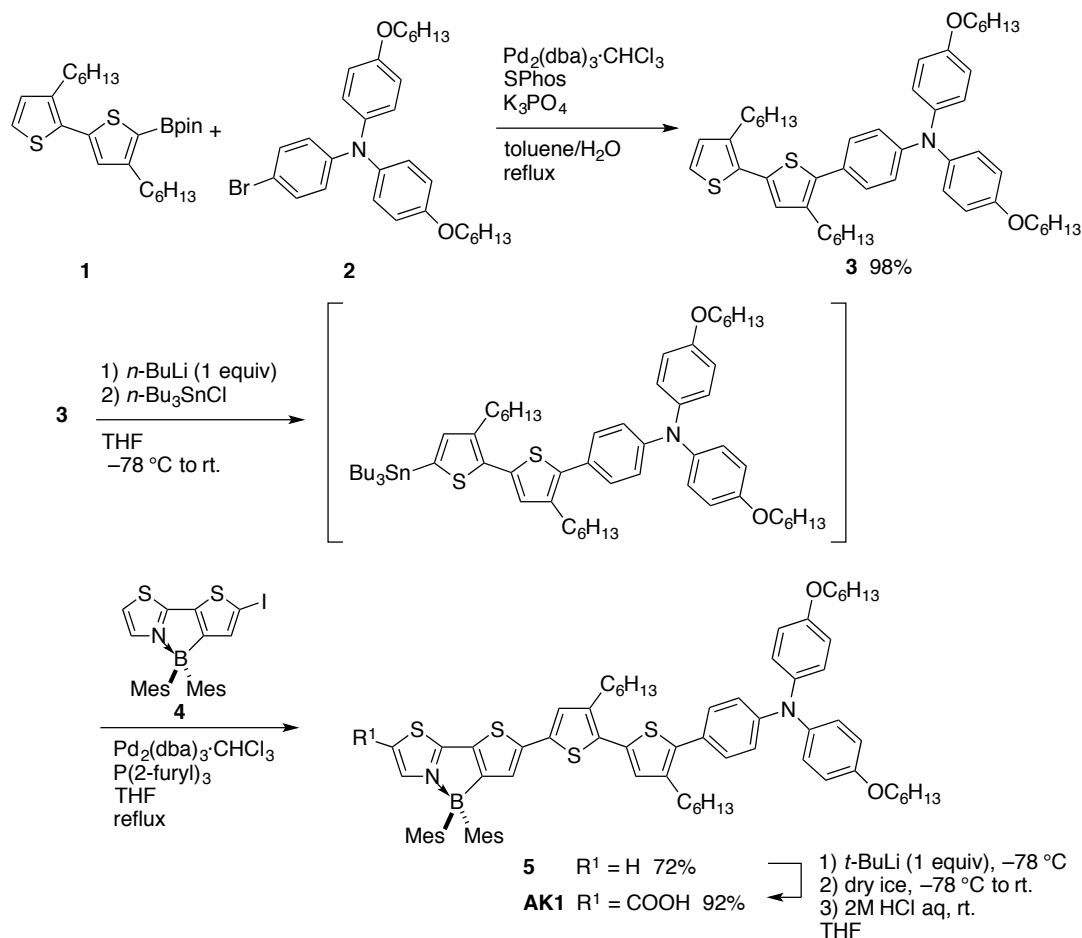
Figure 3. Molecular structures of **AK1–5** and reference compound **AK0**.

Results and Discussion

Synthesis

The outline for the synthesis of **AK1** is shown in Scheme 1. D- π unit **3** was prepared in 98% yield from the Suzuki-Miyaura cross-coupling reaction of **1** and **2**. The iodo derivative of Mes_2B -substituted thienylthiazole **4** was prepared according to a previously reported procedure.²¹ The lithiation of **3** with *n*-BuLi and a subsequent treatment with *n*-Bu $_3$ SnCl, followed by the Stille coupling with **4** gave D- π -A unit **5** in 72% yield. The lithiation of **5** with *t*-BuLi, followed by quenching with crushed dry ice and a work-up with 2 M aqueous HCl, afforded **AK1** in 92% yield.

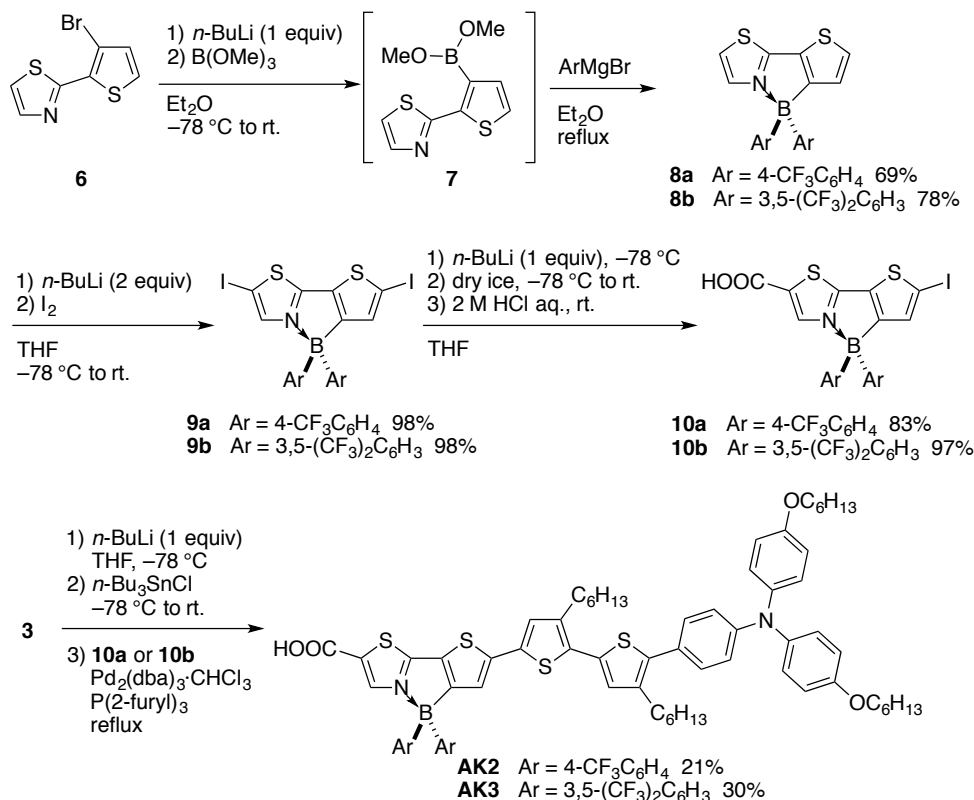
Scheme 1. Synthesis of **AK1**



As shown in Scheme 2, **AK2** and **AK3**, which possess 4- $\text{CF}_3\text{C}_6\text{H}_4$ and 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ substituents on the boron center, respectively, were synthesized by a nucleophilic substitution of dimethoxyboryl-substituted thienylthiazole (**7**). Dimethoxyboryl-substituted thienylthiazole **7** was prepared by lithiation of **6** with *n*-BuLi and a subsequent treatment with $\text{B}(\text{OMe})_3$, and directly used for the ensuing nucleophilic substitution reaction in a one-pot fashion. Subsequently, **7** was treated with the corresponding aryl-Grignard reagents to give **8a** and **8b** in 69% and 78% yields (relative to **6**), respectively. In a similar way to Mes_2B derivative **4**, the treatment of the dilithio derivatives of **8a** and **8b**, which were generated by the treatment of **8a** and **8b** with two equivalents of *n*-BuLi, with iodine furnished diiodo derivatives **9a** and **9b** in 98% yields. The selective monolithiation of **9a** and **9b** with one equivalent of *n*-BuLi, followed by quenching with crushed dry ice and a work-up with 2 M aqueous HCl, afforded **10a** and **10b**, both of which bear a carboxyl group at the 5-position on the

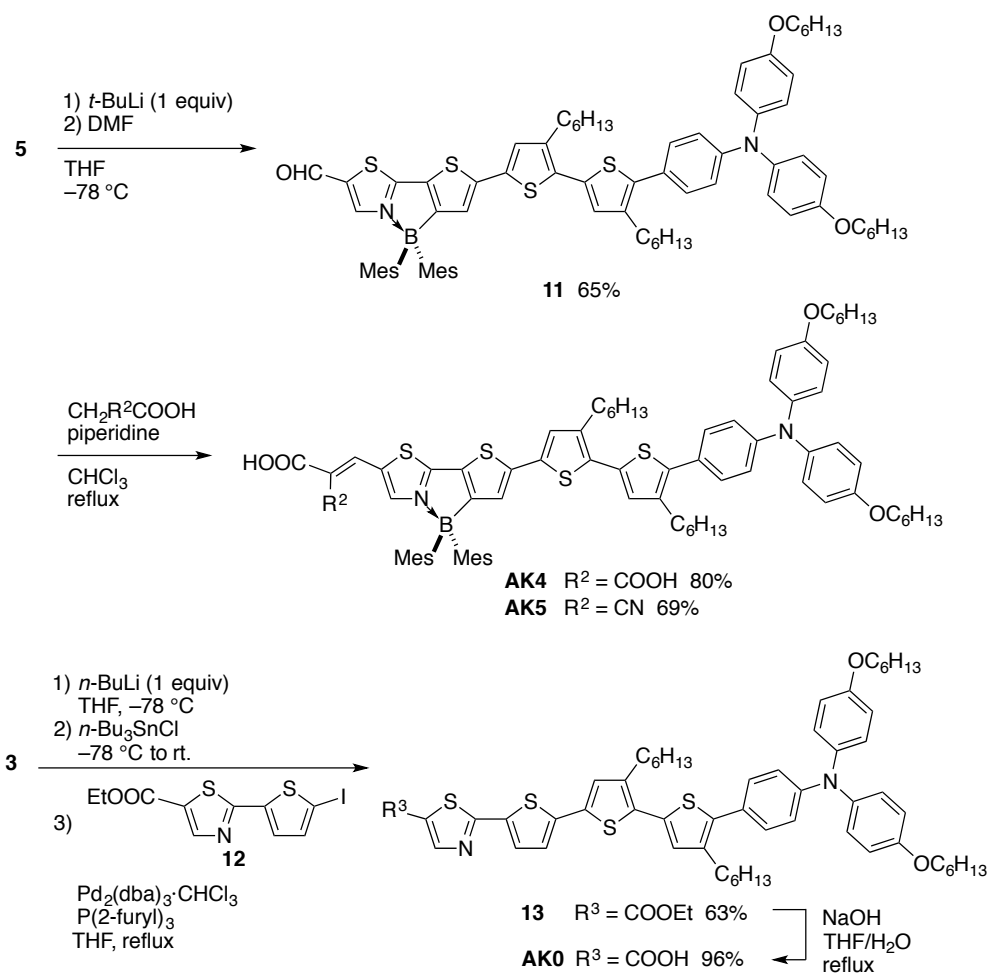
thiazole ring, in 83% and 97% yields, respectively. The Stille coupling of **10a** and **10b** with the stannyl derivative of the D- π unit prepared from **3**, yielded **AK2** and **AK3** in 21% and 30%, respectively.

Scheme 2. Synthesis of AK2 and AK3



As shown in Scheme 3, **AK4** and **AK5**, which bear methylene malonic acid and cyanoacrylic acid anchors, respectively, were synthesized. The lithiation of the aforementioned D- π -A unit **5** (Scheme 1) with *t*-BuLi followed by treatment with DMF afforded formyl derivative **11** in 65% yield. The terminal formyl group of **11** was converted into the anchoring group by the Knoevenagel condensation with the corresponding carboxylic acid, which furnished **AK4** and **AK5** in 80% and 69% yields, respectively. Similarly, the Stille coupling of the stannyl derivative of D- π unit **3** with ethyl 2-(5-iodo-thien-2-yl)thiazole-5-carboxylate **12**, followed by hydrolysis, furnished reference compound **AK0** in 96% yield (Scheme 3).

Scheme 3. Synthesis of AK4, AK5, and AK0



Chemical and Thermal Stability of D- π -A Unit 5

To confirm the chemical stability of the intramolecular B–N bond in the boryl-substituted thienylthiazole a chloroform solution of D- π -A unit **5**, which contains an intramolecular B–N bond, was treated with 1 M aqueous solutions of HCl or NaOH. Upon addition of either of these solutions, no change was observed in the corresponding ^1H NMR spectra. The thermal stability of **5** was examined by a thermogravimetric analysis (TGA), which revealed a 5% weight loss temperature ($T_{\text{d}5}$) at 325 $^\circ\text{C}$ (Figure 4).

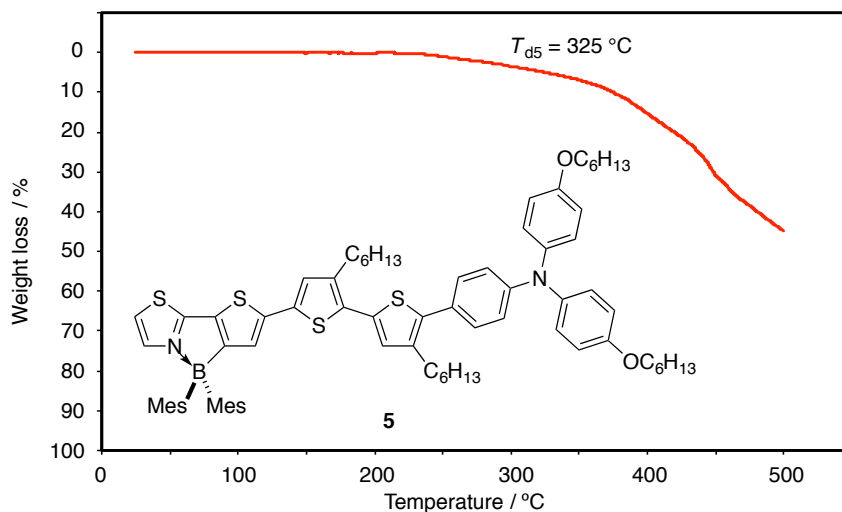


Figure 4. Thermogravimetric analysis of **5** heating at 10 °C/min under N₂.

Electrochemical Properties of AK0–5 in Solution

Cyclic voltammograms for **AK0–5** were recorded in CH₂Cl₂ (oxidation) and in THF (reduction). As shown in Figure 5, **AK0–5** exhibit one reversible reduction wave and two reversible oxidation waves, indicating the stability of the corresponding anionic and cationic species under the applied conditions.

The reduction potential of **AK1** is substantially shifted to less negative potential ($E_{1/2} = -2.16$ V vs. Fc/Fc⁺) compared to that of **AK0** (-2.36 V), demonstrating the impact of the formation of an intramolecular B–N bond on decreasing the LUMO level of the present D– π –A system. In comparison, the reduction potentials of **AK2** (-2.03 V) and **AK3** (-1.78 V) are even further shifted to less negative potentials relative to that of **AK1**. These results clearly suggest that the LUMO levels of such D– π –A systems containing B–N bonds can be further decreased by attaching electron-withdrawing substituents on the boron center. Such modification should be valuable in terms of the fine-tuning of the LUMO levels of organic DSSC dyes, in which the match between the energy levels of the LUMO and the TiO₂ conduction band is highly important in order to ensure efficient electron collection and effective harvesting over a wide range of the solar spectrum.

A comparison of the reduction potentials of **AK4** and **AK5** with that of **AK1** revealed the effect of the anchor unit. The reduction potentials of **AK4** ($E_{1/2} = -1.90$ V) with a methylene malonic acid and that of **AK5** (-1.78 V) with a cyanoacrylic acid are shifted to less negative values compared to that of **AK1** (-2.16 V) with a carboxylic

acid. This result suggests that the LUMO levels in **AK4** and **AK5** decreased relative to **AK1**, which should reflect the order of electron-withdrawing ability of the anchor units: $-\text{COOH} < -\text{CH}=\text{C}(\text{COOH})_2 < -\text{CH}=\text{C}(\text{CN})\text{COOH}$.

Whereas the reduction potentials are affected by the formation of B–N bonds, as well as by the electron-withdrawing ability of the anchoring units and the substituents on the boron center, the oxidation potentials of **AK0–5** are less sensitive to such modifications. The oxidation waves of **AK0–5** were observed at almost the same potential, i.e., within a range of $E_{1/2} = +0.20\text{--}0.22$ V (vs. Fc/Fc^+) for the first oxidation and $+0.52\text{--}0.56$ V for the second oxidation. As a result, the less negatively shifted reduction potentials directly affect the energy gap between the oxidation and reduction potential in **AK0–5**. The energy gaps decrease in the order of **AK0** > **AK1** > **AK2** > **AK3** on account of the formation of the B–N bond and due to the substituents on boron center, and in the order of **AK1** > **AK4** > **AK5** reflecting the effect of the anchor units.

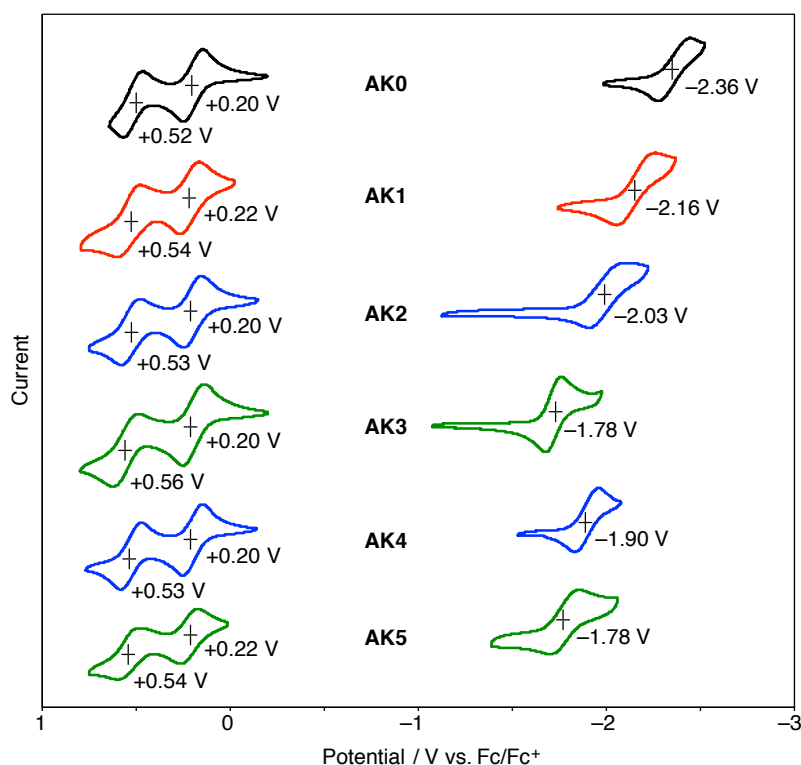


Figure 5. Cyclic voltammograms for **AK0–5** measured in CH_2Cl_2 (oxidation) and THF (reduction); supporting electrolyte: 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$; scan rate: 0.1 V s^{-1} .

Photophysical Properties of AK0–5 in Solution

A THF solution of **AK1** exhibits a broad absorption band at $\lambda_{\text{abs}} = 467$ nm ($\varepsilon = 38,000$ M⁻¹ cm⁻¹) and an emission band at $\lambda_{\text{em}} = 586$ nm ($\Phi_{\text{FL}} = 0.33$) (Figure 6). An examination of the solvent dependency of these spectra revealed that the absorption band is sensitive to solvent polarity. The absorption peak is red-shifted to 481 nm ($\varepsilon = 30,000$ M⁻¹ cm⁻¹) in less polar cyclohexane and blue-shifted to 444 nm ($\varepsilon = 41,000$ M⁻¹ cm⁻¹) in polar DMF. The fluorescence spectrum of **AK1** is less affected by solvent polarity. The fluorescence peak in DMF is slightly red-shifted ($\lambda_{\text{em}} = 602$ nm, $\Phi_{\text{FL}} = 0.03$) compared to those in cyclohexane ($\lambda_{\text{em}} = 585$ nm, $\Phi_{\text{FL}} = 0.39$) and THF ($\lambda_{\text{em}} = 586$ nm, $\Phi_{\text{FL}} = 0.33$) (Figure 6). These results suggest higher polarity in the ground state of **AK1** than in the excited state, and the longest-wavelength absorption contains contributions from the intramolecular charge transfer (ICT) character. According to the Lippert-Mataga plot,²⁴ the difference in dipole moment between the ground and excited state of **AK1** was estimated to be as large as 21.2 D (for details, see Experimental Section, Figure 17).

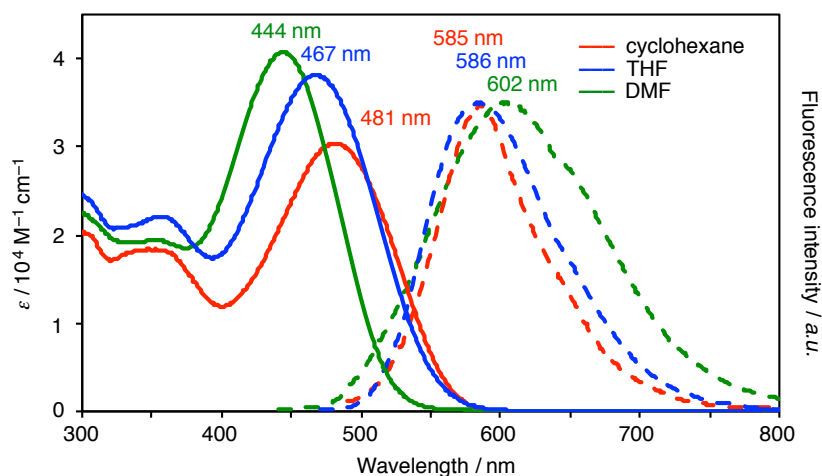


Figure 6. Solvent-dependence of the absorption and fluorescence band of **AK1**.

To evaluate the impact of the intramolecular B–N bond on the photophysical properties, UV/vis absorption spectra for **AK0–3** were also recorded in THF containing 1% trifluoroacetic acid (TFA), which was added to prevent dye aggregation arising from intermolecular interactions of the carboxyl groups. Reflecting the decrease of the LUMO level on account of the formation of the intramolecular B–N coordination bond in **AK1–3**, the absorption of **AK2** ($\lambda_{\text{abs}} = 476$ nm, $\varepsilon = 37,000$ M⁻¹ cm⁻¹) and **AK3** ($\lambda_{\text{abs}} =$

481 nm, $\varepsilon = 36,000 \text{ M}^{-1} \text{ cm}^{-1}$) as well as **AK1** ($\lambda_{\text{abs}} = 469 \text{ nm}$, $\varepsilon = 38,000 \text{ M}^{-1} \text{ cm}^{-1}$) are largely red-shifted compared to that of reference compound **AK0** (434 nm, $\varepsilon = 35,000 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 7). Compared to **AK1**, the absorption bands of **AK2** and **AK3** are red-shifted with respect to the substituents effects on boron center. However, the extent of these shifts seems to be rather small ($\Delta E = 0.03 \text{ eV}$ between **AK1** and **AK2**, $\Delta E = 0.06 \text{ eV}$ between **AK1** and **AK3**), considering the significant decrease in the energy gap ($\Delta E = 0.15 \text{ eV}$ between **AK1** and **AK2**, $\Delta E = 0.40 \text{ eV}$ between **AK1** and **AK3**) estimated from CV. The details on the correlation between the photophysical properties and the electronic structures of these systems are discussed in the section for theoretical calculations (*vide infra*).

