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Benzodipyrrole-based donor–acceptor-type boron complexes as tunable near-infrared-absorbing materials

Tomoya Nakamura,^[a] Shunsuke Furukawa,^{[a],[b]} and Eiichi Nakamura*^[a]

Abstract: Benzodipyrrole-based donor–acceptor boron complexes were designed and synthesized as near-infrared-absorbing materials. The electron-rich organic framework combined with the Lewis acidic boron co-ordination enabled us to tune the LUMO energy level and the HOMO–LUMO gap—that is, the absorption wavelength—by changing the organic acceptor units, the number of boron atoms, and the substituents on the boron atoms.

Near-infrared (NIR)-absorbing materials have attracted considerable attention because of their utility as heat absorbers, optical filters, photosensitizers, and active layers in organic solar cells (OSCs).^{[1],[2]} The molecular design for the OSC application of NIR materials^[3] requires tuning of not only the HOMO–LUMO gap for NIR absorption but also the energy level of the LUMO so as to transfer electrons effectively to an electrode. A popular approach to achieving NIR absorption includes the use of a donor–acceptor (D–A) system, where the gap is tuned by variation of the donor HOMO and the acceptor LUMO levels, making control of the absorption wavelength a rather complex task (Fig. 1a).^[4] We propose here that a benzodipyrrole (BDP) unit can serve as both an electron donor and as an anchor to bind one or two diarylboryl moieties covalently (Fig. 1c) so that the HOMO–LUMO gap and the LUMO level can be tuned by selective lowering of the LUMO level by attachment of one or two substituted diarylboryl group(s) (Fig. 1b). This ability of BDP to anchor a metal atom covalently on each nitrogen atom (trivalent) is unique among donors, such as furans and thiophenes (divalent oxygen and sulfur atoms, respectively). BDP has a low ionization potential^[5] and hence is a good donor, and is readily synthesized with a wide range of structural variety using the synthetic method that we developed recently.^[6] We chose quinoxaline (Qx) and benzo-2,1,3-thiadiazole (BT) moieties as electron acceptors because they also serve as an additional anchor of the boron moieties to be trapped via bidentate ligation. Modification of the substituents on the diarylboron moiety provides an additional possibility for LUMO tuning.^{[7],[8]}

The synthesis of BDP-Qx-based D–A molecules started from the alkylation of 5,8-dibromoquinoxaline (**1a**) to obtain alkylbromoquinoxaline **2a** in 58% yield (Scheme 1). This branched alkyl group was necessary to endow high solubility on the final product **L1** and its derivatives. Sonogashira coupling of

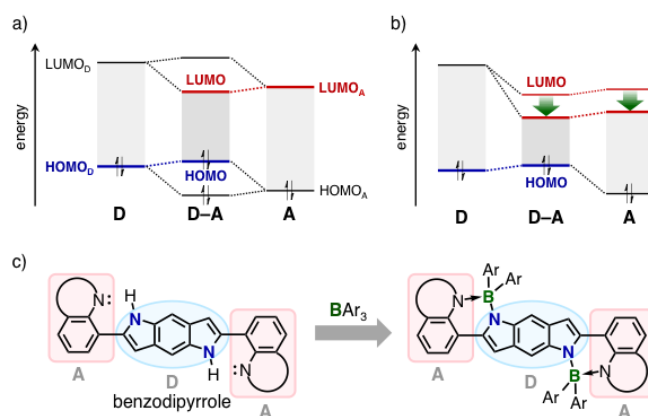


Figure 1. (a) A schematic energy diagram of a representative D–A-type molecule. (b) The expected HOMO–LUMO level tuning in the benzodipyrrole-based D–A-type boron complexes. (c) The molecular design for the D–A-type boron complexes.