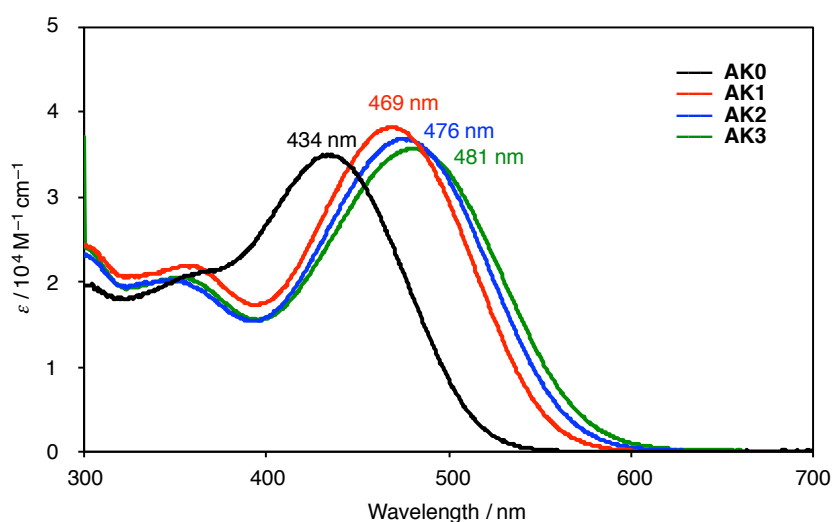


Figure 7. Absorption spectra for **AK0–3** in THF containing 1% TFA.

As shown in Figure 8, the absorption bands of **AK4** and **AK5** were observed at $\lambda_{\text{abs}} = 502 \text{ nm}$ ($\varepsilon = 44,000 \text{ M}^{-1} \text{ cm}^{-1}$) and 520 nm ($\varepsilon = 47,000 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. Compared to **AK1** ($\lambda_{\text{abs}} = 469 \text{ nm}$, $\varepsilon = 38,000 \text{ M}^{-1} \text{ cm}^{-1}$), the absorption bands of **AK4** and **AK5** are red-shifted, accompanied by an increase in extinction coefficients. These results should most likely to be interpreted in terms of the slightly extended π -conjugation upon the addition of a C=C bond in the anchor unit of **AK4** (methylene malonic acid) and **AK5** (cyanoacrylic acid), as well as by their relative electron-withdrawing ability.

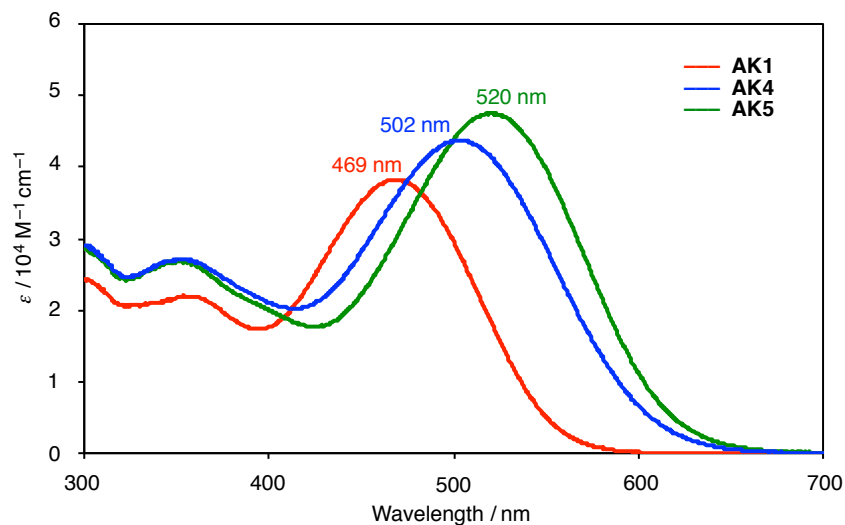


Figure 8. Absorption spectra for **AK1**, **AK4**, and **AK5** in THF containing 1% TFA.

Theoretical Calculations on **AK0–5**

To gain deeper insights into the electronic structures of **AK0–5**, DFT calculations at the B3LYP/6-31G(d) level of theory were carried out on model compounds **AK0'–5'**, in which hexyl groups were replaced with methyl groups (Figure 9). In general, the LUMOs in **AK0'–5'** are delocalized over the π -conjugated skeleton from the anchor via the acceptor to the π -spacer unit. Mes₂B-substituted **AK1'** exhibits a low-lying LUMO level (−2.52 eV), which is decreased by 0.17 eV compared to that of **AK0'** (−2.35 eV) and thus consistent with the observed shift of the reduction potential in the CV measurements (Figure 4). Compared to **AK1'**, the LUMO levels of **AK2'** (−2.82 eV) and **AK3'** (−2.94 eV) are significantly lowered, reflecting the impact of the substituents on the boron center. As far as the effects of the anchoring groups are concerned, the LUMO levels of **AK4'** (−2.97 eV) and **AK5'** (−2.99 eV) are also lower than that of **AK1'** (−2.52 eV). The HOMOs, in contrast, are located on the donor and π -spacer moieties, while the HOMO−1 is delocalized over the π -spacer and the acceptor units. Reflecting the location of the HOMO in this system, the structural modifications arising from the B–N bond in the acceptor unit and from modifications to the anchor unit do not drastically affect the HOMO levels of **AK0'–5'** (−4.66 eV to −4.82 eV). These results are thus in good agreement with the observed oxidation potentials in the CV (Figure 4).

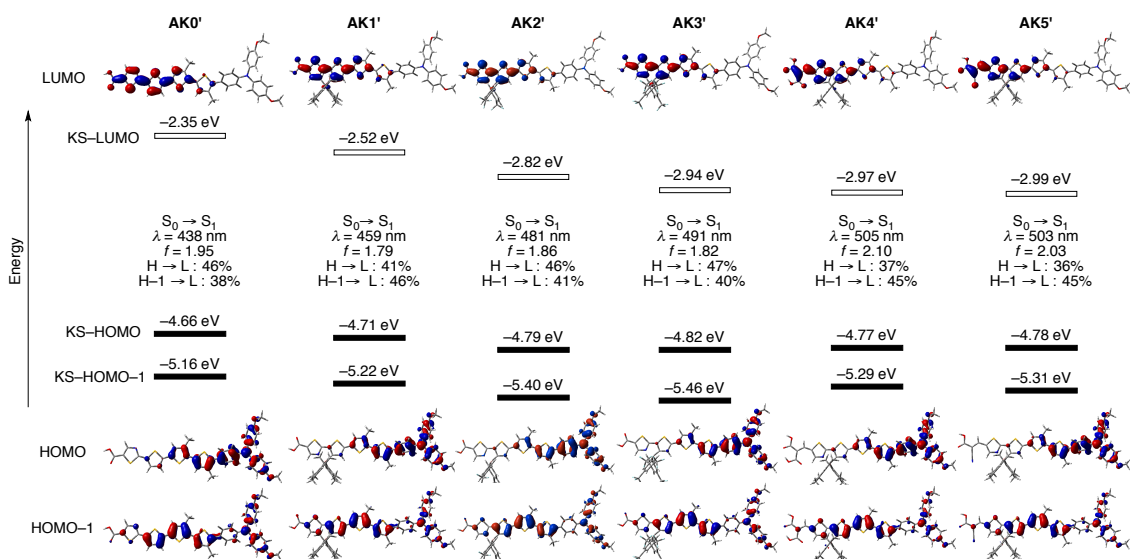


Figure 9. Pictorial representation of the frontier orbitals of **AK0'–5'**: plots of the Kohn-Sham HOMO–1, HOMO, and LOMO and associated energy levels calculated at the B3LYP/6-31G(d) level of theory. Transition energies with oscillator strengths and contributions were calculated at the TD-CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. H $\rightarrow$ L: HOMO $\rightarrow$ LUMO; and H–1 $\rightarrow$ L: HOMO–1 $\rightarrow$ LUMO.

To get further insights into the absorption properties, TD-DFT calculations were conducted on the optimized structures of **AK0'–5'** using various functionals (Figure 10). TD-DFT calculations at the B3LYP/6-31G(d) level of theory on **AK1'** afforded two large absorption bands in the visible region at $\lambda_{\text{abs}} = 629$ nm (oscillator strength: $f = 0.61$) and 501 nm ($f = 0.84$), which correspond to the HOMO $\rightarrow$ LUMO transition (contribution: 99%) and the HOMO–1 $\rightarrow$ LUMO transition (98%), respectively (Figure 11a). Considering the orbitals of **AK1'** (Figure 9), these transitions should exhibit intramolecular charge transfer (ICT) and π - π^* transition character, respectively. However, these results are not consistent with the experimentally observed spectrum, which shows only one broad band in the visible region. Therefore, other functionals that take into account long-range correlations,^{25–29} e.g. CAM-B3LYP/6-31G(d),^{26,27} LC-BLYP/6-31G(d),²⁸ and M06-2X/6-31G(d),²⁹ were used for the TD-DFT calculations on **AK1'**. In sharp contrast to the B3LYP functional, these functionals revealed one large absorption band in the visible region. Whereas the transition energy obtained from LC-BLYP/6-31G(d) showed a slightly over-estimated blue-shifted absorption at 410 nm ($f = 1.74$), the results obtained from CAM-B3LYP/6-31G(d) (459 nm, $f = 1.79$) and

M06-2X/6-31G(d) (461 nm, $f = 1.74$) were in good agreement with the experimentally obtained absorption band at 469 nm (Figure 10). The longest-wavelength absorption band estimated by these functionals considering long-range correlations were composed of two main transitions. For example, the $S_0 \rightarrow S_1$ transition obtained from CAM-B3LYP/6-31G(d) consists of contributions from the HOMO $\rightarrow$ LUMO (41%) and the HOMO-1 $\rightarrow$ LUMO (46%) transitions (Figure 11b). These results indicate the importance of considering long-range correlations for the TD-DFT calculations on such D- π -A systems with intramolecular charge transfer character. TD-DFT calculations at the CAM-B3LYP/6-31G(d) level of theory were also used to generate theoretical absorption profiles for **AK0'** and **AK2'-5'** (Figure 9), and thus the obtained results were also in good agreement with the experimentally observed absorption spectra. Such a contamination of the transition from the HOMO-1 $\rightarrow$ LUMO into the longest absorption would rationalize the observed differences between the HOMO-LUMO gap and the optical band gap.

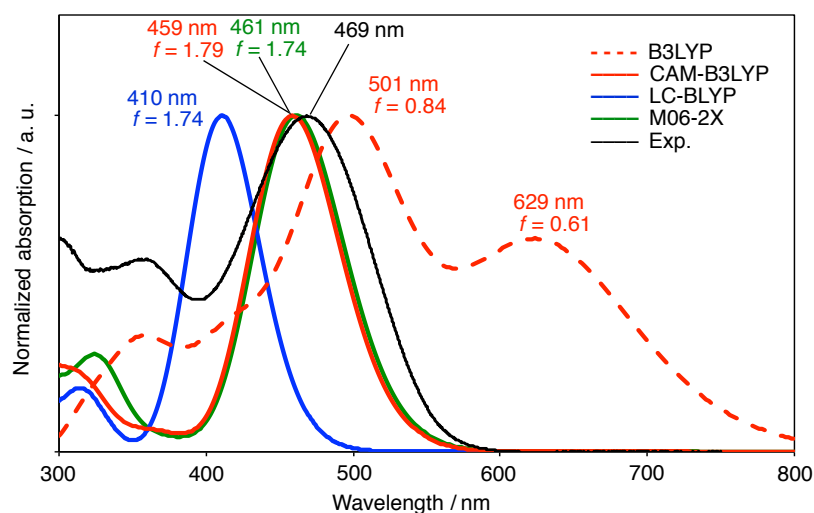


Figure 10. TD-DFT-derived absorption spectra for **AK1'** obtained by using various functionals in combination with the 6-31G(d) basis set: B3LYP (red dashed line), CAM-B3LYP (red line), LC-BLYP (blue line), and M06-2X (green line); full-width half maxima set to 3400 cm^{-1} . The experimentally obtained absorption spectrum for **AK1** in THF with 1% TFA (black line) is included for comparison.

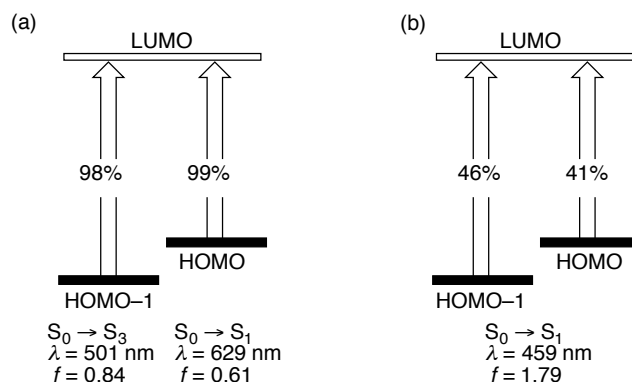


Figure 11. The energy diagram for the frontier orbitals of **AK1'** calculated at the B3LYP/6-31G(d) level of theory, and the estimated transitions derived from TD-DFT calculations at the (a) B3LYP/6-31G(d) and (b) CAM-B3LYP/6-31G(d) level of theory.

Electrochemical and Photophysical Properties of **AK0–5** on TiO_2

Since sensitizers are deposited onto TiO_2 substrates in DSSCs, it is important to evaluate the HOMO and LUMO levels of the dyes upon adsorption on TiO_2 . For that purpose, cyclic voltammograms were recorded using TiO_2 substrates with 2 μm thickness as working electrodes, on which dyes **AK0–5** were adsorbed (for details, see Experimental Section). Each of the **AK0–5**/ TiO_2 substrates exhibit one reversible oxidation wave at $E_{1/2} = +0.35\text{--}0.37$ V (Figure 12), which is positively shifted by 0.14–0.16 V compared to the oxidation waves of dyes in solution (Figure 5). Such positive shifts represent a general trend for **AK0–5**, which is most likely due to the enhanced electron-withdrawing ability resulting from the adsorption of the carboxylic group to a Lewis-acidic Ti center on the TiO_2 surface.

To evaluate the optical band gap of the **AK0–5**/ TiO_2 substrates, absorption spectra were measured (Figure 13). The edges of the absorption spectra of **AK0–5**/ TiO_2 are red-shifted by $\sim 45\text{--}75$ nm (0.16–0.23 eV) compared to those in solution (Figures 7 and 8), suggesting that upon adsorption of dyes onto TiO_2 , the stabilization of the LUMO level is higher than that of the HOMO.

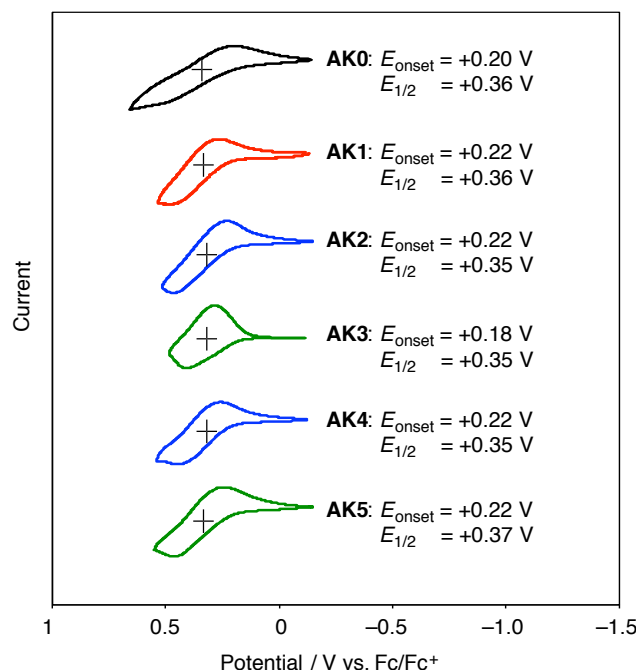


Figure 12. Cyclic voltammograms for **AK0–5/TiO₂** in MeCN); supporting electrolyte: 0.1 M [Bu₄N][PF₆]; scan rate: 0.1 V s⁻¹.

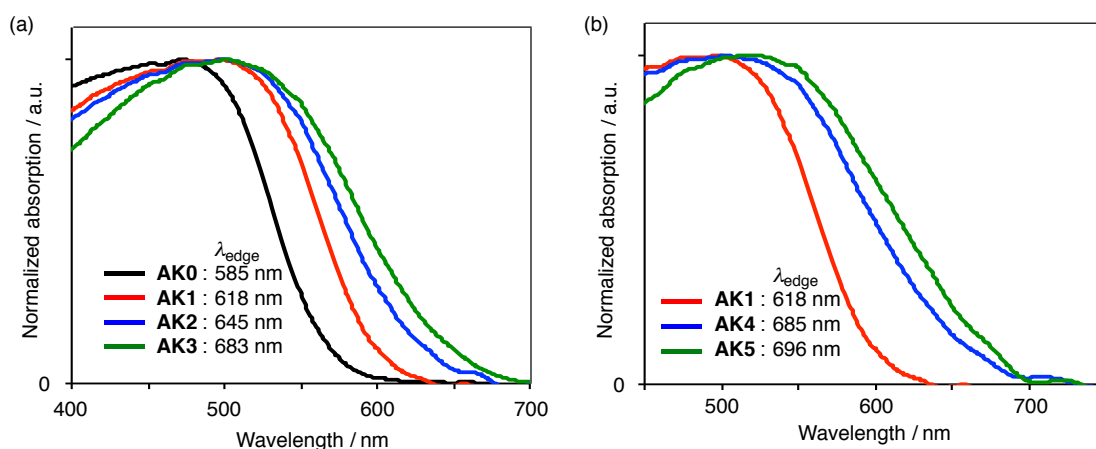


Figure 13. Absorption spectra for **AK0–5/TiO₂**, reflecting the impact of the (a) substituents on boron and (b) anchor units.

Based on the onset oxidation potentials¹⁸ and optical band gaps, the HOMO and LUMO levels of **AK0–5/TiO₂** were estimated and are summarized in Figure 14. The HOMO levels of **AK0–5/TiO₂** are almost identical (–5.28 to –5.32 eV), and located by 0.38 eV below the redox potential of I[–]/I₃[–] (–4.9 eV).^{18,19} In contrast, the LUMO levels are diverse, ranging from –3.18 eV (**AK0**) to –3.54 eV (**AK5**). Even the lowest level estimated for **AK5** is still higher by 0.46 eV than the conduction band of TiO₂ (–4.0

eV).^{17,18} These offset potentials suggest that the driving force for **AK0–5** should be sufficient for efficient charge transfer to the redox couple (I^-/I_3^-) and the semiconductor (TiO_2) in DSSCs.

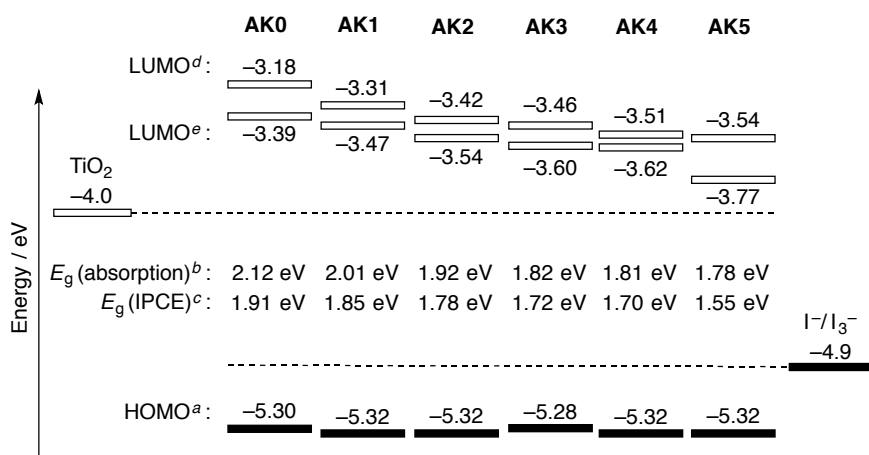


Figure 14. Experimentally determined HOMO and LUMO levels of **AK0–5**. ^aHOMO = $-(E_{\text{onset}} + 5.1)$ eV.¹⁸ ^bObtained from the absorption edge of the dye/ TiO_2 substrates. ^cObtained from the IPCE spectrum edge. ^dLUMO = HOMO + E_g (absorption). ^eLUMO = HOMO + E_g (IPCE).

DSSCs Performance

DSSCs based on **AK0–5**/ TiO_2 substrates (10–16 μm thickness) were fabricated using a solution of 0.1 M LiI, 25 mM I_2 , 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile (for details, see Experimental Section).³⁰ The J - V curves for the prepared devices were measured under AM 1.5G illumination. The DSSC performance of **AK0–3** is summarized in Figure 15 and Table 1. The **AK1** cell exhibited a short-circuit current density (J_{SC}) of 10.3 mA cm^{-2} , open-circuit voltage (V_{OC}) of 0.72 V, and fill factor (FF) of 0.72, giving a power conversion efficiency (PCE, η) of 5.3%. Due to the increased J_{SC} , the performance of the **AK1** cell was thus better than that of **AK0** ($J_{\text{SC}} = 9.5 \text{ mA cm}^{-2}$, $\eta = 4.9\%$). In the incident-photon-to-current conversion efficiency (IPCE) spectra, the **AK1** and **AK0** cells exhibited high external quantum efficiencies (EQE, $\sim 80\%$) at the maximum, while the spectrum of **AK1** (edge: 670 nm) is red-shifted compared to that of **AK0** (edge: 650 nm), thus reflecting the red-shift observed in their absorption spectra in solution and on TiO_2 (Figures 7, 13a). The **AK2** and **AK3** cells show further red-shifts of the IPCE spectra to afford higher J_{SC} values (**AK2**: 12.1, **AK3**: 11.9 mA cm^{-2}) than that of **AK0** (9.5 mA cm^{-2}) and **AK1** (10.3 mA cm^{-2}). As a result, the PCE for **AK2** ($\eta = 6.1\%$) and

AK3 ($\eta = 5.6\%$) are increased.

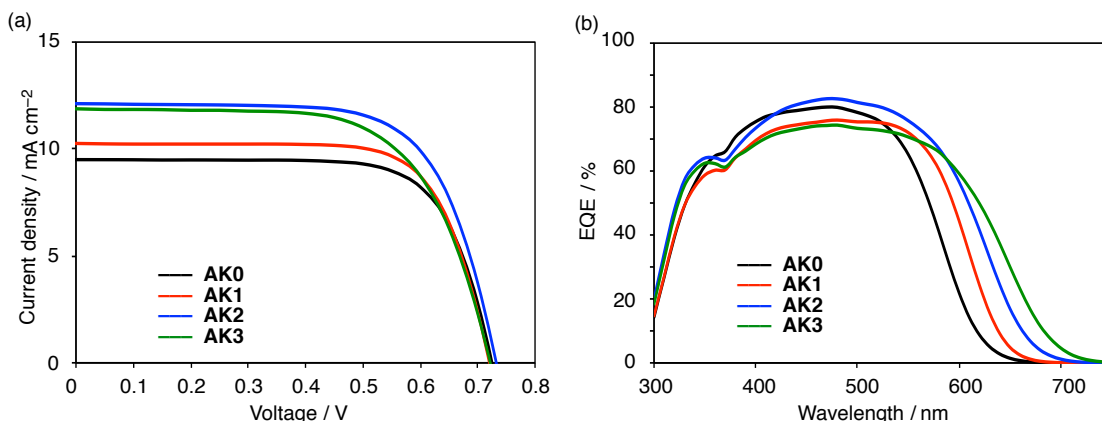


Figure 15. (a) J - V curves and (b) IPCE spectra for DSSCs based on **AK0–3**.

Table 1. Photovoltaic Performance of DSSCs Based on **AK0–3**^a

Dye	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	η [%]
AK0	9.50	0.72	0.72	4.9
AK1	10.3	0.72	0.72	5.3
AK2	12.1	0.73	0.69	6.1
AK3	11.9	0.72	0.65	5.6

^aElectrolyte solution: 0.1 M LiI, 25 mM I₂, 0.6 M DMPII, and 0.5 M TBP in MeCN.

The J - V curves for the devices based on **AK4** and **AK5**, which possess different anchor units, are shown in Figure 16a and Table 2 together with that of **AK1** (carboxy anchor) for comparison. Similar to **AK2** and **AK3**, the **AK4** cell (methylene malonic acid anchor) exhibited higher J_{SC} (12.1 mA cm⁻²) and thus improved PCE ($\eta = 5.9\%$) relative to the **AK1** cell, which reflects the red-shifted absorption. In contrast, the **AK5** cell (cyanoacrylic acid anchor) exhibited comparable J_{SC} (10.7 mA cm⁻²) to that of the **AK1** cell. In the IPCE spectra, the **AK4** cell exhibited a broader spectrum tailing to ~730 nm, while maintaining a high EQE (77%) at the maximum. The IPCE spectrum of the **AK5** cell is significantly red-shifted to 800 nm. However, its EQE is as low as 60% even at the maximum (Figure 16b), resulting in a moderate J_{SC} value (Table 2). Modifications of the components or the DSSC fabrication method were examined, e.g. 1) removal of TBP from the electrolyte solution, which was expected to decrease TiO₂ conduction band edge,^{11a,31,32} or 2) the use of a co-adsorbent such as deoxycholic acid

(DCA), which could suppress the dye aggregation on TiO₂ surface.^{31,33} These modifications, however, did not improve the PCE of the **AK5** cell (Table 2).

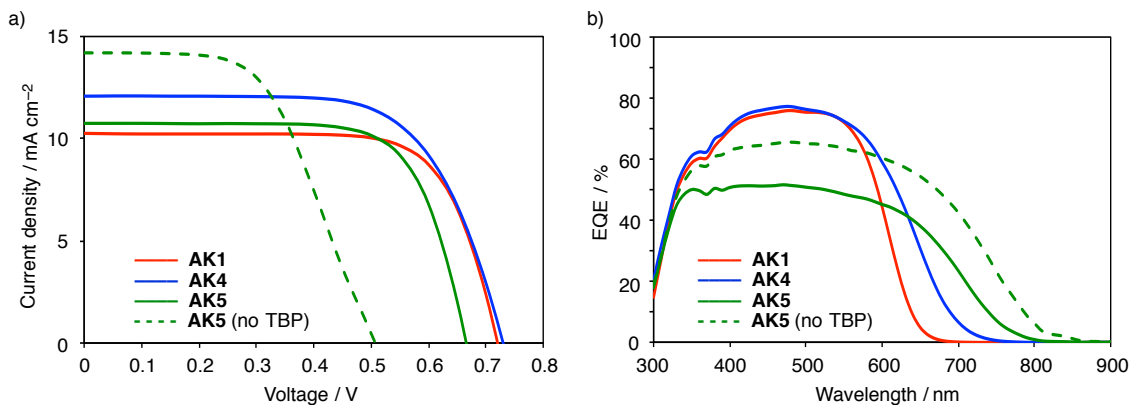


Figure 16. (a) *J*-*V* curves and (b) IPCE spectra for DSSCs based on **AK1**, **AK4**, and **AK5**.

Table 2. Photovoltaic Performance of DSSCs Based on **AK1**, **AK4**, and **AK5**^a

Dye	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	η [%]
AK1	10.3	0.72	0.72	5.3
AK4	12.1	0.73	0.67	5.9
AK5	10.7	0.66	0.71	5.1
AK5 ^b	14.2	0.51	0.54	3.9
AK5 +DCA	10.5	0.66	0.68	4.7

^aElectrolyte solution: 0.1 M LiI, 25 mM I₂, 0.6 M DMPH, and 0.5 M TBP in MeCN.

^bTBP was removed from the electrolyte solution.

To gain insight into the relationship between the electronic structures of dyes and their DSSC performance, the LUMO levels were also estimated from the position of the edge in the IPCE spectra of the cells (Figure 14). Compared to the absorption spectra of the dye/TiO₂ substrates, red-shifts (0.11–0.23 eV) of the spectral edge in IPCE were observed for **AK0–5**, leading to a further decrease in the estimated LUMO levels. Among **AK0–5**, the red-shift of the edge in the IPCE spectrum of **AK5** is significant, considering that the absorption edges of **AK4**/TiO₂ and **AK5**/TiO₂ are comparable (Figure 13b). As a result, the estimated LUMO level of **AK5** (–3.77 eV) becomes close to the conduction band of TiO₂. Interestingly, the IPCE spectrum for the cells using **AK5** without TBP showed a further red-shift to 820 nm (LUMO = –3.80 eV). Although

the reason for this drastic decrease of the LUMO level of **AK5** is not clear at present, the moderate EQE observed for the cells is most likely correlated to the low-lying LUMO level of **AK5**, as the decrease in offset potential might lead to less effective electron injection into TiO₂.

Conclusion

The author designed and synthesized a series of D- π -A dyes (**AK1–5**), which contain an intramolecular B–N coordination bond in the acceptor unit, as sensitizers for dye-sensitized solar cells (DSSCs). A systematic examination of the electrochemical and photophysical properties of **AK1–5** revealed that the formation of intramolecular B–N coordination bonds effectively lowers the LUMO level of the dyes, which leads to a red-shift in the absorption spectrum. The degree of the decreasing the LUMO level and the corresponding absorption shift depend on the electron-withdrawing ability of the substituents on boron. The effect of the anchoring units on the electronic structure of **AK1–5** was also examined. The synergetic effects between the formation of a B–N bond and the electron-withdrawing ability of the anchor group induced a further decrease of the LUMO levels, leading to red-shifts in the IPCE spectra of **AK4** and **AK5**. The photovoltaic performances of DSSCs using these dyes reflect these electronic and structural modifications, and the red-shifted absorptions resulted in an increase of the short-circuit current density (J_{sc}). DSSCs based on **AK1–5** exhibited good power conversion efficiency values (5.1–6.1%). Throughout this study, the author demonstrated the utility of such π -skeletons with intramolecular B–N bonds for the fine-tuning of the electronic structure. This molecular design strategy should thus allow access to several more sophisticated sensitizers for DSSC applications.

Experimental Section

General

Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. ¹H and ¹³C NMR spectra were recorded with a Varian Mercury 300 (300 MHz for ¹H and 75 MHz for ¹³C), a JEOL Resonance ECA-500 (500 MHz for ¹H and 125 MHz for ¹³C), or a Bruker Avance III 800US (200 MHz for ¹³C) spectrometer. Chemical shifts are reported in δ ppm using residual protons in the deuterated solvents for ¹H NMR and using solvent peaks for ¹³C NMR as internal standards. ¹¹B and ¹⁹F NMR spectra were

recorded with JEOL Resonance ECA-500 (160 MHz for ^{11}B and 470 MHz for ^{19}F), or Bruker Avance III 600US (192 MHz for ^{11}B and 565 MHz for ^{19}F) spectrometer. The chemical shifts in ^{11}B and ^{19}F NMR spectra are reported in ppm with reference to $\text{BF}_3\cdot\text{OEt}_2$ (δ 0.00 ppm in ^{11}B NMR) and trifluoromethylbenzene in CDCl_3 (δ -64.0 ppm in ^{19}F NMR) as external standards, respectively. UV/vis absorption measurement was performed with a Shimadzu UV-3150 spectrometer, in degassed spectral grade solvents. Fluorescence measurement was performed with a HORIBA FluoroMax 4P-NIR. Quantum yields were determined with a Hamamatsu Photonics Quantaurus QY C11347 with calibrated integrating sphere system. Cyclic voltammetry (CV) was performed with an ALS/chi-620C electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode. The measurement was carried out under an argon atmosphere using CH_2Cl_2 solutions for oxidation and THF solutions for reduction. The solutions are composed of 1 mM samples containing 0.1 M tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thermogravimetric analysis (TGA) was performed with a SHIMADZU TGA-50 apparatus. Thin layer chromatography (TLC) was performed with plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Silica gel column chromatography was performed using PSQ 60B (Fuji Silysia). The Gel Permeation Chromatography (GPC) was performed with a JAI LC-918 system using toluene as eluent or a LC-908 system using CHCl_3 as eluent, equipped with a RI-50 detector and JAIGEL-2H and 1H columns at the flow rate of 3.8 mL/min. All reactions were carried out under an argon atmosphere. Geometry optimization and TD-DFT calculations were performed by using Gaussian 09 (revision A.02) program.³⁴

Synthesis

4-(3',4-Dihexyl-[2,2'-bithiophen]-5-yl)-*N,N*-bis(4-hexyloxyphenyl)aniline (3).

To a mixture of **1** (4.39 g, 9.54 mmol), **2** (5.01 g, 9.55 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (98.8 mg, 94.5 μmol), SPhos (78.3 mg, 0.191 mmol), and K_3PO_4 (6.08 g, 28.6 mmol) were added degassed toluene (50 mL) and H_2O (10 mL) at room temperature. The reaction mixture was refluxed for 16 h. After cooling down and addition of water, the mixture was extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified

by a silica gel column chromatography (3:1 hexane/toluene) to give 7.27 g (9.35 mmol) of **3** in 98% yield as yellow oil: ^1H NMR (300 MHz, CDCl_3): δ 7.23 (d, $J_{\text{HH}} = 8.7$ Hz, 2H), 7.13 (d, $J_{\text{HH}} = 5.4$ Hz, 1H), 7.08 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 6.95 (s, 1H), 6.93 (d, $J_{\text{HH}} = 8.7$ Hz, 2H), 6.92 (d, $J_{\text{HH}} = 5.4$ Hz, 1H), 6.83 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 3.93 (t, $J_{\text{HH}} = 6.6$ Hz, 4H), 2.77 (t, $J_{\text{HH}} = 7.8$ Hz, 2H), 2.63 (t, $J_{\text{HH}} = 7.8$ Hz, 2H), 1.82–1.75 (m, 4H), 1.68–1.58 (m, 4H), 1.51–1.41 (m, 4H), 1.39–1.25 (m, overlapped, 20H), 0.93–0.85 (m, overlapped, 12H); ^{13}C NMR (75 MHz, CDCl_3): δ 155.57, 148.02, 140.42, 139.07, 138.05, 138.01, 133.20, 131.05, 129.98, 129.58, 128.27, 126.81, 125.85, 123.10, 119.68, 115.23, 68.21, 31.66, 31.59, 30.95, 30.70, 29.30, 29.24, 29.21, 28.78, 25.74, 22.60, 14.10, 14.04 (five aliphatic signals are overlapped); HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{50}\text{H}_{68}\text{NO}_2\text{S}_2$, 778.4686; found, 778.4676; Elemental analysis calcd. (%) for $\text{C}_{50}\text{H}_{67}\text{NO}_2\text{S}_2$: C 77.17, H 8.68, N 1.80; found: C 77.03, H 8.73, N 1.95.

4-(4''-Dimesitylboryl-3',4-dihexyl-5''-(thiazol-2-yl)-[2,2':5',2''-terthiophen]-5-yl)-N,N-bis(4-hexyloxyphenyl)aniline (5**).**

To a solution of **3** (73.0 mg, 93.8 μmol) in THF (1 mL) at -78°C , $n\text{-BuLi}$ (1.47 M in hexane, 66.0 μL , 97.0 μmol) was added dropwise, and the mixture was stirred for 30 min. To the mixture, $n\text{-Bu}_3\text{SnCl}$ (28.0 μL , 94.8 μmol) was added, and the mixture was gradually warmed to room temperature with stirring for 1 h. To the mixture, **4** (51.3 mg, 94.8 μmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (1.90 mg, 1.84 μmol), and trifurylphosphine (1.82 mg, 7.34 μmol) were added, and the mixture was refluxed for 4 h. After addition of water (2 mL), the organic layer was separated and the aqueous layer was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 toluene/hexane, $R_f = 0.46$) to give 80.0 mg (0.0671 mmol) of **5** in 72% yield as red solids: mp $141\text{--}143^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.67 (d, $J_{\text{HH}} = 3.7$ Hz, 1H), 7.28 (s, 1H), 7.25 (d, $J_{\text{HH}} = 8.7$ Hz, 2H), 7.10 (d, $J_{\text{HH}} = 8.9$ Hz, 4H), 7.06 (s, 1H), 7.00 (s, 1H), 6.99 (d, $J_{\text{HH}} = 3.7$ Hz, 1H), 6.95 (d, $J_{\text{HH}} = 8.7$ Hz, 2H), 6.85 (d, $J_{\text{HH}} = 8.9$ Hz, 4H), 6.68 (s, 4H), 3.95 (t, $J_{\text{HH}} = 6.6$ Hz, 4H), 2.76 (t, $J_{\text{HH}} = 7.8$ Hz, 2H), 2.65 (t, $J_{\text{HH}} = 7.8$ Hz, 2H), 2.21 (s, 6H), 1.91 (s, 12H), 1.82–1.77 (m, 4H), 1.69–1.62 (m, 4H), 1.51–1.46 (m, 4H), 1.43–1.26 (m, overlapped, 20H), 0.93 (t, $J_{\text{HH}} = 7.1$ Hz, 6H), 0.902 (t, $J_{\text{HH}} = 7.0$ Hz, 3H), 0.895 (t, $J_{\text{HH}} = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 184.32, 166.18, 155.63, 148.14, 145.96, 143.00, 140.37, 140.11,

139.76, 138.50, 138.25, 137.23, 134.11, 133.91, 132.65, 131.82, 129.56, 129.50, 128.38, 127.92, 127.52, 126.85, 126.64, 125.63, 119.62, 116.05, 115.27, 68.22, 31.65, 31.59, 30.94, 30.46, 29.43, 29.30, 29.21, 28.77, 25.74, 24.30, 22.60, 20.74, 14.10, 14.04 (five aliphatic signals are overlapped); ^{11}B NMR (192 MHz, CDCl_3): δ 2.92; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{75}\text{H}_{92}\text{BN}_2\text{O}_4\text{S}_4$, 1191.6141; found, 1191.6156; elemental analysis calcd. (%) for $\text{C}_{75}\text{H}_{91}\text{BN}_2\text{O}_2\text{S}_4$: C 75.60, H 7.70, N 2.35; found: C 75.47, H 7.76, N 2.42.

2-(5''-(4-(Bis(4-hexyloxyphenyl)amino)phenyl)-4-dimesitylboryl-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carboxylic acid (AK1).

To a solution of **5** (105 mg, 0.088 mmol) in THF (1 mL) at $-78\text{ }^\circ\text{C}$, $t\text{-BuLi}$ (1.55 M in pentane, $57\text{ }\mu\text{L}$, 0.088 mmol) was added dropwise. After the mixture was stirred for 1 h, crashed dry ice was added to the mixture, and the mixture was gradually warmed to room temperature. After addition of 2 M hydrochloric acid aqueous solution, the organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with water, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH_2Cl_2 , then 10:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give 100 mg (0.081 mmol) of **AK1** in 92% yield as dark red solids: mp $98\text{--}100\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 8.23 (s, 1H), 7.28 (s, 1H), 7.23 (d, $J_{\text{HH}} = 8.5\text{ Hz}$, 2H), 7.10 (s, 1H), 7.09 (d, $J_{\text{HH}} = 9.0\text{ Hz}$, 4H), 7.00 (s, 1H), 6.92 (d, $J_{\text{HH}} = 8.5\text{ Hz}$, 2H), 6.84 (d, $J_{\text{HH}} = 9.0\text{ Hz}$, 4H), 6.68 (s, 4H), 3.94 (t, $J_{\text{HH}} = 6.5\text{ Hz}$, 4H), 2.76 (t, $J_{\text{HH}} = 8.0\text{ Hz}$, 2H), 2.63 (t, $J_{\text{HH}} = 8.0\text{ Hz}$, 2H), 2.20 (s, 6H), 1.90 (s, 12H), 1.81–1.75 (m, 4H), 1.65–1.61 (m, 4H), 1.48–1.45 (m, 4H), 1.37–1.27 (m, 20H), 0.91 (t, $J_{\text{HH}} = 7.0\text{ Hz}$, 6H), 0.89 (t, $J_{\text{HH}} = 7.0\text{ Hz}$, 3H), 0.88 (t, $J_{\text{HH}} = 7.0\text{ Hz}$, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.58, 163.59, 155.77, 149.39, 148.34, 143.86, 140.47, 140.20, 140.10, 139.04, 138.47, 134.68, 133.34, 133.27, 132.49, 129.83, 129.67, 129.05, 128.76, 127.97, 126.99, 126.75, 125.61, 124.34, 119.69, 115.41, 68.37, 31.74, 31.70, 31.04, 30.54, 29.54, 29.41, 29.30, 28.87, 25.85, 24.52, 22.70, 20.82, 14.19, 14.14 (two aromatic signals are not observed due to quadrupolar relaxation, and three aliphatic signals are overlapped); ^{11}B NMR (160 MHz, $\text{DMSO-}d_6/\text{CDCl}_3 = 1/1(\text{v/v})$): δ 0.04; HRMS (ESI-TOF) (m/z): $[\text{M}-\text{H}]^-$ calcd. for $\text{C}_{76}\text{H}_{90}\text{BN}_2\text{O}_4\text{S}_4$, 1233.5882; found, 1233.5870.

2-(3-(Bis(4-trifluoromethylphenyl)boryl)thiophen-2-yl)thiazole (8a).

To a solution of **6** (750 mg, 3.05 mmol) in Et₂O (31 mL) at –78 °C, *n*-BuLi (1.60 M in hexane, 1.91 mL, 3.05 mmol) was added dropwise. After the mixture was stirred for 1 h, trimethyl borate (340 µL, 3.05 mmol) was added to the mixture, which was gradually warmed to room temperature with stirring for 48 h. *p*-Trifluoromethylphenylmagnesium bromide solution in Et₂O (30 mL), freshly prepared from *p*-trifluoromethylbromobenzene (2.14 mL, 15.3 mmol) and magnesium tuning (233 mg, 15.3 mmol), was added to the mixture, which was refluxed for 90 h. After addition of saturated NH₄Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (3:1 hexane/CH₂Cl₂) to give 982 mg (2.10 mmol) of **8a** in 69% yield as pale yellow solids: mp 174–175 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.76 (d, *J*_{HH} = 3.6 Hz, 1H), 7.69 (d, *J*_{HH} = 4.6 Hz, 1H), 7.46 (d, *J*_{HH} = 7.7 Hz, 4H), 7.33 (d, *J*_{HH} = 4.6 Hz, 1H), 7.32 (d, *J*_{HH} = 7.7 Hz, 4H), 7.30 (d, *J*_{HH} = 3.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 178.56, 167.73, 152.33, 134.73, 134.62, 132.79, 131.69, 129.18, 128.19 (q, *J*_{CF} = 32.1 Hz), 124.64 (q, *J*_{CF} = 271.8 Hz), 124.18 (q, *J*_{CF} = 3.8 Hz), 117.96; ¹¹B NMR (192 MHz, CDCl₃): δ 0.99; ¹⁹F NMR (565 MHz, CDCl₃): δ –62.83; HRMS (APCI-TOF) (*m/z*): [M][–], calcd. for C₂₃H₁₀BF₁₂NS₂, 467.0408; found, 467.0429; Elemental analysis calcd. (%) for C₂₃H₁₀BF₁₂NS₂: C 53.98, H 2.59, N 3.00; found: C 54.18, H 2.53, N 3.13.

2-(3-(Bis(3,5-bis(trifluoromethyl)phenyl)boryl)thiophen-2-yl)thiazole (8b).

To a solution of **6** (493 mg, 2.00 mmol) in Et₂O (10 mL) at –78 °C, *n*-BuLi (1.60 M in hexane, 1.25 mL, 2.00 mmol) was added dropwise. After the mixture was stirred at –78 °C for 1 h, trimethyl borate (223 µL, 2.00 mmol) was added. The reaction mixture was gradually warmed to room temperature. 3,5-Bis(trifluoromethyl)phenylmagnesium bromide solution in Et₂O (10 mL), freshly prepared from 3,5-bis(trifluoromethyl)bromobenzene (1.72 mL, 10.0 mmol) and magnesium tuning (245 mg, 10.1 mmol), was added and the mixture was refluxed for 90 h. After addition of a saturated NH₄Cl aqueous solution, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified

by a silica gel column chromatography (2:1 hexane/CH₂Cl₂) to give 944 mg (1.57 mmol) of **8b** in 78% yield as pale yellow solids: mp 170–171 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.77 (d, *J*_{HH} = 4.6 Hz, 1H), 7.72 (d, *J*_{HH} = 3.7 Hz, 1H), 7.71 (s, 2H), 7.57 (s, 4H), 7.41 (d, *J*_{HH} = 3.7 Hz, 1H), 7.31 (d, *J*_{HH} = 4.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 176.58, 168.48, 149.57, 135.87, 134.01, 132.26, 132.23 (q, *J*_{CF} = 3.9 Hz), 130.57 (q, *J*_{CF} = 32.3 Hz), 128.84, 123.80 (q, *J*_{CF} = 272.7 Hz), 120.54 (sept, *J*_{CF} = 3.9 Hz), 119.02; ¹¹B NMR (192 MHz, CDCl₃): δ 0.30; ¹⁹F NMR (565 MHz, CDCl₃): δ –63.17; HRMS (APCI-TOF) (*m/z*): [M][–] calcd. for C₂₃H₁₀BF₁₂NS₂, 603.0156; found, 603.0195; Elemental analysis calcd. (%) for C₂₃H₁₀BF₁₂NS₂: C 45.79, H 1.67, N 2.32; found: C 46.09, H 1.62, N 2.47.

2-(3-(Bis(4-trifluoromethylphenyl)boryl)-5-iodothiophen-2-yl)-5-iodothiazole (**9a**).