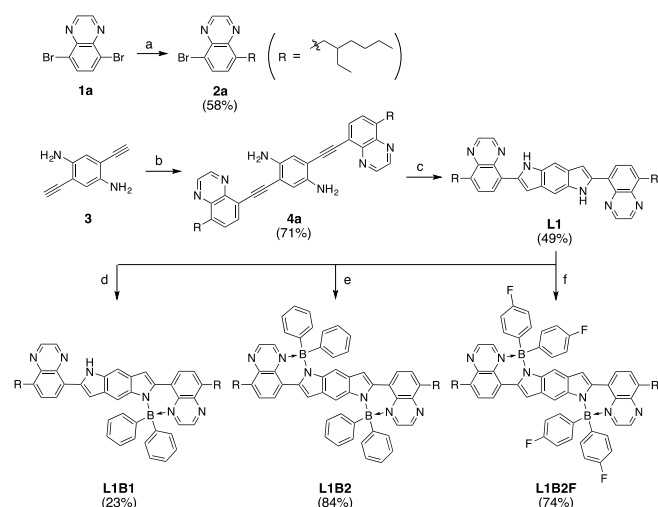
2a with the diethynylphenylenediamine **3** gave the corresponding coupling product **4a** in 71% yield. A zinc-mediated hydroamination reaction^[9] of **4a** gave the D–A molecule, **L1**, in 49% yield. Mononuclear complex **L1B1** was synthesized by the reaction of **L1** with 1.2 equiv of triphenylborane in 23% yield (condition d). The dinuclear boron complex **L1B2** was synthesized using 2.6 equiv of triphenylborane in 84% yield (condition e). The reaction with tris(4-fluorophenyl)borane similarly gave a dinuclear complex **L1B2F** bearing fluorophenyl substituents in 74% yield (condition f). These boron complexes were isolated as stable compounds. Thermogravimetry–differential thermal analysis (TG–DTA) showed that the decomposition temperatures are 435 °C, 363 °C, 318 °C, and 332 °C for **L1**, **L1B1**, **L1B2**, and **L1B2F**, respectively (see the Supporting information, Fig. S1). The thermal stability of the products is high enough for various materials applications. We found that the corresponding boron difluoride complexes are too insoluble in organic solvents to be characterized well. The structures of the obtained D–A molecule and boron complexes were confirmed using NMR. In the ¹H NMR spectra, **L1** showed two protons of pyrrole rings (N–H) at a chemical shift of 11.63 ppm, and one proton was observed at 11.41 ppm for **L1B1**. No signals were observed over a range of 10 ppm in **L1B2** and **L1B2F**, indicating a lack of N–H protons on the pyrrole rings. ¹¹B NMR spectra of **L1B1**, **L1B2**, and **L1B2F** showed signals at 5.55 ppm, 5.13 ppm, and 5.17 ppm, which appear at a much higher magnetic field strength than that of three-co-ordinated triphenylborane (45.8 ppm). The higher magnetic field shifts indicate that the hybridization at the boron centre changes from sp² to sp³,^[10] and the phenomena are observed in related *N,N*-chelating four-co-ordinate boron species.^{[7h],[11]}

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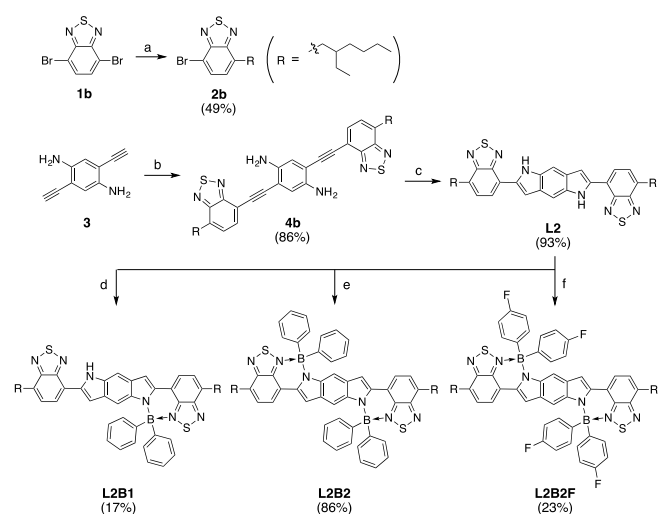
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BDP-BT-based D–A molecules were synthesized in a similar manner (Scheme 2). Alkylation of dibromobenzothiadiazole **1b** gave the corresponding alkylated product **2b** in 49% yield.