To a solution of **8a** (91.0 mg, 0.195 mmol) in THF (1 mL) at –78 °C, *n*-BuLi (1.60 M in hexane, 268 μL, 0.428 mmol) was added dropwise. After the mixture was stirred for 1 h, iodine (514 mg, 0.473 mmol) was added to the mixture. The reaction mixture was gradually warmed to room temperature. After addition of a Na₂SO₃ aqueous solution, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (2:1 hexane/CH₂Cl₂) to give 138 mg (0.192 mmol) of **9a** in 98% yield as pale yellow solids: mp 210–212 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.74 (s, 1H), 7.49 (s, 1H), 7.48 (d, *J*_{HH} = 7.7 Hz, 4H), 7.27 (s, *J*_{HH} = 7.7 Hz, 4H); ¹³C NMR (150 MHz, CDCl₃): δ 179.68, 169.71, 151.04, 140.67, 138.91, 136.62, 132.78, 128.58 (q, *J*_{CF} = 31.8 Hz), 124.52 (q, *J*_{CF} = 271.6 Hz), 124.37 (q, *J*_{CF} = 3.8 Hz), 87.28, 66.22; ¹¹B NMR (192 MHz, CDCl₃): δ 1.28; ¹⁹F NMR (565 MHz, CDCl₃): δ –62.88; HRMS (APCI-TOF) (*m/z*): [M]⁺ calcd. for C₂₁H₁₀BF₆I₂NS₂, 854.8089; found, 854.8070; Elemental analysis calcd. (%) for C₂₁H₁₀BF₆I₂NS₂: C 35.08, H 1.40, N, 1.95; found: C 35.24; N 2.21.

2-(3-(Bis(3,5-bis(trifluoromethyl)phenyl)boryl)-5-iodothiophen-2-yl)-5-iodothiazole (**9b**).

To a solution of **8b** (2.57 g, 4.27 mmol) in THF (22 mL) at –78 °C, *n*-BuLi (1.42 M in hexane, 6.61 mL, 9.39 mmol) was added dropwise. After the mixture was stirred for 1 h, iodine (2.82 g, 11.1 mmol) was added to the mixture. The reaction mixture was

gradually warmed to room temperature with stirring for 5 h. After addition of a Na₂SO₃ aqueous solution, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH₂Cl₂). After removal of the solvent, the resulting solids were washed with hexane and dried *in vacuo* to give 3.56 g (4.16 mmol) of **9b** in 98% yield as pale yellow solids: mp 197–199 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.73 (s, 2H), 7.67 (s, 1H), 7.50 (s, 4H), 7.42 (s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 177.50, 170.46, 148.43, 139.87, 138.41, 137.20, 132.18 (q, *J*_{CF} = 3.8 Hz), 130.80 (q, *J*_{CF} = 32.4 Hz), 123.69 (q, *J*_{CF} = 272.8 Hz), 120.93 (sept, *J*_{CF} = 3.8 Hz), 88.46, 67.21; ¹¹B NMR (193 MHz, CDCl₃): δ 0.66; ¹⁹F NMR (565 MHz, CDCl₃): δ –63.13; HRMS (APCI-TOF) (*m/z*): [M]⁺ calcd. for C₂₃H₈BF₁₂I₂NS₂, 854.8089; found, 854.8071; Elemental analysis calcd. (%) for C₂₃H₈BF₁₂I₂NS₂: C 32.31, H 0.94, N 1.64; found: C 32.57, H 0.90, N 1.67.

2-(3-(Bis(4-trifluoromethylphenyl)boryl)-5-iodothiophen-2-yl)thiazole-5-carboxylic acid (**10a**).

To a solution of **9a** (1.00 g, 1.39 mmol) in THF (13.5 mL) at –78 °C, *n*-BuLi (1.59 M in hexane, 875 μL, 1.39 mmol) was added dropwise. After the mixture was stirred for 1 h, crashed dry ice was added to the mixture. The mixture was gradually warmed to room temperature with stirring for 1 h. After addition of 2 M hydrochloric acid aqueous solution (10 mL), the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was washed with water, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH₂Cl₂, then 10:1 CH₂Cl₂/MeOH) to give 733 mg (0.081 mmol) of **10a** in 83% yield as yellow solids: mp 235–237 °C (decomposed); ¹H NMR (600 MHz, DMSO-*d*₆): δ 14.17 (br s, 1H), 8.87 (s, 1H), 7.70 (s, 1H), 7.49 (d, *J*_{HH} = 7.7 Hz, 4H), 7.38 (d, *J*_{HH} = 7.7 Hz, 4H); ¹³C NMR (150 MHz, DMSO-*d*₆): δ 180.37, 168.43, 161.22, 152.50, 139.47, 138.12, 137.10, 132.96, 130.55, 126.59 (q, *J*_{CF} = 31.4 Hz), 124.70 (q, *J*_{CF} = 271.5 Hz), 123.88 (q, *J*_{CF} = 3.9 Hz), 93.67; ¹¹B NMR (192 MHz, DMSO-*d*₆): δ 0.13; ¹⁹F NMR (565 MHz, DMSO-*d*₆): δ –61.30; HRMS (ESI-TOF) (*m/z*): [M–H][–] calcd. for C₂₂H₁₀BF₆INO₂S₂, 635.9200; found, 635.9175; Elemental analysis calcd. (%) for C₂₂H₁₁BF₆INO₂S₂: C 41.47, H 1.74, N 2.20; found: C

41.67, H 1.73, N 2.34.

2-(3-(Bis(3,5-bis(trifluoromethyl)phenyl)boryl)-5-iodothiophen-2-yl)thiazole-5-carboxylic acid (10b).

To a solution of **9b** (5.00 g, 5.85 mmol) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$, *n*-BuLi (1.53 M in hexane, 3.80 mL, 5.81 mmol) was added dropwise. After the mixture was stirred for 1 h, crashed dry ice was added and the mixture was gradually warmed to room temperature with stirring for 1 h. After addition of 2 M hydrochloric acid aqueous solution, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with water, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH_2Cl_2 , then 6:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give 4.38 g (5.67 mmol) of **10b** in 97% yield as yellow solids: mp $228\text{--}230\text{ }^{\circ}\text{C}$ (decomposed); ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 14.20 (br s, 1H), 9.29 (s, 1H), 7.83 (s, 2H), 7.75 (s, 4H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 178.15, 169.19, 161.28, 149.98, 140.04, 138.00, 137.98, 132.79, 130.87, 129.08 (q, $J_{\text{CF}} = 32.0\text{ Hz}$), 123.78 (q, $J_{\text{CF}} = 272.8\text{ Hz}$), 120.04 (sept, $J_{\text{CF}} = 3.7\text{ Hz}$), 94.03; ^{11}B NMR (192 MHz, $\text{DMSO}-d_6$): δ -0.82 ; ^{19}F NMR (565 MHz, $\text{DMSO}-d_6$): δ -61.53 ; HRMS (ESI-TOF) (m/z): $[\text{M}-\text{H}]^-$ calcd. for $\text{C}_{24}\text{H}_8\text{BF}_{12}\text{INO}_2\text{S}_2$, 771.8948; found, 771.8969; Elemental analysis calcd. (%) for $\text{C}_{24}\text{H}_9\text{BF}_{12}\text{INO}_2\text{S}_2$: C 37.28, H 1.17, N 1.81; found: C 37.48, H 1.11, N 2.03.

2-(5''-(4-(Bis(4-hexyloxyphenyl)amino)phenyl)-4-(bis(4-trifluoromethylphenyl)boryl)-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carboxylic acid (AK2).

To a solution of **3** (321 mg, 0.412 mmol) in THF (4 mL) at $-78\text{ }^{\circ}\text{C}$, *n*-BuLi (1.60 M in hexane, 258 μL , 0.412 mmol) was added dropwise. After the mixture was stirred for 1 h, *n*-Bu₃SnCl (112 μL , 0.412 mmol) was added to the mixture. The reaction mixture was gradually warmed to room temperature with stirring for 7.5 h. To the mixture, **10a** (265 mg, 0.416 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (8.42 mg, 8.13 μmol), and trifurylphosphine (7.71 mg, 33.2 μmol) were added, and the mixture was refluxed for 22 h. After addition of 1 M hydrochloric acid aqueous solution (5 mL), the organic layer was separated and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with water, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH_2Cl_2) followed by

preparative thin layer chromatography (10:1 CH₂Cl₂/MeOH) to give 114 mg (0.088 mmol) of **AK2** in 21% yield as dark red solids: mp 170–171 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.29 (s, 1H), 7.47 (d, *J*_{HH} = 6.0 Hz, 4H), 7.35 (s, 1H), 7.32 (d, *J*_{HH} = 6.0 Hz, 4H), 7.23 (d, *J*_{HH} = 8.5 Hz, 2H), 7.19 (s, 1H), 7.09 (d, *J*_{HH} = 9.0 Hz, 4H), 7.02 (s, 1H), 6.93 (d, *J*_{HH} = 8.5 Hz, 2H), 6.84 (d, *J*_{HH} = 8.5 Hz, 4H), 3.94 (t, *J*_{HH} = 6.5 Hz, 4H), 2.78 (t, *J*_{HH} = 8.0 Hz, 2H), 2.64 (t, *J*_{HH} = 8.0 Hz, 2H), 1.79–1.75 (m, 4H), 1.69–1.61 (m, 4H), 1.49–1.45 (m, 4H), 1.43–1.38 (m, 4H), 1.37–1.26 (m, 20H), 0.91 (t, *J*_{HH} = 7.0 Hz, 6H), 0.90–0.86 (m, 6H); ¹³C NMR (125 MHz, DMSO-*d*₆/CDCl₃ = 3/1(v/v)): δ 168.90, 160.91, 155.31, 152.18, 148.43, 147.91, 139.87, 139.39, 138.15, 137.91, 132.69, 132.55, 131.76, 131.41, 129.92, 129.06, 128.39, 126.89, 126.73, 126.62, 125.48, 124.69, 124.23, 123.61 (q, *J*_{CF} = 3.6 Hz), 123.31, 118.49, 115.16, 67.49, 30.91, 30.11, 29.70, 28.90, 28.73, 28.62, 28.48, 28.38, 28.02, 25.10, 21.97, 21.93, 21.91, 13.71 (two aromatic signals are not observed due to quadrupolar relaxation, and three aliphatic signal are overlapped); ¹¹B NMR (160 MHz, DMSO-*d*₆/CDCl₃ = 1/1(v/v)): δ 1.50; ¹⁹F NMR (470 MHz, DMSO-*d*₆/CDCl₃ = 1/1(v/v)): δ –61.48; HRMS (ESI-TOF) (*m/z*): [M–H][–] calcd. for C₇₂H₇₆BF₆N₂O₄S₄, 1285.4691; found, 1285.4638.

2-(4-(Bis(3,5-bis(trifluoromethyl)phenyl)boryl)-5''-(4-(bis(4-hexyloxyphenyl)amino)phenyl)-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carboxylic acid (AK3).

To a solution of **3** (80.9 mg, 0.104 mmol) in THF (1 mL) at –78 °C, *n*-BuLi (1.49 M in hexane, 75.2 μL, 0.104 mmol) was added dropwise. After the mixture was stirred for 1 h, *n*-Bu₃SnCl (31.0 μL, 0.114 mmol) was added to the mixture. The reaction mixture was gradually warmed to room temperature with stirring for 8 h. To the mixture, **10b** (81.0 mg, 0.105 mmol), Pd₂(dba)₃·CHCl₃ (2.32 mg, 2.24 μmol), and trifurylphosphine (2.10 mg, 9.04 μmol) were added, and the reaction mixture was refluxed for 66 h. After addition of 1 M hydrochloric acid aqueous solution, the organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was washed with water, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH₂Cl₂, then 10:1 CH₂Cl₂/MeOH) followed by preparative thin layer chromatography (7:1 CH₂Cl₂/MeOH) to give 43.7 mg (30.7 μmol) of **AK3** in 30% yield as dark red solids: mp 210–212 °C; ¹H NMR (500 MHz, THF-*d*₈): δ 10.82 (s, 1H), 8.82 (s, 1H), 7.81 (s,

2H), 7.79 (s, 4H), 7.57 (s, 1H), 7.39 (s, 1H), 7.23 (d, $J_{\text{HH}} = 9.0$ Hz, 2H), 7.10 (s, 1H), 7.06 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 6.89 (d, $J_{\text{HH}} = 9.0$ Hz, 2H), 6.85 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 6.78 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 3.94 (t, $J_{\text{HH}} = 6.5$ Hz, 4H), 2.82 (t, $J_{\text{HH}} = 7.5$ Hz, 2H), 2.67 (t, $J_{\text{HH}} = 8.0$ Hz, 2H), 1.86–1.58 (m, 8H), 1.52–1.29 (m, 24H), 0.94–0.85 (m, 12H); ^{13}C NMR (200 MHz, THF- d_8): δ 171.51, 157.10, 151.39, 151.18, 149.65, 141.26, 141.24, 140.27, 139.28, 134.19, 134.05, 133.70, 133.09, 131.83, 131.27 (q, $J_{\text{CF}} = 32$ Hz), 130.37, 130.24, 129.75, 127.86, 126.14, 125.47, 125.03 (q, $J_{\text{CF}} = 270$ Hz), 121.18, 120.17, 116.09, 68.78, 32.63, 32.62, 32.58, 31.82, 31.35, 30.31, 30.20, 30.14, 30.09, 29.54, 26.93, 26.74, 23.53, 23.49, 14.42, 14.40, 14.37 (two aromatic signals are not observed due to quadrupolar relaxation); ^{11}B NMR (160 MHz, CDCl_3) δ -0.81; ^{19}F NMR (470 MHz, CDCl_3): δ -62.48; HRMS (ESI-TOF) (m/z): $[\text{M}-\text{H}]^-$ calcd. for $\text{C}_{74}\text{H}_{74}\text{BF}_{12}\text{N}_2\text{O}_2\text{S}_2$, 1421.4438; found, 1421.4401.

2-(5''-(4-(Bis(4-hexyloxyphenyl)amino)phenyl)-4-dimesitylboryl-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carbaldehyde (11).

To a solution of **5** (238 mg, 0.20 mmol) in THF (4 mL) at -78 °C, $t\text{-BuLi}$ (1.55 M in pentane, 129 μL , 0.20 mmol) was added dropwise. After the mixture was stirred for 1 h, DMF (15 μL , 0.20 mmol) was added, and the mixture was gradually warmed to room temperature. After addition of a saturated NH_4Cl aqueous solution, the organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic layer was dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:3 hexane/toluene) to give 158 mg (0.130 mmol) of **11** in 65% yield as dark red solids: mp 152–154 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.81 (s, 1H), 8.16 (s, 1H), 7.30 (s, 1H), 7.24 (d, $J_{\text{HH}} = 8.8$ Hz, 2H), 7.13 (s, 1H), 7.10 (d, $J_{\text{HH}} = 8.9$ Hz, 4H), 7.02 (s, 1H), 6.94 (d, $J_{\text{HH}} = 8.8$ Hz, 2H), 6.85 (d, $J_{\text{HH}} = 8.9$ Hz, 4H), 6.70 (s, 4H), 3.95 (t, $J_{\text{HH}} = 6.5$ Hz, 4H), 2.77 (t, $J_{\text{HH}} = 7.9$ Hz, 2H), 2.64 (t, $J_{\text{HH}} = 7.9$ Hz, 2H), 2.21 (s, 6H), 1.91 (s, 12H), 1.81–1.76 (m, 4H), 1.69–1.61 (m, 4H), 1.50–1.45 (m, 4H), 1.43–1.27 (m, overlapped, 20H), 0.92 (t, $J_{\text{HH}} = 7.1$ Hz, 6H), 0.90 (t, $J_{\text{HH}} = 7.1$ Hz, 3H), 0.89 (t, $J_{\text{HH}} = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.45, 180.35, 169.83, 155.69, 150.55, 148.27, 145.09, 141.83, 140.32, 140.07, 140.03, 139.10, 138.39, 135.46, 134.68, 133.67, 133.03, 132.28, 129.80, 129.56, 129.33, 128.73, 128.16, 126.91, 126.58, 125.42, 119.54, 115.28, 68.23, 31.65, 31.63, 31.59, 30.94, 30.42, 29.43, 29.30, 29.20, 28.77, 25.75, 24.45, 22.61, 22.60,

20.74, 14.10, 14.09, 14.04 (two aliphatic peaks are overlapped); ^{11}B NMR (192 MHz, CDCl_3): δ 3.72; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{76}\text{H}_{92}\text{BN}_2\text{O}_3\text{S}_4$, 1219.6090; found, 1219.6024; Elemental analysis calcd. (%) for $\text{C}_{76}\text{H}_{91}\text{BN}_2\text{O}_3\text{S}_4$: C 74.84, H 7.52, N 2.30; found: C 74.92, H 7.45, N 2.22.

2-((2-(5''-(4-(Bis(4-hexyloxyphenyl)amino)phenyl)-4-dimesitylboryl-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazol-5-yl)methylene)malonic acid (AK4).

To a solution of **11** (120 mg, 98.4 μmol) in chloroform (1 mL), malonic acid (31.0 mg, 0.298 mmol) and piperidine (29.0 μL , 0.294 mmol) were added, and the mixture was refluxed for 14 h. After cooling down to room temperature, 2 M hydrochloric acid aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined organic layer was dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by preparative thin layer chromatography (8:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give 102 mg (78.0 μmol) of **AK4** in 80% yield as dark purple solids: mp 224–226 $^\circ\text{C}$; ^1H NMR (500 MHz, $\text{THF}-d_8$): δ 10.82 (s, 2H), 9.05 (s, 1H), 8.33 (s, 1H), 8.22 (s, 1H), 7.69 (s, 1H), 7.31 (s, 1H), 7.24 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 7.01 (s, 1H), 7.06 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 6.90 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 6.85 (d, $J_{\text{HH}} = 9.0$ Hz, 4H), 6.59 (s, 4H), 3.96 (t, $J_{\text{HH}} = 8.5$ Hz, 4H), 2.72 (t, $J_{\text{HH}} = 7.0$ Hz, 2H), 2.68 (t, $J_{\text{HH}} = 7.5$ Hz, 2H), 2.22 (s, 6H), 2.13 (s, 12H), 1.81–1.75 (m, 4H), 1.69–1.42 (m, 8H), 1.39–1.29 (m, overlapped, 20H), 0.94–0.88 (m, overlapped, 12H); ^{13}C NMR (200 MHz, $\text{THF}-d_8$): δ 170.79, 157.08, 153.20, 149.59, 141.29, 141.06, 140.43, 139.92, 139.62, 139.19, 134.53, 133.89, 133.38, 133.02, 132.21, 130.46, 130.38, 130.35, 129.52, 129.43, 127.85, 127.58, 126.29, 120.22, 116.09, 68.78, 32.65, 32.59, 31.82, 31.35, 30.64, 30.31, 30.25, 30.18, 30.15, 30.11, 29.56, 26.74, 23.53, 23.50, 14.44, 14.37 (two aliphatic and one aromatic peaks are overlapped, and two aromatic signals are not observed due to quadrupolar relaxation); ^{11}B NMR (160 MHz, $\text{DMSO}-d_6/\text{CDCl}_3 = 3/1(\text{v/v})$): δ 0.17; HRMS (FAB) (m/z): $[\text{M}^+]$ calcd. for $\text{C}_{79}\text{H}_{93}\text{BN}_2\text{O}_6\text{S}_4$, 1304.6022; found, 1304.6013.

(E)-3-(2-(5''-(4-(Bis(4-hexyloxyphenyl)amino)phenyl)-4-dimesitylboraneyl-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazol-5-yl)-2-cyanoacrylic acid (AK5).

To a solution of **11** (58.4 mg, 0.048 mmol) in chloroform (2 mL), cyanoacetic acid (8.1 mg, 0.096 mmol) and piperidine (9.5 μL , 0.096 mmol) were added, and the mixture

was refluxed for 60 h. After cooling down to room temperature, 2 M hydrochloric acid aqueous solution was added. The organic layer was separated and the aqueous layer was extracted with Et₂O three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by preparative thin layer chromatography (6:1 CH₂Cl₂/MeOH) to give 42.5 mg (0.033 mmol) of **AK5** in 69% yield as dark purple solids: mp 110–112 °C; ¹H NMR (500 MHz, DMSO-*d*₆/CDCl₃ = 3/1(v/v)): δ 8.70 (s, 1H), 8.62 (s, 1H), 7.28 (s, 1H), 7.21 (s, 1H), 7.17 (d, *J*_{HH} = 8.5 Hz, 2H), 7.02 (s, 1H), 7.01 (d, *J*_{HH} = 9.0 Hz, 4H), 6.83 (d, *J*_{HH} = 9.0 Hz, 4H), 6.79 (d, *J*_{HH} = 8.5 Hz, 2H), 6.55 (s, 4H), 3.89 (t, *J*_{HH} = 6.5 Hz, 4H), 2.71 (t, *J*_{HH} = 7.5 Hz, 2H), 2.58 (t, *J*_{HH} = 7.5 Hz, 2H), 2.09 (s, 6H), 1.80 (s, 12H), 1.72–1.66 (m, 4H), 1.61–1.54 (m, 4H), 1.42–1.37 (m, 4H), 1.34–1.21 (m, 20H), 0.86 (t, *J*_{HH} = 7.0 Hz, 6H), 0.83 (t, *J*_{HH} = 7.0 Hz, 3H), 0.81 (t, *J*_{HH} = 6.5 Hz, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆/CDCl₃ = 3/1(v/v)): δ 167.97, 162.64, 155.29, 148.49, 147.87, 146.79, 144.19, 141.72, 139.83, 139.39, 139.29, 138.19, 137.87, 133.16, 132.41, 132.10, 131.35, 129.29, 129.18, 129.01, 128.63, 128.45, 128.11, 126.67, 125.56, 124.28, 118.54, 115.83, 115.12, 67.48, 30.92, 30.13, 29.74, 28.74, 28.63, 28.52, 28.42, 28.04, 25.11, 24.02, 21.98, 21.93, 20.24, 13.71 (five aliphatic peaks are not overlapped); ¹¹B NMR (160 MHz, DMSO-*d*₆/CDCl₃ = 3/1(v/v)): δ 1.15; HRMS (FAB) (*m/z*): [M]⁺ calcd. for C₇₉H₉₂BN₃O₄S₄, 1285.6064; found, 1285.6022.

Ethyl 2-(5-iodothiophen-2-yl)thiazole-5-carboxylate (**12**).