Scheme 1. Synthesis of quinoxaline-based D–A-type boron complexes. Reagents and conditions: (a) RMgBr (1.7 equiv), ZnCl₂ (1.7 equiv), Pd(PPh₃)₄ (5 mol%), THF, reflux, 1.5 h; (b) **2a** (2.2 equiv), Pd(PPh₃)₄ (2 mol%), PPh₃ (4 mol%), CuI (4 mol%), Et₃N, 80 °C, 14 h; (c) ZnI₂ (2.1 equiv), toluene, reflux, 3 h; (d) BPh₃ (1.2 equiv), toluene, reflux, 3 d; (e) BPh₃ (2.6 equiv), toluene, reflux, 5 h; (f) B(4-FC₆H₄)₃ (7.4 equiv), toluene, reflux, 2 h.



Scheme 2. Synthesis of benzothiadiazole-based D–A-type boron complexes. Reagents and conditions: (a) RMgBr (1.1 equiv), ZnCl₂ (1.1 equiv), Pd(PPh₃)₄ (5 mol%), THF, reflux, 22 h; (b) **2b** (2.2 equiv), Pd(PPh₃)₄ (2 mol%), PPh₃ (4 mol%), CuI (4 mol%), Et₃N, 80 °C, 1.5 h; (c) ZnI₂ (2.2 equiv), toluene, reflux, 1 h; (d) BPh₃ (1.4 equiv), toluene, reflux, 23 h; (e) BPh₃ (10 equiv), toluene, reflux, 1 h; (f) B(4-FC₆H₄)₃ (8.2 equiv), toluene, reflux, 2 h.

Sonogashira coupling of **2b** with diethynylphenylenediamine **3** gave the coupled product **4b** in 86% yield. Zinc-mediated intramolecular hydroamination of **4b** gave **L2** in 93% yield. By the reaction of **L2** with the corresponding triarylborane, mononuclear boron complex **L2B1** (17%), dinuclear boron complex **L2B2** (86%), and fluorophenyl-substituted **L2B2F**

(23%) were synthesized. These analogues are also thermally stable with high decomposition temperatures of 417 °C (**L2**), 241 °C (**L2B1**), 267 °C (**L2B2**), and 256 °C (**L2B2F**) (see the Supporting information, Fig. S1).

Photophysical and electrochemical properties of the synthesized compounds were investigated and are summarized in Fig. 2 and Table 1. As we expected, absorption wavelengths of the boron complexes were significantly red-shifted compared with those of the parent D–A molecules. The absorption maximum derived from the HOMO–LUMO transition was observed at 507 nm ($\log \epsilon = 4.30$) in **L1**, whereas the maxima were red-shifted to 713 nm ($\log \epsilon = 3.59$) in **L1B1** and 791 nm ($\log \epsilon = 3.67$) in **L1B2**. Installation of the more electron-deficient BT unit (**L2** series) red-shifted the absorption greatly, with maxima at 537 nm ($\log \epsilon = 4.33$) in **L2**, 757 nm ($\log \epsilon = 3.67$) in **L2B1**, and 850 nm ($\log \epsilon = 3.82$) in **L2B2**. Thus, the absorption wavelengths are tunable not only by the choice of acceptor units but also by the number of boron atoms on the BDP skeleton. The broad absorption of boron complexes up to 1100 nm suggested their potential utility as NIR-absorbing materials. It is notable that the 4-fluorophenyl substituents at the boron atoms have little influence on the optical properties because they lower both HOMO and LUMO to the same extent (see below). The longest absorption maxima were 791 nm ($\log \epsilon = 3.76$) in **L1B2F** and 842 nm ($\log \epsilon = 3.83$) in **L2B2F**. We also measured the absorption spectra of these compounds in film, which were red-shifted compared with those in CH₂Cl₂ (see the Supporting information, Fig. S2). The parent D–A-type molecules showed weak fluorescence with an emission maximum of 602 nm ($\Phi_F = 1.0 \times 10^{-4}$) in **L1** and 736 nm ($\Phi_F = 4.4 \times 10^{-4}$) in **L2** (see the Supporting information, Fig. S3). No detectable fluorescence signals were observed for any of the boron complexes.

Electrochemical properties of the above molecules were measured using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The BDP-Qx boron complexes **L1B1** and

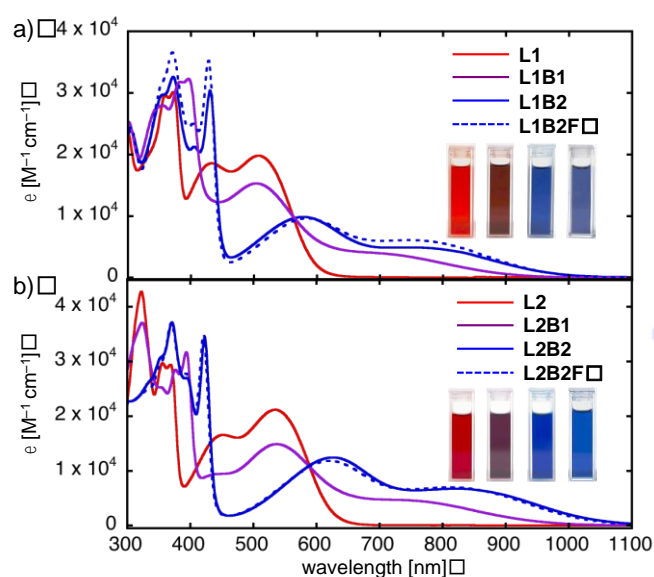


Figure 2. UV-vis-NIR absorption spectra of (a) quinoxaline-based D–A-type molecules and (b) benzothiadiazole-based D–A-type molecules in CH₂Cl₂.

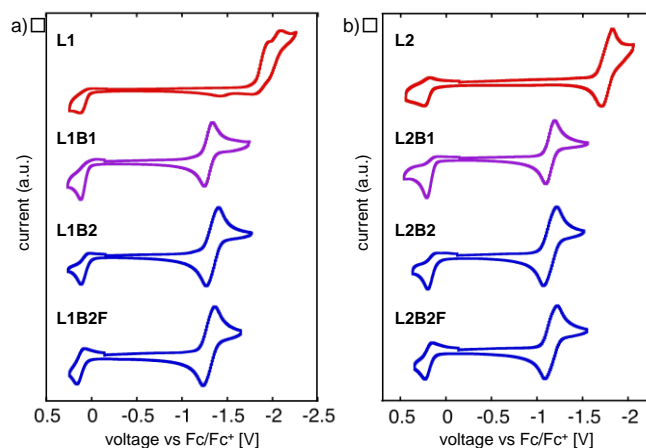
Table 1. Photoelectronic properties of the synthesized D–A molecules and boron complexes.