To a solution of ethyl 2-(thiophen-2-yl)thiazole-5-carboxylate (86.2 mg, 0.360 mmol) in CHCl₃ (0.5 mL) and AcOH (0.5 mL), NIS (86.4 mg, 0.384 mmol) was added. The mixture was refluxed for 28 h. After cooling down to room temperature, a saturated Na₂SO₃ aqueous solution was added, and the mixture was extracted with Et₂O three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 hexane/CH₂Cl₂) to give 131 mg (0.359 mmol) of **12** in quantitative yield as pale yellow solids: mp 133–135 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.27 (s, 1H), 7.25 (d, *J*_{HH} = 3.9 Hz, 1H), 7.22 (d, *J*_{HH} = 3.9 Hz, 1H), 4.37 (q, *J*_{HH} = 7.2 Hz, 2H), 1.38 (t, *J*_{HH} = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 165.14, 161.10, 148.84, 142.33, 138.00, 128.89, 128.39, 79.21, 61.75, 14.26; HRMS (APCI-TOF) (*m/z*): [M]⁺ calcd. for C₁₀H₈INO₂S₂, 364.9041; found, 364.9077; Elemental analysis calcd. (%)

for C₁₀H₈INO₂S₂: C 32.89, H 2.21, N 3.84; found: C 33.03, H 2.14, N 3.96.

Ethyl 2-(5''-(4-(bis(4-hexyloxyphenyl)amino)phenyl)-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carboxylate (13).

To a solution of **3** (300 mg, 0.386 mmol) in THF (3.9 mL) at -78 °C, *n*-BuLi (1.56 M in hexane, 0.272 mL, 0.424 mmol) was added dropwise. After the mixture was stirred for 1 h, *n*-Bu₃SnCl (0.115 mL, 0.424 mmol) was added to the mixture, and the mixture was gradually warmed to room temperature with stirring for 6.5 h. To the mixture, **12** (141 mg, 0.386 mmol), Pd₂(dba)₃·CHCl₃ (8.1 mg, 7.8 μmol), and trifurylphosphine (7.2 mg, 31 μmol) were added, and the mixture was refluxed for 14 h. After cooling down to room temperature, a saturated NH₄Cl aqueous solution was added, and the mixture was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:2 hexane/CH₂Cl₂) followed by gel permeation chromatography (JAIGEL 1H/2H) eluted with toluene to give 247 mg (0.243 mmol) of **13** in 63% yield as red solids: mp 63–65 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.31 (s, 1H), 7.50 (d, *J*_{HH} = 3.9 Hz, 1H), 7.23 (d, *J*_{HH} = 8.4 Hz, 2H), 7.12 (d, *J*_{HH} = 3.9 Hz, 1H), 7.10 (s, 1H), 7.09 (d, *J*_{HH} = 9.0 Hz, 4H), 7.00 (s, 1H), 6.93 (d, *J*_{HH} = 8.4 Hz, 2H), 6.84 (d, *J*_{HH} = 9.0 Hz, 4H), 4.38 (q, *J*_{HH} = 7.2 Hz, 2H), 3.94 (t, *J*_{HH} = 6.6 Hz, 4H), 2.77 (t, *J*_{HH} = 7.8 Hz, 2H), 2.64 (t, *J*_{HH} = 7.8 Hz, 2H), 1.82–1.72 (m, 4H), 1.70–1.61 (m, 4H), 1.51–1.28 (m, overlapped, 27H), 0.93–0.86 (m, overlapped, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 166.21, 161.16, 155.60, 148.91, 148.13, 141.51, 140.28, 139.88, 138.67, 138.20, 134.27, 133.00, 132.40, 132.00, 129.50, 128.80, 128.45, 127.84, 127.81, 126.82, 125.48, 123.91, 119.54, 115.21, 68.15, 61.59, 31.62, 31.55, 30.91, 30.38, 29.40, 29.26, 29.19, 28.75, 25.71, 22.57, 14.25, 14.06, 14.00 (five aliphatic signals are overlapped); HRMS (APCI-TOF) (*m/z*): [M]⁻ calcd. for C₆₀H₇₄N₂O₄S₄, 1014.4531; found, 1014.4541; Elemental analysis calcd. (%) for C₆₀H₇₄N₂O₄S₄: C 70.97, H 7.35, N 2.76; found: C 70.91, H 7.34, N 2.85.

2-(5''-(4-(bis(4-hexyloxyphenyl)amino)phenyl)-4',4''-dihexyl-[2,2':5',2''-terthiophen]-5-yl)thiazole-5-carboxylic acid (AK0).

To a solution of **13** (95.7 mg, 0.094 mmol) in THF (2.0 mL), 2 M NaOH aqueous solution (2.0 mL) was added, and the mixture was refluxed for 12 h. After cooling down

to room temperature, the mixture was acidified with 2M HCl aqueous solution and was extracted with Et₂O three times. The combined organic layer was washed with water, dried over MgSO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (9:1 CH₂Cl₂/MeOH) to give 89.4 mg (0.091 mmol) of **AK0** in 96% yield as red solids: mp 111–113 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.39 (s, 1H), 7.54 (d, *J*_{HH} = 4.0 Hz, 1H), 7.23 (d, *J*_{HH} = 8.5 Hz, 2H), 7.14 (d, *J*_{HH} = 4.0 Hz, 1H), 7.12 (s, 1H), 7.09 (d, *J*_{HH} = 8.5 Hz, 4H), 7.01 (s, 1H), 6.93 (d, *J*_{HH} = 8.5 Hz, 2H), 6.84 (d, *J*_{HH} = 8.5 Hz, 4H), 3.94 (t, *J*_{HH} = 6.5 Hz, 4H), 2.78 (t, *J*_{HH} = 8.0 Hz, 2H), 2.65 (t, *J*_{HH} = 8.0 Hz, 2H), 1.79–1.75 (m, 4H), 1.67–1.62 (m, 4H), 1.48–1.28 (m, 24H), 0.91 (t, *J*_{HH} = 7.0 Hz, 6H), 0.89 (t, *J*_{HH} = 7.5 Hz, 3H), 0.88 (t, *J*_{HH} = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 167.60, 164.30, 155.68, 150.60, 148.24, 142.14, 140.36, 140.06, 138.85, 138.34, 134.10, 132.99, 132.34, 132.27, 129.59, 129.37, 128.61, 128.10, 126.90, 126.43, 125.53, 124.10, 119.59, 115.31, 68.26, 31.66, 30.94, 30.46, 29.43, 29.31, 29.21, 28.78, 25.75, 22.61, 14.10, 14.03 (six aliphatic signals are overlapped); HRMS (ESI-TOF) (*m/z*): [M–H][–] calcd. for C₅₈H₆₉BN₂O₄S₄, 985.4146; found, 985.4126.

Lippert-Mataga Plot for **AK1**

The change in dipole moment from the ground state to the excited state ($\mu_e - \mu_g = \Delta\mu$) for **AK1** was estimated by the Lippert-Mataga plot (Equation 1),²⁴ in which $\Delta\nu$ is the Stokes shift, C is a constant, ϵ_0 ($= 8.854 \times 10^{-12}$ F/m) is the permittivity of vacuum, h ($= 6.626 \times 10^{-34}$ J/s) is the Planck's constant, c ($= 2.9979 \times 10^{10}$ cm/s) is the speed of the light, a is the radius of the cavity, μ_e and μ_g are the dipole moments in the excited state and ground state, respectively. In the Equation 2, the function of orientation polarizability is defined as Δf , in which ϵ and n are the dielectric constant and refractive index of solvent, respectively. The value for the radius of the cavity (a) was determined as 8.73 Å by DFT calculations at the B3LYP/6-31G(d) level of theory. Accordingly, $\Delta\mu$ value is determined to be 21.2 D, suggesting that **AK1** has intramolecular charge transfer (ICT) character.

$$\Delta\nu = \nu_{\text{abs}} - \nu_{\text{FL}} = \Delta f(\mu_e - \mu_g)^2 / 2\pi\epsilon_0 h c a^3 + C \quad 1$$

$$\Delta f = (\epsilon - 1) / (2\epsilon + 1) - (n^2 - 1) / (2n^2 + 1) \quad 2$$

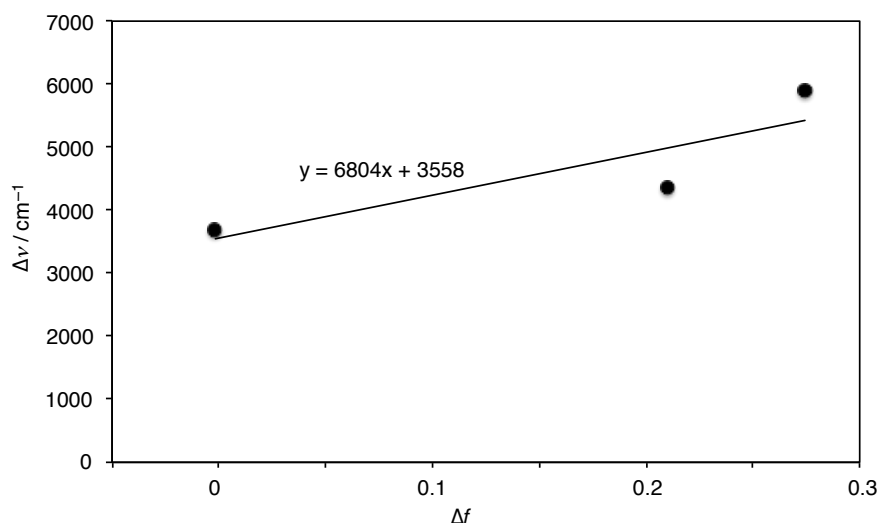


Figure 17. The Lippert-Mataga plot for AK1.

Measurements of Electrochemical and Photophysical Properties of Dyes Adsorbed on TiO₂

Dye-adsorbing TiO₂ layer was prepared as follow: The TiO₂ layer (Solaronix, T/SP, particle size: 15–20 nm) was coated on the FTO glass plates (Asahi Glass Co. Ltd, 1.8 mm thick) by a screen printing. The electrodes coated with the TiO₂ pastes were gradually heated at 200 °C for 10 min and then at 500 °C for 30 min. After cooling down to room temperature, the TiO₂ electrodes were immersed into the dye solution (0.1 mM in toluene), and kept at 30 °C for 6 h. Then, cyclic voltammetry was carried out using dye-adsorbing TiO₂ electrodes as a working electrode under an argon atmosphere in MeCN with 0.1 M *n*-Bu₄N⁺PF₆[−] as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. The UV/vis absorption spectra were also measured with dye-adsorbing TiO₂ electrodes. The thickness of the TiO₂ electrodes was 2 μm. The thickness of TiO₂ electrode was measured with SURFCOM 130A (ACCRETECH, TOKYO SEIMITSU Co., Ltd.).

Fabrication of DSSCs

The fabrication method of DSSC is modified from the reported procedure.³⁰ At first, FTO glass plates (Asahi Glass Co. Ltd, 1.8 mm thick) were treated in a UV-O₃ system for 15 min. The paste for the transparent nanocrystalline-TiO₂ layer (Solaronix, HT/SP, particle size: 10–15 nm) was coated on the FTO glass plates by screen printing at the

size of 4 mm $\times$ 4 mm. After that, the plates were left in petri dish for 1 min at room temperature, dried in an oven for 3 min at 120 °C, and cooled down to room temperature. Next, the paste for the transparent nanocrystalline-TiO₂ layer (Solaronix, T/SP, particle size: 15–20 nm) was coated twice on the glass plates by screen printing and dried by the same procedure as previous layer. This printing–leaving–drying–cooling procedure was repeated twice for the paste (SOLARONIX, T/SP) and then twice for the paste (Solaronix, D/SP, particle size: 15–20 nm). The electrodes coated with the TiO₂ pastes were gradually heated from room temperature to 200 °C for 10 min, kept at 200 °C for 10 min, heated again from 200 to 500 °C for 15 min, and kept at 500 °C for 30 min. The TiO₂ films were treated with in 0.1 M TiCl₄ aqueous solution at 70 °C for 30 min and washed with water. After the printing–leaving–drying–cooling procedure using the paste for the scattering layer (Solaronix, R/SP, particle size: >100 nm) one time, the electrodes coated with the TiO₂ pastes were gradually heated in the same way as before. The thickness of the TiO₂ electrodes was 10–16 μ m. The TiO₂ electrodes were immersed into the dye solutions (0.1 mM in toluene) and kept at 30 °C for 16 h for adsorption of the dyes.

The counter electrodes were prepared by sputtering of Pt on an FTO plates and the glass plates were drilled.

An organic electrolyte solution was composed of 0.1 M LiI, 25 mM I₂, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) with/without 0.5 M TBP in acetonitrile.

The dye-adsorbing TiO₂ electrode and the Pt counter electrode were assembled into a sandwich-type cell with film spacer (30 μ m thickness) between the electrodes. The electrolyte solution (7 μ L) was injected into the cell from a drilled hole on the Pt counter electrode. After the holes were sealed with glass plate, the cell was fixed with clips. Finally, solder was deposited on the edges of the TiO₂ electrode and the Pt counter electrode.

Photovoltaic Measurements

The photovoltaic performances of the fabricated DSSCs were evaluated by the incident-photon to current conversion efficiency (IPCE) spectra and the photocurrent-voltage (*J-V*) measurements of the cells with the area of 0.16 cm² by using a square shade mask in air without sealing. The (IPCE) spectra were recorded on a

SMO-250III system. The J - V curves were measured with an OTENTO-SUNIII (BUNKOKEIKI Co., Ltd.) and a Keithley model 2400 (BUNKOKEIKI Co., Ltd.) under the simulated sunlight irradiation of AM-1.5G one sun condition (100 mW cm^{-2}). The light intensity of the illumination source was adjusted by using standard silicon photodiodes: BS520 for J - V measurements and SiPD S1337-1010BQ for IPCE measurements.

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Chapter 5

D- π -A Dyes Containing Diketopyrrolopyrrole and Boryl-Substituted Thienylthiazole Units for Dye-Sensitized Solar Cells with High J_{SC} Values

Abstract: The organic D- π -A dyes **HS1** and **HS2** were synthesized as low-band-gap sensitizers with diketopyrrolopyrrole and boryl-substituted thienylthiazole moieties as π -spacer and acceptor units, respectively. Dye-sensitized solar cells containing these dyes exhibited high J_{SC} values (≤ 19.8 mA/cm²), as the absorption of **HS1** and **HS2** extends into the NIR region.

Introduction

As mentioned in Chapter 4, in order to develop excellent photosensitizers for dye-sensitized solar cells, the fine-tuning of their electronic structure is highly required.¹ So far, several Ru-based^{2–4} and porphyrin-based NIR sensitizers^{5–7} have achieved high power conversion efficiencies (η) in DSSCs on account of their high short-circuit current density (J_{sc}) owing to effective use of a large photon flux in the visible/NIR region of the solar spectrum. Examples include Ru-based **CYC-B1** ($J_{sc} = 23.9 \text{ mA cm}^{-2}$)³ and **DX1** (26.8 mA cm^{-2})⁴, as well as porphyrin-based **SM315** (18.1 mA cm^{-2})⁶ and **GY50** (18.5 mA cm^{-2})⁷ (Figure 1). Despite their advantages regarding the versatility of their molecular design, examples for organic D- π -A dyes^{8–11} with high J_{sc} values still remain limited to **DA2** (17.6 mA cm^{-2})⁹, **Ant3** (18.4 mA cm^{-2})¹⁰ and **RK1** (20.3 mA cm^{-2})¹¹. Therefore, the development of efficient organic D- π -A sensitizers with tunable electronic structure is highly desirable.

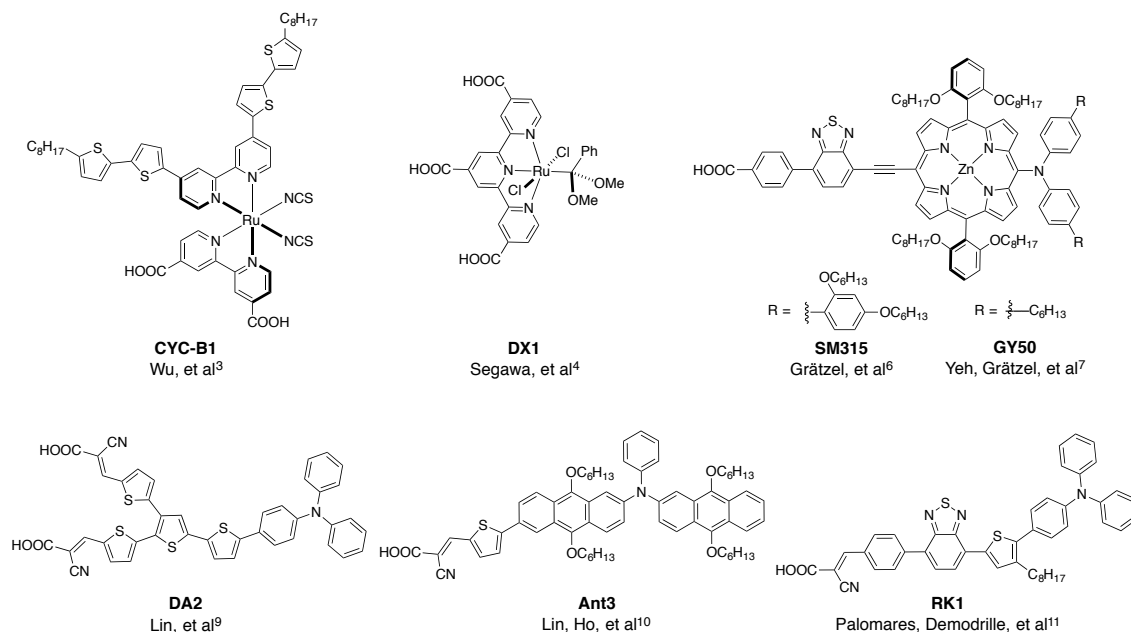


Figure 1. Examples of photosensitizers exhibiting high J_{sc} value in DSSCs.

In Chapter 4, the author described that D- π -A dyes **AK1–5** with a boryl-substituted thienylthiazole as the key electron-accepting unit are susceptible to tuning of their electronic structure. In contrast, the optical band-gap was not directly affected by the modification of the HOMO-LUMO gap due to a contribution of the HOMO-1 $\rightarrow$ LUMO transition to the longest-wavelength absorption. To overcome this drawback, the author focused on diketopyrrolopyrrole (DPP)^{13,14} as a narrow π - π^* -gap π -spacer unit, and

subsequently designed and synthesized D- π -A dyes **HS1** and **HS2** (Figure 2). In this chapter, the impact of the DPP unit on the electrochemical and photophysical properties of **HS1** and **HS2**, as well as on the photovoltaic performance of DSSCs based on these dyes, were investigated.

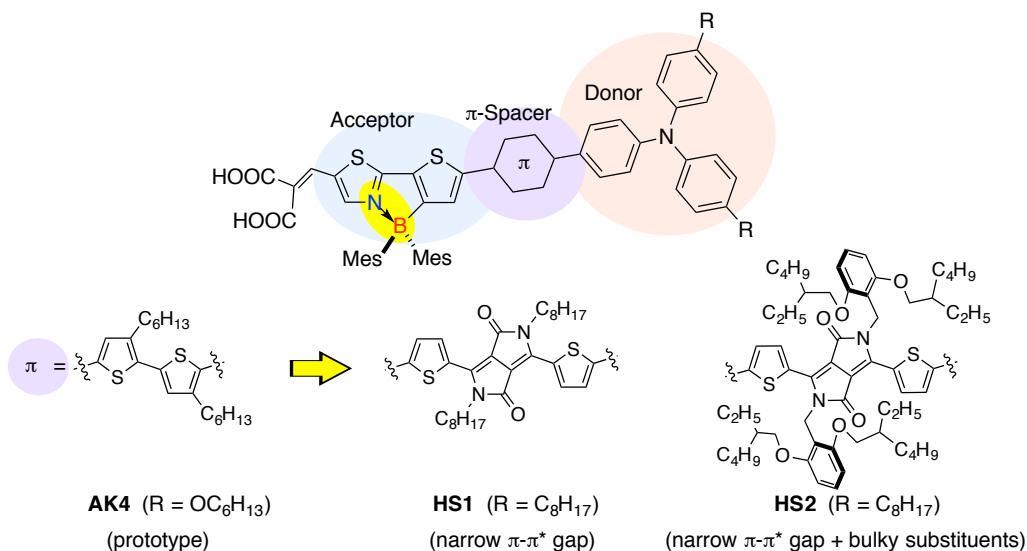


Figure 2. Chemical structures of **HS1**, **HS2**, and reference compound **AK4**.

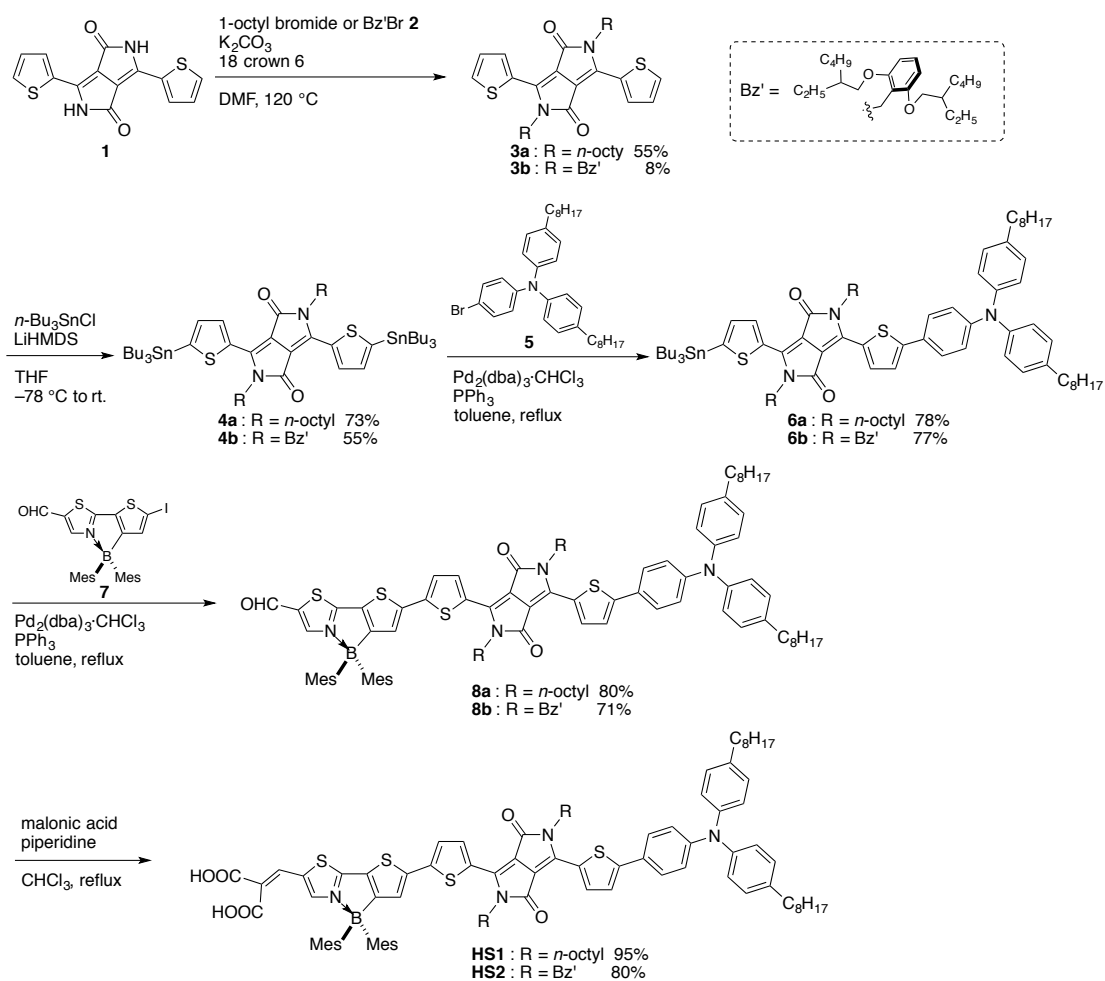
Results and Discussion

Synthesis

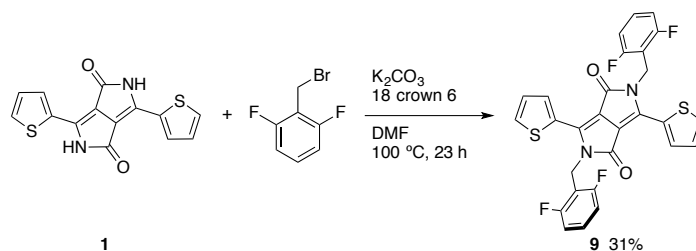
The outline for synthesis of **HS1** and **HS2** is shown in Scheme 1. Nucleophilic substitution reaction between **1**¹⁵ and octyl bromide or 2-bromomethyl-1,3-bis(2-ethylhexyloxy)benzene (**2**) with K₂CO₃ and 18-crown-6 in DMF at 120 °C afforded *N*-substituted diketopyrrolopyrrole derivatives **3a** and **3b** in 55% and 8% yields, respectively. The lithiation of **3a** and **3b** with lithium hexamethyldisilazide (LiHMDS) and a subsequent treatment with *n*-Bu₃SnCl gave distanylated products **4a** and **4b** in 73% and 55 % yields, respectively. Then, Stille coupling reaction between distanylated **4a** and **4b** and bromo derivative of the donor unit **5** gave **6a** and **6b** as D-A units in 78% and 77% yields, respectively. And then, the acceptor unit of boryl-substituted thienylthiazole was introduced to the D-A unit by Stille coupling reaction of **6a/6b** with iodo derivative of boryl-substituted thienylthiazole **7** to furnish **8a** and **8b** in 80% and 71% yields, respectively. The terminal formyl group of **8a** and **8b** was converted to -CH=C(COOH)₂ group as the anchor unit by Knoevenagel condensation with malonic acid, which gave **HS1** and **HS2**

as green solids in 95% and 80% yields, respectively. In addition, As a model compound to evaluate the steric effect, compound **9** was also synthesized in 31% yield by nucleophilic substitution reaction between **1** and 2,6-difluorobenzyl bromide with K_2CO_3 and 18-crown-6 in DMF at 120 °C (Scheme 2).