	$\lambda_{\text{abs}}^{\text{[a]}}$ [nm]	$\log \epsilon$	$\lambda_{\text{em}}^{\text{[b]}}$ [nm]	$\phi_{\text{F}}^{\text{[c]}}$	$\square_{\text{HOMO}}^{\text{[d]}}$ [eV]	$\square_{\text{LUMO}}^{\text{[e]}}$ [eV]
L1	507	4.30	602	1.00×10^{-4}	-4.86	-2.98
L1B1	713	3.59	–	–	-4.84	-3.54
L1B2	791	3.67	–	–	-4.84	-3.51
L1B2F	791	3.76	–	–	-4.91	-3.55
L2	537	4.33	736	4.4×10^{-4}	-4.98	-3.06
L2B1	757	3.67	–	–	-4.93	-3.69
L2B2	850	3.82	–	–	-4.91	-3.66
L2B2F	842	3.83	–	–	-4.98	-3.70

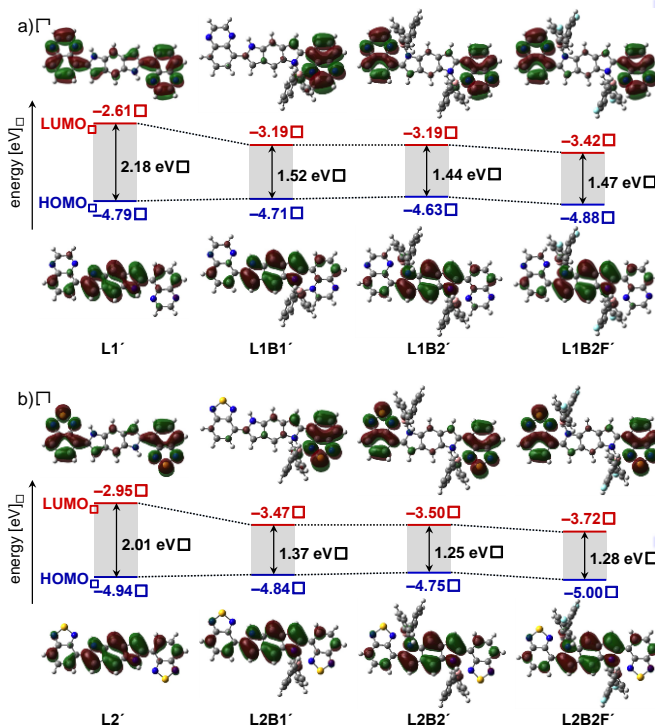
[a] Absorption maxima λ_{max} determined by curve fitting with multi-Gaussian peaks. [b] Emission maxima λ_{em} upon excitation at the absorption maximum wavelengths. [c] Fluorescence quantum yield ϕ_{F} determined with Rhodamine 6G as a standard. The quantum yield of Rhodamine 6G was measured by an absolute method to be 0.82 in dichloromethane. [d] HOMO energy levels estimated from DPV measurements in CH_2Cl_2 . [e] LUMO energy levels estimated from DPV measurements in CH_2Cl_2 .

L1B2 showed a reversible reduction wave, while the free-base ligand **L1** showed two irreversible reduction waves (Fig. 3a). Reduction potentials were estimated by DPV to be -1.84 V (vs. Supporting information, Fig. S4). In addition, these compounds showed irreversible oxidation waves. The obtained oxidation potentials were $+0.04$ V in **L1**, $+0.02$ V in **L1B1**, and $+0.02$ V in **L1B2**. These results suggest that the LUMO energy levels are substantially lowered by complexation with boron atoms, from -2.98 eV (**L1**) to -3.54 eV (**L1B1**) and -3.51 eV (**L1B2**), while the HOMO energies show only a small change, -4.86 eV (**L1**), -4.84 eV (**L1B1**), and -4.84 eV (**L1B2**) (Table 1). From these electrochemical results, we concluded that the observed red-shifted absorptions originate from the lowering of LUMO energy levels upon the formation of boron complexes. A similar trend was observed also in the BT-based D–A molecules. Lowering of LUMO levels by complexation with boron atoms was observed, from -3.06 eV (**L2**) to -3.69 eV (**L2B1**) and -3.66 eV (**L2B2**), while HOMO energies showed a much smaller change with -4.98 eV (**L2**), -4.93 eV (**L2B1**), and -4.91 eV (**L2B2**). The lower HOMO–LUMO levels and smaller band gaps of BT-based boron complexes would be ascribed to the stronger electron-accepting property of the BT unit than that of the Qx unit. This indicates that the present strategy is applicable to other acceptor units with co-ordination ability. Furthermore, lowering of HOMO and LUMO levels was accomplished by the introduction of electron-withdrawing 4-fluorophenyl boryl groups (**F** series). The HOMO and LUMO energy levels of **L1B2F** were -3.55 eV and -4.91 eV, respectively, which were lower than those of **L1B2** by 0.07 eV and 0.04 eV, respectively. Similarly, the HOMO and LUMO levels of **L2B2F** were -3.70 eV and -4.98 eV, respectively, which were lower than those of **L2B2** by 0.07 eV and 0.04 eV, respectively.