Scheme 1. Synthetic route of **HS1** and **HS2**



Scheme 2. Synthesis of compound **9**



Crystal Structure of **9** and Evaluation of Steric Effects of Benzyl Groups on DPP Unit

Single-crystal X-ray diffraction analysis on a model compound **9** revealed that the phenyl groups adopt an orthogonal arrangement with respect to the DPP skeleton (Figure 3). This result indicates the steric protection on the π -skeleton in **HS2** by a the 2,6-dialkoxybenzyl groups (Figure 4).

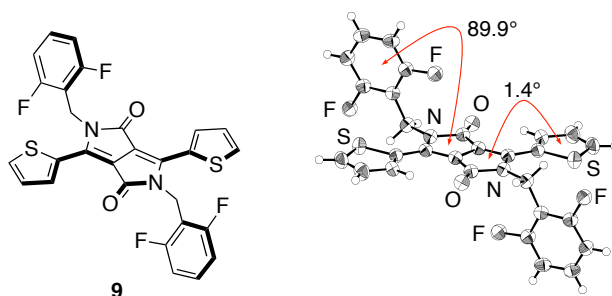


Figure 3. Chemical structure and ORTEP drawing of **9** (50% probability for thermal ellipsoids).

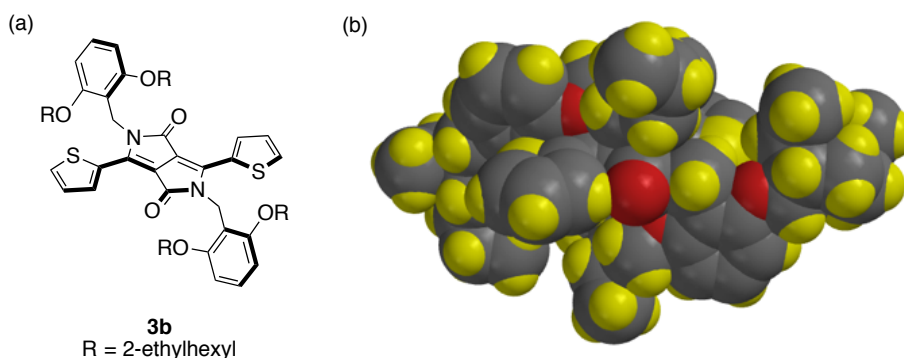


Figure 4. (a) Chemical structure and (b) space filling model of **3b**.

Theoretical Calculations

To assess the effect of the DPP unit on the electronic structure of such D- π -A dyes, DFT calculations were conducted at the B3LYP/6-31G(d) level of theory on model compounds **AK4'** and **HS'**, in which the long alkyl groups were replaced with methyl groups (Figure 5). In **AK4'**, the HOMO is located on the triarylamine donor, whereas the HOMO-1 corresponds to the π -orbital, which is delocalized over the bithiophene and boryl-substituent thienylthiazole moieties. TD-DFT calculations at the CAM-B3LYP/6-31G(d) level of theory suggested that the longest-wavelength absorption of **AK4'** is composed of the HOMO $\rightarrow$ LUMO transition (37%), which

exhibits intramolecular charge transfer character, and the π - π^* transition from the HOMO-1→LUMO (45%). Unfortunately, such a mixed absorption profile hampers a controlled modulation of the optical band gap by tuning the frontier orbitals. However, when DPP was used as a π -spacer unit in **HS'**, the π -orbital, which is delocalized over the DPP unit, is effectively elevated to the HOMO. TD-DFT calculations suggested that the major contribution to the longest-wavelength absorption of **HS'** is the HOMO→LUMO transition with π - π^* character (67%), which would lead to a substantial red-shift of the absorption wavelength with increased oscillator strength.

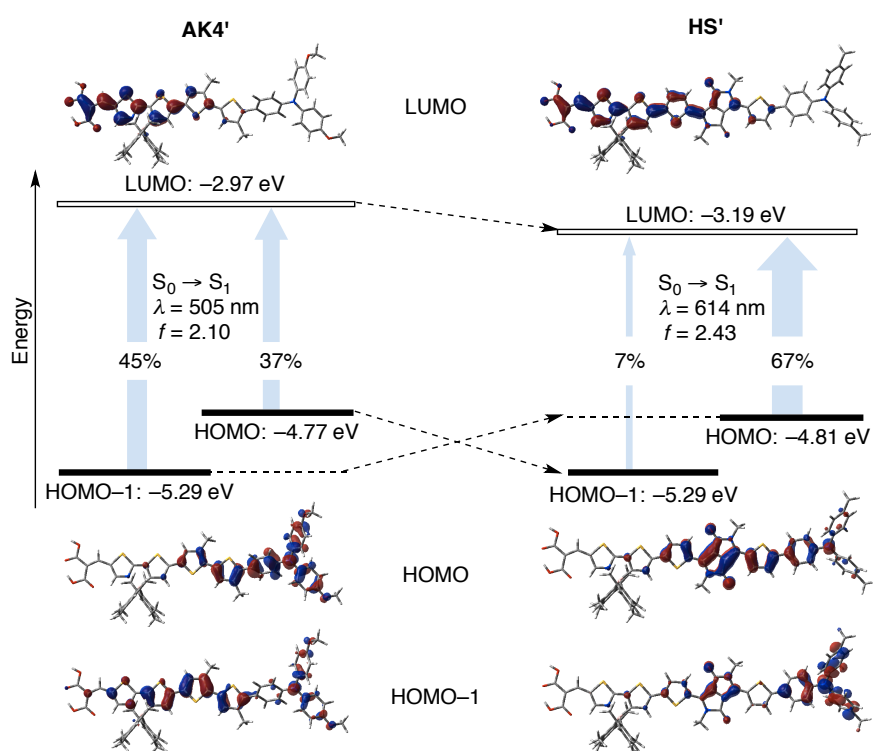


Figure 5. Comparison of the theoretical transition energies, oscillator strengths, and the individual contributions to the longest-wavelength absorption of **AK4'** and **HS'** obtained from TD-DFT calculations at the CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

Photophysical Properties of **HS1** and **HS2** in Solution and on TiO_2

The absorption spectra of **HS1** and **HS2** in solution (Figure 6) exhibit substantially red-shifted absorption bands and increase extinction coefficients relative to those of **AK4** ($\lambda_{\text{abs}} = 502$ nm, $\log \varepsilon = 4.64$). The longest-wavelength absorption bands of **HS1** and **HS2** in THF with 1% TFA are observed at $\lambda_{\text{abs}} = 640$ and 669 nm ($\log \varepsilon = 4.89$ and 4.88) and $\lambda_{\text{abs}} = 642$ nm ($\log \varepsilon = 4.83$), respectively (Figure 6). An examination of the

solvent dependency of these spectra revealed that the longest-wavelength absorption bands of **HS1** and **HS2** are less sensitive to solvent polarity (Figure 7) whereas **AK4** shows a blue-shifted absorption in polar solvents (See Chapter 4). This result indicates a large contribution from the π - π^* transition in **HS1** and **HS2**. To determine the effects of the substituents on the DPP unit, the absorption spectra for films of **HS1** and **HS2** were examined (Figure 6). A film of **HS1**, cast from CH_2Cl_2 solution, exhibits a broader band with red-shifted absorption edge compared to that in solution, whereas a film of **HS2** shows an almost identical peak to that in solution. This result suggests that octyl-substituted **HS1** forms aggregates in the film due to intermolecular π - π interactions, whereas the bulky substituents in **HS2** effectively suppress such aggregation even in the film.

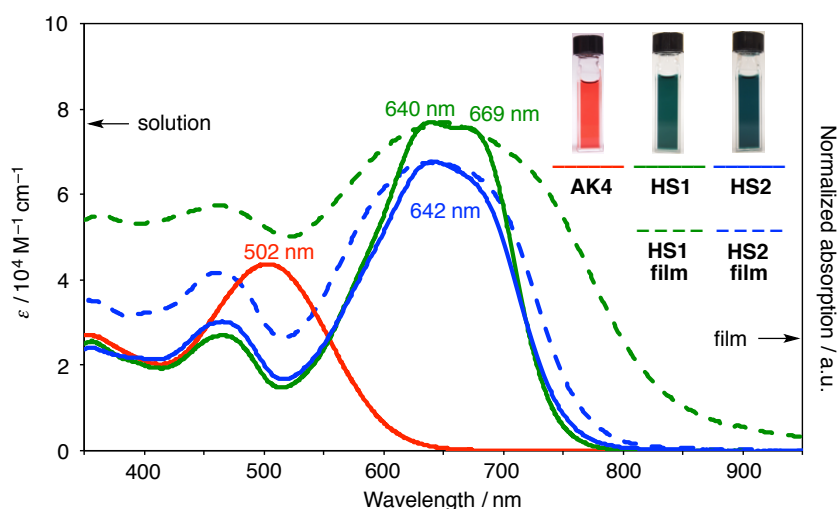


Figure 6. UV/vis absorption spectra for **HS1**, **HS2**, and **AK4** in THF containing 1% TFA, and for films of **HS1** and **HS2**.

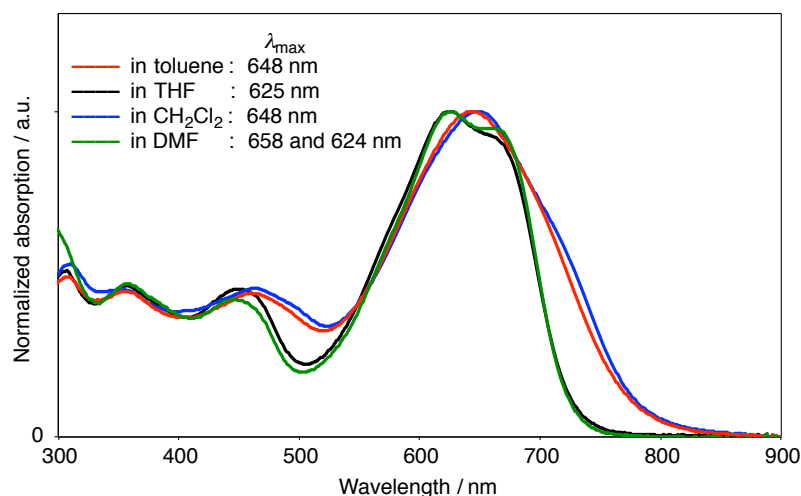


Figure 7. Solvent effects: UV/vis absorption spectra of **HS1** in toluene, THF, CH_2Cl_2 , and DMF.

As the sensitizers are deposited onto TiO_2 substrate in DSSCs, absorption spectra were also measured for dye/ TiO_2 adsorbates (for details, see Experimental Section). The absorption edge of **HS1**/ TiO_2 was observed at $\lambda_{\text{edge}} = 840$ nm, which is red-shifted by 40 nm compared to that of **HS2**/ TiO_2 (800 nm) (Figure 8), as observed in the films (Figure 6). Considering that the absorption edges of **HS1** and **HS2** in solution are almost identical ($\lambda_{\text{edge}} = 770$ nm), the peak tailing observed for **HS1**/ TiO_2 relative to **HS2**/ TiO_2 should most likely be attributed to the aggregation of **HS1** on the TiO_2 surface.

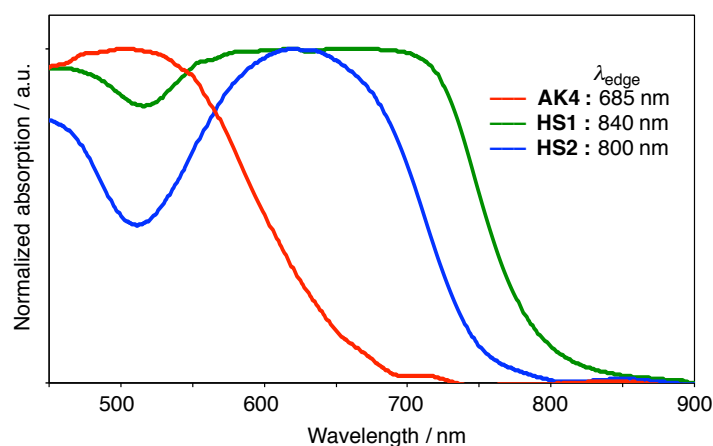


Figure 8. UV/vis absorption spectra of **HS1**, **HS2**, and **AK4** adsorbing TiO_2 electrode.

Electrochemical Properties of HS1 and HS2 in Solution and on TiO₂

Cyclic voltammograms were recorded for solutions of **HS1** and **HS2** in THF (reduction) and CH₂Cl₂ (oxidation). **HS1** and **HS2** exhibit one reversible reduction wave at $E_{1/2} = -1.49$ V (vs. Fc/Fc⁺) and -1.67 V, respectively, i.e., at substantially less negative potentials than that of **AK4** (-1.90 V) (Figure 9). The oxidation waves for **HS1** and **HS2** were observed at $E_{1/2} = +0.29$ and $+0.17$ V (vs. Fc/Fc⁺), respectively, which are comparable to that of **AK4** ($+0.20$ V). Both the oxidation and reduction waves of **HS2** occur at slightly negative potential relative to those of **HS1**, which is most likely due to the electron-donating effect of the 2,6-dialkoxybenzyl groups on the DPP unit. This notion is also supported by the results of DFT calculations; the HOMO and LUMO levels of **HS2'** are at -4.60 and -3.04 eV, respectively.

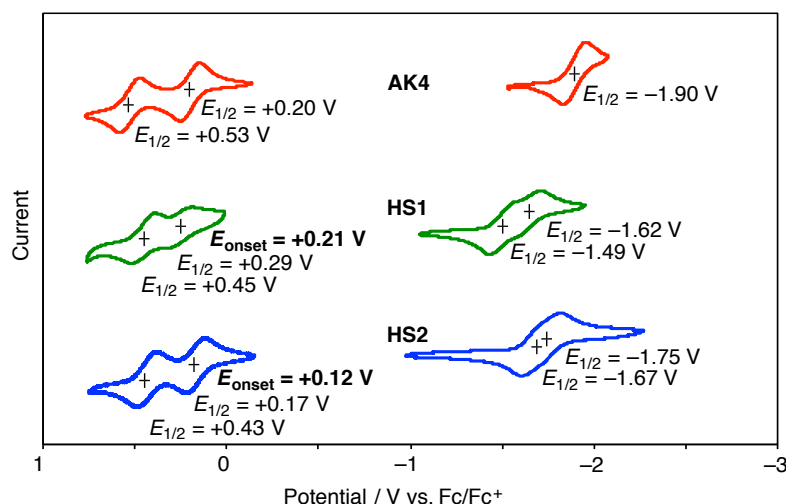


Figure 9. Cyclic voltammograms of **HS1**, **HS2**, and **AK4** measured in CH₂Cl₂ for oxidation and in THF for reduction with 0.1 M [*n*-Bu₄N⁺][PF₆⁻] as a supporting electrolyte at a scan rate of 0.1 V s⁻¹.

Cyclic voltammograms for dye/TiO₂ adsorbates were also recorded (for details, see Experimental Section). For **HS1**/TiO₂ ($E_{1/2} = +0.52$ V vs. Fc/Fc⁺) and **HS2**/TiO₂ ($+0.36$ V), similar oxidation potentials to that of **AK4** were observed (See Chapter 4), while their onset potentials were positively shifted by 0.14 V compared to those in solution (Figure 10).

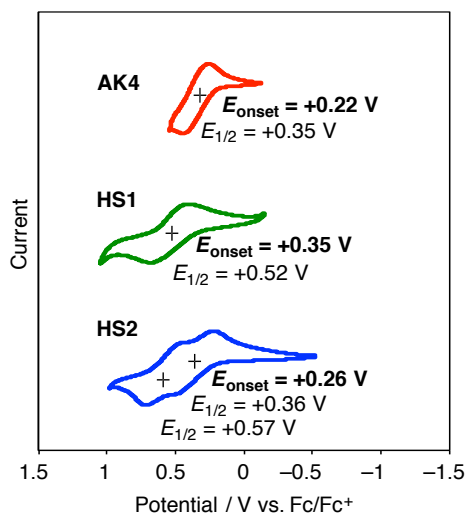


Figure 10. Cyclic voltammograms of **HS1**, **HS2**, and **AK4** using dye-adsorbing TiO_2 electrode as working electrode in MeCN containing $[n\text{-Bu}_4\text{N}^+][\text{PF}_6^-]$ as a supporting electrolyte, at a scan rate of 100 mV s^{-1} .

Experimentally Determined HOMO and LUMO Levels of HS1 and HS2

Based on the obtained onset oxidation potentials, absorption edges, and optical band gaps, the HOMO and LUMO levels were estimated for **HS1** and **HS2** in solution and for **HS1**/ TiO_2 and **HS2**/ TiO_2 (Figure 11). The HOMO levels of **HS1**/ TiO_2 (-5.45 eV) and **HS2**/ TiO_2 (-5.36 eV) are slightly lower or comparable to that of **AK4**/ TiO_2 (-5.32 eV), while the LUMO levels are decreased significantly. The potential differences between the LUMO of **HS2**/ TiO_2 (-3.81 eV) and the conduction band of TiO_2 (-4.0 eV)^{16,17} is suitably large (0.19 eV), while that of **HS1**/ TiO_2 (-3.97 eV) is relatively small (0.03 eV).

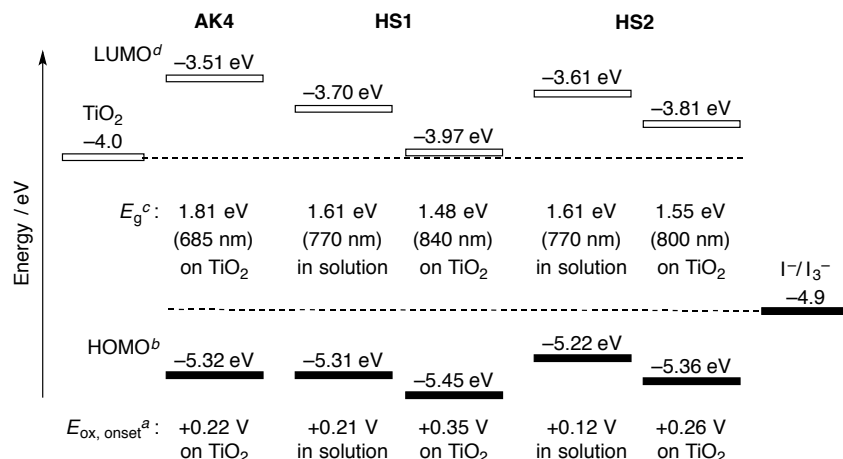


Figure 11. Experimentally determined energy diagrams for **HS1**, **HS2**, and **AK4**. ^aMeasured in MeCN with 0.1 M $[n\text{-Bu}_4\text{N}^+][\text{PF}_6^-]$ as the supporting electrolyte. Potentials are referenced against the internal standard Fc/Fc^+ ; ^bHOMO = $-(E_{\text{ox, onset}} + 5.10)$ eV¹⁷; ^c $E_g = 1240/\lambda_{\text{edge}}$; ^dLUMO = HOMO + E_g .

DSSC Performance

In order to determine how the electronic structure of the dyes affects the DSSC performances, DSSCs containing **HS1** or **HS2** and the standard I^-/I_3^- redox electrolyte in MeCN were fabricated,¹⁸ and their performances were investigated. Their J - V characteristics under AM 1.5G irradiation are summarized in Table 1 (for details, see Experimentl Section). The **HS1** cell, which contains 0.5 M 4-*tert*-butylpyridine (TBP) in the electrolyte, exhibited only a moderate short-circuit current density ($J_{\text{SC}} = 7.8 \text{ mA cm}^{-2}$); together with an open-circuit voltage of $V_{\text{OC}} = 0.61 \text{ V}$ and a fill factor of $\text{FF} = 0.68$. As a result, the **HS1** cell exhibited a low PCE of $\eta = 3.3\%$ (Figure 12a). In the incident-photon-to-current-conversion efficiency (IPCE) spectrum (Figure 12b), this **HS1** cell exhibited a broad spectrum tailing to the NIR region ($\sim 820 \text{ nm}$), which is significantly red-shifted relative to that of **AK4** ($\sim 730 \text{ nm}$). However, the external quantum efficiency (EQE) of this **HS1** cell remained as low as $\sim 30\%$ over the entire spectral range, due to the small potential difference between the LUMO level of **HS1** and the conduction band of TiO_2 . It is known that adding TBP to the I^-/I_3^- redox electrolyte elevates the TiO_2 band edge potential, which leads to an increase of V_{OC} , and also decreases the recombination of electrons in TiO_2 by preventing access of triiodide to the TiO_2 surface.^{19,20} Focusing on the former effect, TBP was removed from the electrolyte of the **HS1** cell. The resulting device exhibited decreased V_{OC} (0.44 V) and FF (0.49) values, but a substantially increased J_{SC} value (19.8 mA cm^{-2}), resulting in an

increased PCE ($\eta = 4.3\%$). In the IPCE spectrum, the EQE was increased to 75%, accompanied by a further red-shift of the spectrum tailing up to 900 nm. In order to prevent dye aggregation on the surface of TiO_2 , deoxycholic acid (DCA) was added as a co-adsorbent.^{19,21} Upon adding 2 mM DCA to the dye solution for deposition on TiO_2 , the **HS1** cell without TBP showed slightly improved V_{oc} (0.48 V) and FF (0.53) values, while maintaining a high J_{sc} (19.4 mA cm^{-2}) value, which afforded the highest PCE ($\eta = 4.9\%$) for **HS1** in this study.