Density functional theory (DFT) calculations of model compounds revealed the origin of the boron effects. In the model

**Figure 3.** CV of (a) quinoxaline-based D–A-type molecules and (b) benzothiadiazole-based D–A-type molecules in CH_2Cl_2 , measured with 0.1 M Bu_4NPF_6 as a supporting electrolyte at a scan rate of 100 mV s^{-1} .

compounds denoted with a prime sign, 2-ethylhexyl groups were replaced by hydrogen atoms (Fig. 4). In **L1'**, the HOMO is predominantly distributed in the central BDP core, while the LUMO is mainly distributed on the Qx moiety. The LUMO of the monoboryl complex **L1B1'** is localized at the boron-complex Qx group, as one would expect. The dinuclear **L1B2'** shows the same LUMO value as that of mononuclear **L1B1'** (-3.19 eV). Both the HOMO and the LUMO levels of **L1B2F'** were lowered by a similar amount as those of **L1B2'**, and the gap remained

**Figure 4.** Calculated HOMOs and LUMOs, and their energy levels for the model compounds of (a) quinoxaline-based D–A-type molecules and (b) benzothiadiazole-based D–A-type molecules, obtained at the B3LYP/6-31+G(d) level of theory.

little changed (1.44 eV vs. 1.47 eV), as reflected in their absorption maxima mentioned above. These trends seen for the HOMO and LUMO levels are consistent with the experimental values obtained from the DPV measurements (see above). The theoretical calculations of BT-based molecules (Fig. 4b) showed a similar trend to those of the Qx analogues, while the HOMO and LUMO levels were lower, and the HOMO–LUMO gaps were a little smaller.

In summary, BDP-based D–A-type boron complexes represent a new class of NIR-absorbing materials. The BDP donor unit allows the D–A-type molecules to be further functionalized to change the photophysical and electrochemical properties of the compounds. Boron complexation caused both a significant red-shift of the NIR absorption and lowering of the LUMO energy levels compared with those of the parent D–A-type molecules. In addition, further tuning of the absorption wavelength and energy levels was made possible by changing the number of boryl substituents and installation of a fluorine group on the diarylboron atoms.

Acknowledgements

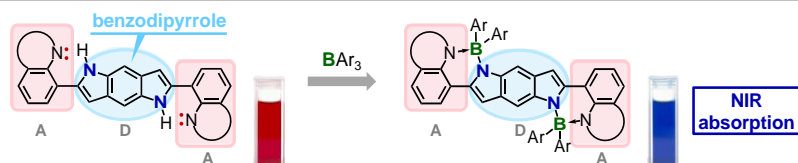
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Keywords: boron • donor–acceptor type molecule • energy level tuning • heterocycles • near-infrared absorption

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Layout 2:

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Tomoya Nakamura, Shunsuke Furukawa, and Eiichi Nakamura*

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Benzodipyrrole-based donor-acceptor boron complexes were designed and synthesized as near-infrared-absorbing materials. The electron-rich organic framework combined with the Lewis acidic boron co-ordination enabled us to tune the LUMO energy level and the HOMO-LUMO gap—that is, the absorption wavelength—by changing the organic acceptor units, the number of boron atoms, and the substituents on the boron atoms.

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