Table 1. Photovoltaic Performance of DSSCs Based on **HS1**^a and **AK4**^b

Dye	TBP	J_{sc}	V_{oc}	FF	η
	[M]	[mA cm^{-2}]	[V]		[%]
HS1	0.5	7.8	0.61	0.68	3.3
HS1	None	19.8	0.44	0.49	4.3
HS1+DCA	0.5	7.1	0.61	0.73	3.2
HS1+DCA	None	19.4	0.48	0.53	4.9
AK4	0.5	12.1	0.73	0.67	5.9

^a I^-/I_3^- -based electrolyte solution: 0.6 M DMPII, 0.1 M LiI, 0.1 M I_2 , and 0.5 M or no TBP in MeCN. ^b Electrolyte solution: 0.6 M DMPII, 0.1 M LiI, 0.025 M I_2 , and 0.5 M TBP in MeCN.

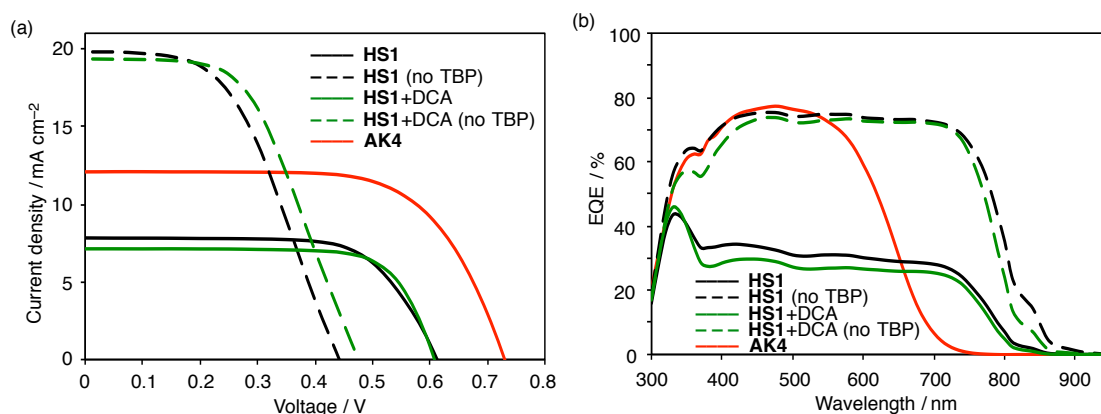


Figure 12. Photovoltaic performance of DSSC devices containing **HS1** or **AK4**: (a) J - V curves and (b) IPCE spectra. Solid and dashed lines represent the conditions in the presence or absence of TBP, respectively.

The **HS2** cell, using the optimum conditions for the **HS1** cell, exhibited a higher V_{OC} (0.59 V) value than the **HS1** cell as well as comparable FF (0.53) and J_{SC} (18.9 mA cm⁻²) values with high EQE = 77%, resulting in a higher PCE (η = 5.9%) (Table 2 and Figure 13). The **HS2** cell containing 0.5 M TBP afforded a PCE beyond 6%, arising from good V_{OC} (0.68) and FF (0.66) values in combination with increased J_{SC} (13.6 mA cm⁻²) and EQE (~60%) values relative to those of **HS1** under the same conditions (J_{SC} = 7.1 mA cm⁻², EQE = ~30%). Such higher J_{SC} values obtained for the **HS2** cells even with TBP should be attributed to the larger offset potential (0.19 eV) between the LUMO level of **HS2** and the TiO₂ band edge. However, the fact that J_{SC} and EQE in the **HS2** cell slightly decreased under the condition with TBP might suggest that the offset potential of 0.19 eV is not large enough for efficient electron injection into the elevated TiO₂ conduction band arising from the effect of TBP. On the other hand, regardless of the presence or absence of TBP, all of the **HS2** cells afforded higher V_{OC} values than those of the **HS1** cells, which indicates that the synergy between the steric bulk around the DPP unit and the co-adsorbent effectively reduces unfavorable electron back-transfer to triiodide on the TiO₂ surface.²² Toward further improvement of performance of **HS2**, [Co(bpy)₃]^{2+/3+} redox couple²³ were applied instead of I⁻/I₃⁻ couple, which resulted in significant increment of V_{OC} (0.75 V) instead of decrease of J_{SC} (8.3 mA cm⁻²) to afford moderate PCE (η = 4.5%).

Table 2. Photovoltaic Performance of DSSCs Based on **HS2**^a

Dye	Redox Couple	TBP [M]	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	η [%]
HS2	I ⁻ /I ₃ ⁻	0.5	10.9	0.65	0.64	4.6
HS2	I ⁻ /I ₃ ⁻	None	18.1	0.48	0.46	4.0
HS2 +DCA	I ⁻ /I ₃ ⁻	0.5	13.6	0.68	0.66	6.1
HS2 +DCA	I ⁻ /I ₃ ⁻	None	18.9	0.59	0.53	5.9
HS2 +DCA	Co ^{2+/3+}	0.5	8.3	0.75	0.73	4.5

^a I⁻/I₃⁻-based electrolyte solution: 0.6 M DMPII, 0.1 M LiI, 0.1 M I₂, and 0.5 M or no TBP in MeCN. Co^{2+/3+}-based electrolyte solution: 0.1 M LiClO₄, 0.25 M Co(bpy)₃(PF₆)₂, 0.035 M Co(bpy)₃(PF₆)₃ and 0.5 M or no TBP in MeCN.

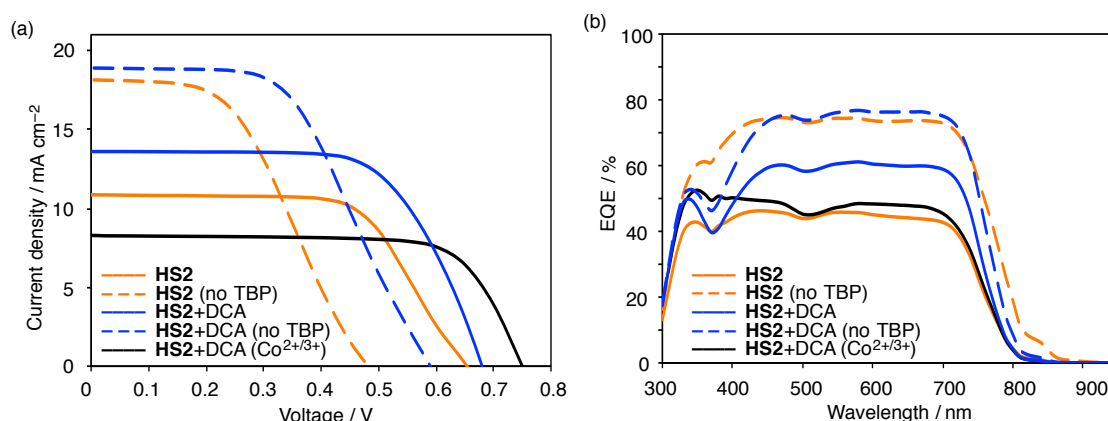


Figure 13. Photovoltaic performance of DSSC devices containing **HS2**: (a) J - V curves and (b) IPCE spectra. Solid and dashed lines represent the conditions in the presence or absence of TBP, respectively.

Conclusion

The organic D- π -A dyes **HS1** and **HS2** were designed and synthesized as low-band-gap sensitizers with diketopyrrolopyrrole (DPP) and boryl-substituted thienylthiazole moieties as π -spacer and acceptor units, respectively. Owing to a narrow π - π^* gap derived from the electronic structure of π -spacer unit, the absorption bands of **HS1** and **HS2** were significantly red-shifted compared to **AK4** with bithiophene π -spacer. The dye-sensitized solar cells (DSSCs) containing **HS1** and **HS2** exhibited high short-circuit current density ($J_{SC} \leq 19.8 \text{ mA/cm}^2$), as the absorption extends into the NIR region. Throughout this study, the author has demonstrated the importance of fine-tuning of the electronic structure of the dyes, especially in terms of the offset potential for efficient electron injection into TiO_2 . In the molecular design of these DSSC sensitizers, it should be also important to consider the decrease of the HOMO and LUMO levels ($\sim 0.14 \text{ eV}$) upon adsorption of the dyes onto TiO_2 , as well as the increase of the TiO_2 conduction band as a result of the presence of TBP. Considering that the presence of TBP in the **HS2** cell increased the V_{OC} value by $+0.09 \text{ V}$, the optimal LUMO level for the dyes on TiO_2 would be ca. -3.70 eV , which corresponds to the KS-LUMO level of ca. -2.93 eV at the B3LYP/6-31G(d) level of theory. Following the design principles outlined herein, it should be possible to attain several other bespoke DSSC sensitizers.

Experimental Section

General

Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. ^1H and ^{13}C NMR spectra were recorded with a JEOL Resonance ECA-500 (500 MHz for ^1H , 125 MHz for ^{13}C , and 160 MHz for ^{11}B), or a Bruker Avance III 800US (200 MHz for ^{13}C) spectrometer. Chemical shifts are reported in δ ppm using residual protons in the deuterated solvents for ^1H NMR as internal standard, using solvent peaks for ^{13}C NMR as internal standards, and using $\text{BF}_3 \cdot \text{OEt}_2$ for ^{11}B NMR (δ 0.00 ppm) as an external standard. UV/vis absorption measurement was performed with a Shimadzu UV-3150 spectrometer, in degassed spectral grade solvents. Fluorescence measurement was performed with a HORIBA FluoroMax 4P-NIR. Quantum yields were determined with a Hamamatsu Photonics Quantaurs QY C11347 with calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on an ALS/chi-620C electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode. The measurement was carried out under an argon atmosphere using CH_2Cl_2 solutions for oxidation and THF solutions for reduction of 1 mM samples with 0.1 M tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Silica gel column chromatography was performed using PSQ 60B (Fuji Silysia). The gel permeation chromatography was performed on JAI LC-9130NEXT system equipped with JAIGEL-2HR and 2.5HR columns and RI-50 detector using toluene as eluent at the flow rate of 10 mL/min, JAI LC-918 system equipped with JAIGEL-1H and 2H columns and RI-50 detector using toluene as eluent at the flow rate of 3.8 mL/min, or JAI LC-908 system equipped with JAIGEL-1H and 2H columns and RI-50 detector using CHCl_3 as eluent at the flow rate of 3.8 mL/min. All reactions were carried out under an argon atmosphere. Geometry optimization and TD-DFT calculations were performed by using Gaussian 09 (revision A.02) program.²⁴ Synthesis, properties, DSSC fabrication, and DSSC performance of **AK4** were shown in Chapter 4.

Synthesis

2-Bromomethyl-1,3-bis(2-ethylhexyloxy)benzene (**2**).

To a solution of 1,3-bis(2-ethylhexyloxy)-2-methylbenzene²⁵ (14.9 g, 42.7 mmol) in CCl₄ (160 mL), NBS (8.36 g, 47.0 mmol) and benzoyl peroxide (20.7 mg, 85.4 μ mol) were added, and the mixture was refluxed for 12 h. After cooling down to room temperature, the mixture was filtered through celite. The obtained solution was evaporated under reduced pressure to give 20.4 g of **2** as orange oil, which was used for next reaction without further purification; ¹H NMR (500 MHz, CDCl₃): δ 7.19 (t, J_{HH} = 8.5 Hz, 1H), 6.49 (d, J_{HH} = 8.0 Hz, 2H), 4.69 (s, 2H), 3.91 (d, J_{HH} = 5.0 Hz, 4H), 1.79–1.74 (m, 2H), 1.59–1.42 (m, 8H), 1.38–1.30 (m, 8H), 0.96–0.88 (m, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 158.14, 129.96, 114.66, 104.01, 70.47, 39.54, 30.64, 29.12, 24.02, 23.56, 23.05, 14.09, 11.22; HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₂₃H₄₀BrO₂, 426.2206; found, 427.2201.

2,5-Bis(2,6-bis(2-ethylhexyloxy)benzyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**3b**).

To a solution of **1** (2.00 g, 6.67 mmol) in DMF (100 mL), K₂CO₃ (3.69 g, 26.7 mmol) and 18-crown-6 (352 mg, 1.33 mmol) were added, and the mixture was heated at 120 °C. To the mixture, a solution of **2** (8.56 g, < 20 mmol) in DMF (50 mL) via cannular was added, and the mixture was heated at 120 °C for 48 h. After cooling down to room temperature, a saturated NH₄Cl aqueous solution was added, and the mixture was extracted with EtOAc three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (9:1 hexane/EtOAc, R_f = 0.39) to give 545 mg (0.549 mmol) of **3b** in 8% yield as red solids; Mp 108.8–109.9 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.53 (d, J_{HH} = 4.0 Hz, 2H), 7.41 (d, J_{HH} = 4.5 Hz, 2H), 7.07 (dd, J_{HH} = 4.5, 4.0 Hz, 2H), 7.05 (d, J_{HH} = 8.5 Hz, 2H), 6.42 (d, J_{HH} = 8.0 Hz, 4H), 5.37 (s, 4H), 3.73 (d, J_{HH} = 5.5 Hz, 8H), 1.61–1.56 (m, 4H), 1.38–1.16 (m, 32H), 0.83 (t, J_{HH} = 7.0 Hz, 12H), 0.78 (t, J_{HH} = 7.5 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 161.82, 158.15, 140.52, 133.41, 130.4, 130.02, 128.10, 127.55, 112.48, 108.14, 104.23, 71.01, 39.18, 37.47, 30.16, 28.86, 23.58, 22.98, 14.09, 10.78; HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₆₀H₈₅N₂O₆S₂, 993.5844; found, 993.5800.

2,5-Dioctyl-3,6-bis(5-tributylstannylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4a).

To a solution of **3a** (8.05 g, 15.3 mmol), which was prepared in 55% yield according to the literature,¹⁵ in THF (60 mL) at $-78\text{ }^{\circ}\text{C}$, *n*-Bu₃SnCl (9.02 mL, 33.3 mmol) and LiHMDS (1.30 M in THF, 25.9 mL, 33.7 mmol) were added dropwise. After the mixture was stirred for 20 min, the reaction mixture was gradually warmed to room temperature over 3 h. After addition of a saturated NH₄Cl aqueous solution, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 hexane/toluene) to give 12.3 g (11.1 mmol) of **4a** in 73% yield as red-purple oil; ¹H NMR (500 MHz, CD₂Cl₂): δ 9.07 (d, $J_{\text{HH}} = 4.0$ Hz, 2H), 7.37 (d, $J_{\text{HH}} = 4.0$ Hz, 2H), 4.10 (t, $J_{\text{HH}} = 8.0$ Hz, 4H), 1.75–1.72 (m, 4H), 1.64–1.60 (m, 12H), 1.45–1.25 (m, 32H), 1.22–1.19 (m, 12H), 0.93–0.90 (t, $J_{\text{HH}} = 7.5$ Hz, 18H), 0.89–0.87 (t, $J_{\text{HH}} = 7.0$ Hz, 6H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 161.56, 146.22, 139.56, 136.93, 136.14, 135.73, 42.45, 32.22, 30.36, 29.67, 29.33, 27.63, 27.30, 23.05, 14.25, 13.82, 11.47; HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₅₄H₉₃N₂O₂S₂Sn₂, 1105.4731; found, 1105.4667.

2,5-Bis(2,6-bis(2-ethylhexyloxy)benzyl)-3,6-bis(5-tributylstannylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4b).

To a solution of **3b** (123 mg, 0.124 mmol) in THF (5 mL) at $-78\text{ }^{\circ}\text{C}$, *n*-Bu₃SnCl (80.0 μL , 0.295 mmol) and LiHMDS (1.30 M in THF, 0.240 mL, 0.312 mmol) were added dropwise. After the mixture was stirred for 20 min, the reaction mixture was gradually warmed to room temperature over 3 h. After addition of a saturated NaHCO₃ aqueous solution, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by GPC (JAIGEL-2HR and 2.5HR, 10 mL/min, toluene, $R_t = 22.7$ min) to give 107 mg (68.1 μmol) of **4b** in 55% yield as red-purple oil; ¹H NMR (500 MHz, CD₂Cl₂): δ 8.78 (d, $J_{\text{HH}} = 3.5$ Hz, 2H), 7.21 (d, $J_{\text{HH}} = 3.5$ Hz, 2H), 7.09 (t, $J_{\text{HH}} = 8.0$ Hz, 2H), 6.78 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 5.39 (s, 4H), 3.76 (d, $J_{\text{HH}} = 6.0$ Hz, 8H), 1.61–1.50 (m, 16H), 1.38–1.27 (m, 28H), 1.26–1.18 (m, 16H), 1.14–1.11 (m, 12H), 0.90 (t, $J_{\text{HH}} = 7.5$ Hz,

18H), 0.86 (t, $J_{\text{HH}} = 7.0$ Hz, 12H), 0.80 (t, $J_{\text{HH}} = 7.5$ Hz, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 162.00, 158.68, 144.80, 140.38, 136.62, 136.22, 134.97, 128.34, 113.44, 107.75, 104.73, 71.68, 39.66, 38.03, 30.56, 29.27, 27.62, 24.02, 23.44, 14.32, 13.80, 11.30, 11.08; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{84}\text{H}_{137}\text{N}_2\text{O}_6\text{S}_2\text{Sn}_2$, 1573.7984; found, 1573.7929.

3-(5-(4-(Bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-6-(5-tributylstannylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (6a).

To a solution of **4a** (12.3 g, 11.1 mmol) and **5** (1.53 g, 2.80 mmol) in toluene (60 mL), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (27.8 mg, 26.9 μmol) and PPh_3 (29.2 mg, 111 μmol) were added, and the mixture was refluxed for 35 h. After cooling down to room temperature, water was added to the reaction mixture, and the mixture was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 hexane/toluene, $R_f = 0.30$) to give 2.81 g (2.20 mmol) of **6a** in 78% yield as blue-purple oil; ^1H NMR (500 MHz, CD_2Cl_2): δ 9.06 (d, $J_{\text{HH}} = 3.5$ Hz, 1H), 8.98 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.52 (d, $J_{\text{HH}} = 9.0$ Hz, 2H), 7.39 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.36 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.12 (d, $J_{\text{HH}} = 8.0$ Hz, 4H), 7.04 (d, $J_{\text{HH}} = 8.0$ Hz, 4H), 6.99 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 4.10 (t, $J_{\text{HH}} = 7.5$ Hz, 2H), 4.08 (t, $J_{\text{HH}} = 7.5$ Hz, 2H), 2.58 (t, $J_{\text{HH}} = 7.5$ Hz, 4H), 1.77–1.73 (m, 4H), 1.44–1.41 (m, 4H), 1.64–1.59 (m, 8H), 1.39–1.24 (m, 44H), 1.22–1.89 (m, 6H), 0.93–0.83 (m, 21H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 161.53, 161.49, 150.42, 149.46, 146.25, 145.00, 139.76, 139.26, 139.13, 137.10, 136.93, 136.08, 135.72, 129.72, 127.99, 127.10, 125.81, 125.59, 123.46, 121.63, 107.88, 107.17, 42.50, 42.41, 35.72, 32.27, 32.20, 31.93, 30.35, 29.85, 29.74, 29.65, 29.61, 29.31, 27.61, 27.29, 27.22, 23.06, 23.03, 14.26, 13.80, 11.46 (eight aliphatic signals were not observed due to overlapping); HRMS (APCI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{76}\text{H}_{111}\text{N}_3\text{O}_2\text{S}_2\text{Sn}$, 1281.7150; found, 1281.7180.

2,5-Bis(2,6-bis(2-ethylhexyloxy)benzyl)-3-(5-(4-(bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-6-(5-tributylstannylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (6b).

To a solution of **4b** (107 mg, 68.1 μmol) and **5** (16.6 mg, 30.3 μmol) in toluene (1 mL), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (3.01 mg, 2.91 μmol) and PPh_3 (3.21 mg, 2.2 μmol) were added,

and the mixture was refluxed for 15 h. After cooling down to room temperature, water was added to the reaction mixture, and the mixture was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by GPC (JAIGEL-2HR and 2.5HR, 10 mL/min, toluene, R_t = 21.4 min) to give 40.6 mg (23.2 μ mol) of **6b** in 77% yield as blue-purple oil; ¹H NMR (500 MHz, CD₂Cl₂): δ 8.78 (d, J_{HH} = 3.5 Hz, 1H), 8.67 (d, J_{HH} = 4.0 Hz, 1H), 7.38 (d, J_{HH} = 8.5 Hz, 2H), 7.22 (d, J_{HH} = 4.0 Hz, 1H), 7.21 (d, J_{HH} = 3.5 Hz, 1H), 7.10 (d, J_{HH} = 8.5 Hz, 4H), 7.08 (t, J_{HH} = 8.0 Hz, 2H), 7.00 (d, J_{HH} = 8.5 Hz, 4H), 6.94 (d, J_{HH} = 9.0 Hz, 2H), 6.49 (d, J_{HH} = 8.5 Hz, 2H), 6.47 (d, J_{HH} = 8.0 Hz, 2H), 5.39 (s, 4H), 3.76 (d, J_{HH} = 5.0 Hz, 2H), 3.75 (d, J_{HH} = 5.0 Hz, 2H), 2.57 (t, J_{HH} = 8.0 Hz, 4H), 1.64–1.51 (m, 14H), 1.39–1.26 (m, 36H), 1.23–1.18 (m, 12H), 1.13–1.06 (m, 6H), 0.94–0.85 (m, 21H), 0.84–0.76 (m, 18H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 162.00, 161.94, 158.71, 158.66, 149.51, 148.97, 145.15, 144.96, 140.24, 140.14, 138.97, 136.58, 136.23, 135.73, 135.00, 129.65, 129.16, 128.47, 128.35, 126.91, 126.51, 125.37, 122.99, 121.94, 113.37, 113.23, 108.33, 107.80, 104.72, 71.67, 39.64, 38.09, 37.83, 35.70, 32.27, 31.93, 30.53, 29.84, 29.74, 29.64, 29.28, 29.23, 28.22, 27.59, 27.48, 23.98, 23.42, 23.38, 23.05, 17.85, 15.72, 14.28, 14.26, 14.25, 13.79, 13.96, 11.27, 11.04, 11.02 (one aromatic signal is overlapped); HRMS (APCI-TOF) (m/z): [M+H]⁺, calcd. for C₁₀₆H₁₅₆N₃O₆S₂Sn, 1751.0479; found, 1751.0510.

2-(3-Dimesitylboryl-5-iodothiophen-2-yl)thiazole-5-carbaldehyde (**7**).

To a solution of 2-(3-(dimesitylboraneyl)-5-iodothiophen-2-yl)-5-iodothiazole^{12a} (202 mg, 0.303 mmol) in THF (6 mL) at –78 °C, *n*-BuLi (1.47 M in hexane, 0.202 mL, 0.297 mmol) was added dropwise. After the mixture was stirred for 15 min, ethyl formate (26.7 μ L, 0.331 mmol) was added to the reaction mixture, and the mixture was gradually warmed to room temperature over 1 h. After addition of a saturated NH₄Cl aqueous solution, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 hexane/CH₂Cl₂, R_f = 0.24) to give 152 mg (0.267 mmol) of **7** in 88% yield as yellow solids; Mp 239.8 °C (decomposed); ¹H NMR (500 MHz, CD₂Cl₂): δ 9.84 (s, 1H), 8.19 (s, 1H), 7.45 (s, 1H), 6.66 (s, 4H), 2.17 (s, 6H), 1.84 (s, 12H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 180.10, 169.20, 144.99, 140.92, 140.23, 137.21, 135.34,

135.10, 130.16, 90.49, 24.54, 20.76 (two aromatic signals are not observed due to quadrupolar relaxation.); ^{11}B NMR (160 MHz, CD_2Cl_2): δ 3.41; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{26}\text{H}_{26}\text{BINOS}_2$, 570.0593; found, 570.0537.

2-(5'-(4-(5-(4-(bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrol-1-yl)-4-dimesitylboryl-[2,2'-bithiophen]-5-yl)thiazole-5-carbaldehyde (8a).

To a solution of **7** (124 mg, 0.218 mmol) and **6a** (259 mg, 0.202 mmol) in toluene (10 mL), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (4.82 mg, 4.66 μmol) and PPh_3 (4.30 mg, 16.4 μmol) were added, and the mixture was refluxed for 13 h. After cooling down to room temperature, water was added, and the mixture was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:2 hexane/ CH_2Cl_2 , $R_f = 0.50$) to give 231 mg (0.161 mmol) of **8a** in 80% yield as green solids; Mp 98.3–98.8 $^\circ\text{C}$; ^1H NMR (500 MHz, CD_2Cl_2): δ 9.84 (s, 1H), 9.06 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 8.91 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 8.21 (s, 1H), 7.53 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 7.49 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.45 (s, 1H), 7.41 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.13 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 7.04 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 6.99 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 6.69 (s, 4H), 4.10 (t, $J_{\text{HH}} = 8.0$ Hz, 2H), 4.07 (t, $J_{\text{HH}} = 8.0$ Hz, 2H), 2.59 (d, $J_{\text{HH}} = 8.0$ Hz, 4H), 2.18 (s, 6H), 1.90 (s, 12H), 1.76–1.73 (m, 4H), 1.63–1.58 (m, 4H), 1.45–1.41 (m, 4H), 1.37–1.27 (m, 36H), 0.94–0.83 (m, 12H); ^{13}C NMR (200 MHz, $\text{THF}-d_8$): δ 182.43, 170.28, 161.72, 161.34, 151.67, 150.20, 148.57, 146.11, 145.80, 141.44, 140.80, 140.66, 139.46, 138.69, 138.34, 137.85, 136.75, 134.85, 131.44, 130.64, 130.58, 130.17, 129.66, 129.13, 128.66, 128.33, 127.94, 127.68, 126.65, 126.05, 124.29, 122.46, 110.01, 108.54, 42.68, 42.58, 36.25, 32.86, 32.80, 32.78, 32.59, 30.93, 30.89, 30.62, 30.59, 30.45, 30.34, 30.29, 30.23, 30.19, 30.16, 30.14, 30.13, 27.71, 27.70, 23.55, 23.53, 23.51, 20.89, 14.42; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{90}\text{H}_{110}\text{BN}_4\text{O}_3\text{S}_4$, 1433.7562; found, 1433.7599.

2-(5'-(2,5-Bis(2,6-bis(2-ethylhexyloxy)benzyl)-4-(5-(4-(bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-4-dimesitylboryl-[2,2'-bithiophen]-5-yl)thiazole-5-carbaldehyde (8b).

To a solution of **6b** (40.6 mg, 23.2 μ mol) and **7** (14.2 mg, 25.0 μ mol) in toluene (1 mL), Pd₂(dba)₃·CHCl₃ (3.00 mg, 2.90 μ mol) and PPh₃ (3.01 mg, 11.5 μ mol) were added, and the mixture was refluxed for 15 h. After cooling down to room temperature, water was added, and the mixture was extracted with toluene three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (1:1 hexane/CH₂Cl₂, *R_f* = 0.16) to give 31.2 mg (16.4 μ mol) of **8b** in 71% yield as green solids; Mp 83.2–84.5 °C; ¹H NMR (500 MHz, CDCl₃): δ 9.82 (s, 1H), 8.79 (d, *J*_{HH} = 4.0 Hz, 1H), 8.62 (d, *J*_{HH} = 4.5 Hz, 1H), 8.16 (s, 1H), 7.47 (s, 1H), 7.37 (d, *J*_{HH} = 8.5 Hz, 2H), 7.23 (d, *J*_{HH} = 4.0 Hz, 1H), 7.21 (d, *J*_{HH} = 4.0 Hz, 1H), 7.09 (t, *J*_{HH} = 8.5 Hz, 1H), 7.08 (d, *J*_{HH} = 8.5 Hz, 4H), 7.07 (t, *J*_{HH} = 8.5 Hz, 1H), 7.01 (d, *J*_{HH} = 8.5 Hz, 4H), 6.96 (d, *J*_{HH} = 8.5 Hz, 2H), 6.68 (s, 4H), 6.46 (d, *J*_{HH} = 8.5 Hz, 4H), 5.43 (s, 2H), 5.38 (s, 2H), 3.75 (d, *J*_{HH} = 6.0 Hz, 4H), 3.72 (d, *J*_{HH} = 5.5 Hz, 4H), 2.58–2.55 (m, 4H), 2.20 (s, 6H), 1.89 (s, 12H), 1.64–1.54 (m, 8H), 1.37–1.12 (m, 58H), 0.91–0.74 (m, 30H); ¹³C NMR (200 MHz, THF-*d*₈): δ 182.45, 170.23, 162.27, 161.86, 159.38, 159.34, 150.86, 149.70, 149.26, 146.16, 145.93, 141.65, 141.06, 140.60, 139.20, 138.68, 138.06, 137.40, 135.80, 134.77, 132.72, 130.56, 130.39, 130.09, 129.67, 129.28, 129.06, 128.22, 127.46, 127.38, 127.34, 125.84, 123.73, 122.68, 113.67, 113.65, 110.36, 109.09, 105.34, 105.32, 71.98, 71.77, 54.89, 40.38, 40.35, 37.90, 36.22, 32.84, 32.57, 31.21, 31.19, 30.66, 30.61, 30.43, 30.33, 30.28, 30.22, 29.84, 24.55, 23.90, 23.53, 20.92, 14.51, 14.48, 14.41, 11.35, 11.30 (two aromatic signals are not observed due to quadrupolar relaxation.); HRMS (APCI-TOF) (*m/z*): [M+H]⁺, calcd. for C₁₂₀H₁₅₄BN₄O₇S₄, 1902.0792; found, 1902.0715.

2-((2-(5'-(4-(5-(4-(Bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-4-dimesitylboryl-[2,2'-bithiophen]-5-yl)thiazol-5-yl)methylene)malonic acid (HS1).

To a solution of **8a** (622 mg, 0.434 mmol) in chloroform (8 mL), malonic acid (270 mg, 1.60 mmol) and piperidine (257 μ L, 2.60 mmol) were added, and the mixture was refluxed for 21 h. After cooling down to room temperature, a 1 M HCl aqueous solution

was added. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by silica gel column chromatography (4:1 toluene/MeOH, *R_f* = 0.29) to give 628 mg (0.418 mmol) of **HS1** in 95% yield as green solids; Mp 220.1–222.1 °C; ¹H NMR (500 MHz, THF-*d*₈): δ 10.91 (s, 1H), 9.19 (d, *J*_{HH} = 4.0 Hz, 1H), 9.07 (d, *J*_{HH} = 3.5 Hz, 1H), 8.33 (s, 1H), 8.27 (s, 1H), 7.56 (d, *J*_{HH} = 8.0 Hz, 2H), 7.52 (d, *J*_{HH} = 4.0 Hz, 1H), 7.50 (d, *J*_{HH} = 4.0 Hz, 1H), 7.12 (d, *J*_{HH} = 8.0 Hz, 4H), 7.04 (s, 1H), 7.02 (d, *J*_{HH} = 8.5 Hz, 4H), 6.99 (d, *J*_{HH} = 8.5 Hz, 2H), 6.60 (s, 4H), 4.16–4.12 (m, 4H), 2.50–2.35 (m, 4H), 2.13 (s, 6H), 1.90 (s, 12H), 1.76–1.58 (m, 8H), 1.48–1.20 (m, 40H), 0.95–0.82 (m, 12H); ¹³C NMR (200 MHz, THF-*d*₈): δ 171.47, 169.63, 167.71, 161.67, 161.38, 151.42, 150.12, 145.81, 143.45, 142.12, 140.63, 140.47, 139.41, 138.50, 138.12, 138.07, 136.93, 136.08, 135.69, 131.61, 130.89, 130.76, 130.45, 130.15, 130.08, 130.00, 129.66, 129.57, 128.75, 128.38, 127.65, 127.56, 127.35, 126.69, 126.02, 125.75, 125.46, 124.25, 122.47, 109.73, 108.54, 54.89, 42.67, 42.59, 39.93, 36.24, 32.77, 32.58, 31.00, 30.89, 30.67, 30.44, 30.34, 30.22, 30.19, 30.16, 30.14, 27.70, 23.54, 23.52, 23.50, 21.29, 20.91, 19.11, 14.45, 14.42, 14.38, 14.20 (two aromatic signals are not observed due to quadrupolar relaxation.); HRMS (FAB) (*m/z*): [M+H]⁺, calcd. for C₉₃H₁₁₁BN₄O₆S₄, 1518.7494; found, 1518.7503.

2-((2-(5'-(2,5-Bis(2,6-bis(2-ethylhexyloxy)benzyl)-4-(5-(4-(bis(4-octylphenyl)amino)phenyl)thiophen-2-yl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrol-1-yl)-4-dimesitylboryl-[2,2'-bithiophen]-5-yl)thiazol-5-yl)methylene)malonic acid (HS2).

To a solution of **8b** (213 mg, 0.112 mmol) in chloroform (2 mL), malonic acid (35.2 mg, 0.338 mmol) and piperidine (33.0 μL, 0.334 mmol) were added, and the mixture was refluxed for 21 h. After cooling down to room temperature, a 1 M HCl aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The mixture was purified by silica gel column chromatography (10:1 CH₂Cl₂/MeOH, *R_f* = 0.18) to give 177 mg (89.2 μmol) of **HS2** in 80% yield as green solids; Mp 137.2–138.4 °C; ¹H NMR (500 MHz, acetone-*d*₆): δ 8.97 (d, *J*_{HH} = 4.0 Hz, 1H), 8.88 (d, *J*_{HH} = 4.0 Hz, 1H), 8.39 (s, 1H), 8.29 (s, 1H), 7.52 (d, *J*_{HH} = 8.5 Hz, 2H), 7.51 (d, *J*_{HH} = 4.0 Hz, 1H),

7.46 (d, $J_{\text{HH}} = 4.0$ Hz, 1H), 7.30 (s, 1H), 7.19 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 7.15 (t, $J_{\text{HH}} = 8.5$ Hz, 1H), 7.11 (t, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.04 (d, $J_{\text{HH}} = 8.5$ Hz, 4H), 6.95 (d, $J_{\text{HH}} = 9.0$ Hz, 2H), 6.619 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 6.618 (s, 4H), 6.610 (d, $J_{\text{HH}} = 8.5$ Hz, 2H), 5.50 (s, 2H), 5.44 (s, 2H), 3.84 (d, $J_{\text{HH}} = 6.0$ Hz, 4H), 3.81 (d, $J_{\text{HH}} = 5.5$ Hz, 4H), 2.61 (t, $J_{\text{HH}} = 8.0$ Hz, 4H), 2.13 (s, 6H), 1.92 (s, 12H), 1.67–1.57 (m, 8H), 1.44–1.15 (m, 52H), 0.90–0.77 (m, 30H); ^{13}C NMR (200 MHz, THF- d_8): δ 171.51, 162.24, 161.91, 159.41, 159.37, 150.57, 149.64, 147.19, 147.07, 145.98, 143.62, 141.80, 141.28, 140.60, 139.15, 139.04, 138.65, 137.21, 137.19, 135.99, 135.97, 134.34, 132.89, 132.05, 130.53, 130.54, 130.09, 129.81, 129.25, 129.01, 128.37, 127.46, 127.44, 126.73, 125.83, 123.69, 122.77, 113.78, 113.75, 110.08, 109.16, 105.34, 105.31, 71.99, 71.76, 40.42, 40.40, 40.37, 38.20, 37.91, 36.24, 32.86, 32.60, 31.24, 31.21, 30.46, 30.36, 30.24, 29.86, 28.89, 24.58, 24.56, 23.92, 23.91, 23.55, 20.97, 14.53, 14.50, 14.43, 11.39, 11.37, 11.32; ^{11}B NMR (160 MHz, acetone- d_6): δ -3.68; HRMS (MALDI-TOF) (m/z): $[\text{M}]^+$, calcd. for $\text{C}_{123}\text{H}_{155}\text{BN}_4\text{O}_{10}\text{S}_4$, 1987.07173; found, 1987.07063.

2,5-Bis(2,6-difluorobenzyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (9).

To a solution of **1** (3.00 g, 9.99 mmol) in DMF (30 mL), K_2CO_3 (5.53 g, 40.0 mmol), 18-crown-6 (128 mg, 0.484 mmol), and 2,6-difluorobenzil bromide (5.18 g, 25.0 mmol) were added, and the mixture was heated at 100 °C for 23 h. After cooling down to room temperature, water was added to the mixture, and the resulting red solids was collected by filtration. The solids was washed with water and dried under reduced pressure. The mixture was purified by silica gel short column chromatography (CH_2Cl_2 , $R_f = 0.59$) followed by recrystallization from CH_2Cl_2 /hexane solution to give 1.74 g (3.14 mmol) of **9** in 31% yield as red rod-shaped crystals; Mp 305.2–306.0 °C; ^1H NMR (500 MHz, DMF- d_7): δ 8.67 (d, $J_{\text{HH}} = 4.0$ Hz, 2H), 8.05 (d, $J_{\text{HH}} = 5.0$ Hz, 2H), 7.41 (t, $J_{\text{HH}} = 8.5$ Hz, 2H), 7.47 (dd, $J_{\text{HH}} = 4.0, 5.0$ Hz, 2H), 7.05 (t, $J_{\text{HH}} = 8.5$ Hz, 4H), 5.47 (s, 4H); ^{13}C NMR (200 MHz, DMF- d_7): δ 167.29 (d, $J_{\text{CF}} = 8.0$ Hz), 166.62, 166.06 (d, $J_{\text{CF}} = 8.0$ Hz), 139.80 (d, $J_{\text{CF}} = 2.0$ Hz), 135.75 (t, $J_{\text{CF}} = 10.0$ Hz), 135.11, 134.10, 118.39 (t, $J_{\text{CF}} = 16.0$ Hz), 117.51 (dd, $J_{\text{CF}} = 4.0, 20.0$ Hz), 113.11, 41.56 (t, $J_{\text{CF}} = 4.0$ Hz); ^{19}F NMR (470 MHz, DMF- d_7): δ -115.94; HRMS (APCI-TOF) (m/z): $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{28}\text{H}_{17}\text{F}_4\text{N}_2\text{O}_2\text{S}_2$, 553.0662; found, 553.0648.

X-ray Crystal Structure of **9**

The single crystal was obtained by diffusion of hexane into a solution of compound **9** in CH₂Cl₂. Intensity data were collected at 100 K using a diffractometer equipped with an ADSC Quantun315 CCD detector with synchrotron radiation at a wavelength of 0.85 Å at the SPring-8 beamline BL38B1. A total of 15664 reflections were measured with a maximum 2 θ angle of 60°, of which 1923 were independent reflections ($R_{\text{int}} = 0.0622$). The structure was solved by direct methods (SHELXS-97²⁶) and refined by the full-matrix least-squares on F^2 (SHELXL-97²⁶). The molecule sits on symmetric axis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C₁₄H₈F₂NOS; FW = 276.27, crystal size 0.05 × 0.03 × 0.03 mm³, Monoclinic, $P2_1/n$, $a = 5.54230(10)$ Å, $b = 16.6137(3)$ Å, $c = 12.5768(3)$ Å, $\beta = 91.5191(8)^\circ$, $V = 1157.64(4)$ Å³, $Z = 4$, $D_c = 1.585$ g cm⁻³. The refinement converged to $R_1 = 0.0603$, $wR_2 = 0.1641$ ($I > 2\sigma(I)$), GOF = 1.110.

Measurements of Electrochemical and Photophysical Properties of Dyes Adsorbed on TiO₂

Dye-adsorbing TiO₂ layer was prepared as follow: The TiO₂ layer (Dyesol, 30 NR-D, particle size: 30 nm) was coated on the FTO glass plates (Asahi Glass Co. Ltd, 1.8 mm thick) by a screen printing. The electrodes coated with the TiO₂ pastes were gradually heated at 200 °C for 10 min and then at 500 °C for 30 min. After cooling down to room temperature, the TiO₂ electrodes were immersed into the dye solution (0.1 mM in toluene), and kept at 30 °C for 6 h. Then, cyclic voltammetry was carried out using dye-adsorbing TiO₂ electrodes as a working electrode under an argon atmosphere in MeCN with 0.1 M *n*-Bu₄N⁺PF₆⁻ as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. The UV/vis absorption spectra were also measured with dye-adsorbing TiO₂ electrodes. The thickness of the TiO₂ electrodes was 2 μm, measured with SURFCOM 130A (ACCRETECH, TOKYO SEIMITSU Co., Ltd.).

Fabrication of DSSCs

The fabrication method of DSSC is modified from the reported procedure.¹⁸ FTO glass plates (Asahi Glass Co. Ltd, 1.8 mm thick) were treated in a UV-O₃ system for 15

min. The paste for the transparent nanocrystalline-TiO₂ layer (Solaronix, HT/SP, particle size: 10–15 nm) was coated on the FTO glass plates by screen printing at the size of 4 mm × 4 mm. After that, the plates were left in petri dish for 1 min at room temperature, dried in oven for 3 min at 120 °C, and cooled down to room temperature. Next, the paste for the transparent nanocrystalline-TiO₂ layer (Dyesol, 30 NR-D, particle size: 30 nm) was coated on the glass plates by screen printing and dried by the same procedure as previous layer. This printing–leaving–drying–cooling procedure were repeated for another paste (Solaronix, R/SP, particle size: >100 nm). The electrodes coated with the TiO₂ pastes were gradually heated from room temperature to 200 °C for 10 min, kept at 200 °C for 10 min, heated again from 200 to 500 °C for 15 min, and kept at 500 °C for 30 min. After the TiO₂ films were treated with in a 0.1 M TiCl₄ aqueous solution at 70 °C for 30 min and washed with water, the electrodes coated with the TiO₂ pastes were gradually heated in the same way as before. The thickness of the TiO₂ electrodes was 5–7 μm, according to the measurement with SURFCOM 130A (ACCRETECH, TOKYO SEIMITSU Co., Ltd.). The TiO₂ electrodes were immersed into the dye solutions (0.1 mM in toluene) containing no or 2 mM deoxycholic acid (DCA) and kept at 30 °C for 16 h to adsorb the dyes.

The counter electrodes were prepared by sputtering of Pt on an FTO plates and the glass plates were drilled two holes.

The organic electrolyte solution based on I[−]/I₃[−] redox couple was composed of 0.1 M LiI, 0.1 M I₂, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) with/without 0.5 M TBP in acetonitrile. The one based on [Co(bpy)₃]^{2+/3+} redox couple was composed of 0.1 M LiClO₄, 0.25 M Co(bpy)₃(PF₆)₂, 35 mM Co(bpy)₃(PF₆)₃ and 0.5 M or no TBP in acetonitrile.

The dye-adsorbing TiO₂ electrode and the Pt counter electrode were assembled into a sandwich-type cell with film spacer (30 μm thickness) between the electrodes. The electrolyte solution (7 μL) was injected into the cell from a drilled hole on the Pt counter electrode. After the holes were sealed with glass plate, the cell was fixed with clips. Finally, solder was deposited on the edges of the TiO₂ electrode and the Pt counter electrode.

Photovoltaic Measurements

The photovoltaic performances were measured in the same manners as those of Chapter 4. See Chapter 4.

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List of Publications

Chapter 1

Shimogawa, H.; Mori, H.; Wakamiya, A.; Murata, Y.

“Impacts of Dibenzo- and Dithieno-fused Structures at the *b*, *g* Bonds in the BODIPY Skeleton”

Chem. Lett. **2013**, 42, 986–988.

Chapter 2

Shimogawa, H.; Wakamiya, A.; Murata, Y.

“NIR Dye Based on BF₂-Bridged Azafulvene Dimer as an Electron-Accepting Unit”

Submitted.

Chapter 3

Shimogawa, H.; Yoshikawa, O.; Aramaki, Y.; Murata, M.; Wakamiya, A.; Murata, Y.

“4,7-Bis[3-(dimesitylboryl)thien-2-yl]benzothiadiazole: Solvato-, Thermo-, and Mechanochromism Based on the Reversible Formation of an Intramolecular B–N Bond”

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Chapter 4

Shimogawa, H.; Endo, M.; Taniguchi, T.; Nakaike, Y.; Kawaraya, M.; Segawa, H.; Murata, Y.; Wakamiya, A.

“D– π –A Dyes with an Intramolecular B–N Coordination Bond as a Key Scaffold for Electronic Structural Tuning and Their Application in Dye-Sensitized Solar Cells”

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Chapter 5

Shimogawa, H.; Endo, M.; Nakaike, Y.; Murata, Y.; Wakamiya, A.

“D– π –A Dyes with Diketopyrrolopyrrole and Boryl-substituted Thienylthiazole Units for Dye-Sensitized Solar Cells with High J_{sc} Values”

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Other Publication

- (1) Wang, S.; Yang, D.-T.; Lu, J.; Shimogawa, H.; Gong, S.; Wang, X.; Møllerup, S. K.; Wakamiya, A.; Chang, Y.-L.; Yang, C.; Lu, Z.-H.
“In Situ Solid-State Generation of (BN)₂-Pyrenes and Electroluminescent Devices”
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