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π-Extended Planarized Triphenylboranes with Thiophene Spacers

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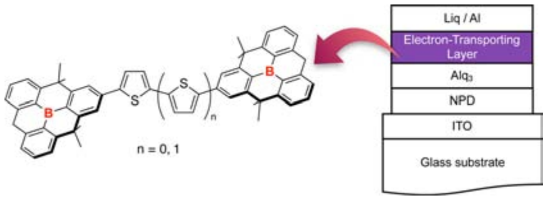
ABSTRACT



Planarized triphenylboranes extended with thiophene or bithiophene spacers were synthesized, which showed intense fluorescences in solution and reversible redox waves for reduction in cyclic voltammetry. Organic light-emitting diodes (OLEDs) using these compounds as an electron-transporting material were fabricated.

Introduction of a tricoordinate boron moiety into a π-conjugated skeleton is a potent strategy to gain a high electron-accepting ability due to the π-conjugation through a vacant p orbital of the B-atom.[1] By taking advantage of this feature, various fascinating B-containing π-electron systems have been developed as emissive materials,[2] two-photon absorption materials,[3] and anion sensors.[4] Of particular note is their use as an electron-transporting material for organic light-emitting diodes (OLEDs). Shirota et al. demonstrated that amorphous oligothiophenes bearing dimesityboryl groups ($-$BMes$_2$) at their termini showed high performance as the electron-transporting materials.[5] Their pioneering studies stimulated further development of various types of triarylboranes for such a purpose.[6] A key issue in their molecular design is the kinetic stabilization of the compounds by

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steric protection of the B-atom. Indeed, the tricoordinate boranes with bulky aryl groups, such as mesityl,[7] 2,4,6-triisopropylphenyl,[8] and 2,4,6-tri-*tert*-butylphenyl groups,[9] are substantially stable toward air and moisture. However, the bulky substituents prevent the intermolecular interactions in the solid state, which gives rise to a detrimental effect on the solid-state properties like charge carrier mobility. Therefore, an alternative strategy for the stabilization of the tricoordinate boranes not relying on the bulky substituents is required.

In this context, we recently designed and synthesized triphenylboranes **1** that have three methylene bridges to fix the three benzene rings coplanar to a plane of the B-center (Figure 1a), and demonstrated that boranes **1** have a high stability toward air, moisture, and silica gel despite the absence of the steric protection.[10] The planarized triphenylboranes **1** showed a characteristic fluorescence property due to the structural constraint.[11] We also isolated a radical anion of **1** and revealed its structure.[12] In addition, the boranes **1** were useful precursors for some intriguing π-electron systems, such as borataanthracenes[13] and boracyclophanes.[14] We now envisioned that the planarized triphenylboranes can also be utilized as a key building unit for the electron-transporting materials in OLEDs. To demonstrate the potential of the planarized boranes to this end, we designed π-extended planarized triphenylboranes **2** and **3** linked with thiophene or 2,2′-bithiophene as a π-spacer (Figure 1b). Here, we report the robust synthesis of the one-dimensionally extended planarized triphenylboranes and their structures and fundamental photophysical and electrochemical properties. The OLEDs using these compounds as an electron-transporting material were successfully fabricated by a vacuum vapor deposition technique.

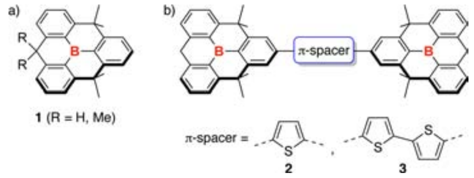
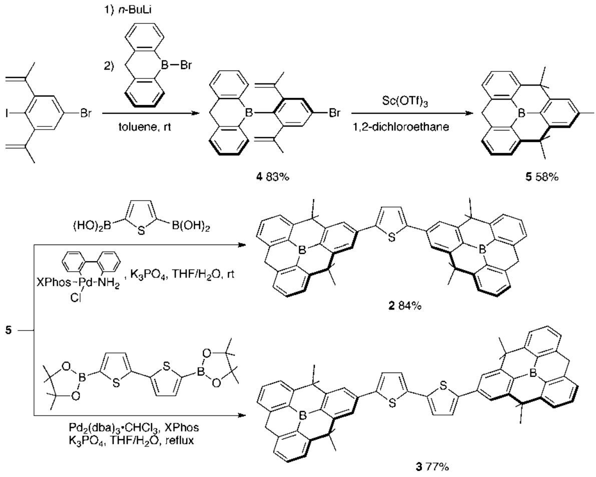


Figure 1. (a) Planarized triphenylboranes. (b) 1-D π-extension of the planarized triphenylboranes with π-spacers.

For the synthesis of the one-dimensionally extended planarized triphenylboranes, we first synthesized the bromo-substituted planarized triphenylborane **5** as a key precursor (Scheme 1). Borane **4** was obtained by the reaction of 9-bromo-9,10-dihydro-9-boraanthracene with 4-bromo-2,6-di-(2-propenyl)phenyllithium in 83% yield. Treatment of **4** with a stoichiometric amount of $Sc(OTf)_3$ (2 equiv) promoted the intramolecular 2-fold Friedel–Crafts cyclization to afford **5** in 58% yield. **5** was stable enough to perform the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction under basic conditions, despite the absence of steric protection. Thus, the reaction between **5** and thiophenediboronic acid or bithiophenediboronic ester produced **2** and **3** in good yields (Scheme 1).[15] **2** and **3** were sufficiently stable toward air and moisture and were purified by silica gel column chromatography without any special precautions. Notably, these compounds have high thermal stabilities. The decomposition temperatures with a 5% weight loss (T_{d5}) of **2** and **3** under N_2 were 418 and 447 °C, respectively.

The UV–vis absorption and fluorescence properties of **2** and **3** in THF are summarized in Table 1 (see also Figure S18a in the Supporting Information, SI). While the thiophene derivative **2** showed an absorption maximum

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



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(λ_{abs}) at 391 nm, the λ_{abs} of the bithiophene derivative **3** was red-shifted to 418 nm, indicative of the effective extension of the π conjugation. Compound **2** exhibited an intense blue fluorescence with a maximum (λ_{em}) of 441 nm. Its fluorescence quantum yield (Φ_F) was 0.92. On the other hand, the bithiophene derivative **3** showed a greenish fluorescence with the λ_{em} of 482 nm (Φ_F = 0.25). The lower Φ_F of **3** compared to that of **2** results from the increased nonradiative decay process, according to their excited state dynamics study (Table S1). Compounds **2** and **3** also showed weak fluorescences in the solid state (Φ_F of 0.14 for **2** and 0.19 for **3**). The fluorescence maximum wavelengths were red-shifted in both cases with the λ_{em} of 471 and 531 nm for **2** and **3**, respectively (Figure S18b).

Compounds **2** and **3** showed reversible redox waves in the cyclic voltammograms for both the oxidation and reduction processes (Figure S19), indicative of the high stability of the produced species under the measurement conditions. The half wave potentials ($E_{1/2}$) of **2** and **3** are also summarized in Table 1. While the oxidation potential was +0.67 V for **3** (vs Fc/Fc$^+$) in CH_2Cl_2, the first reduction potentials of **2** and **3** were comparable to each other (−2.27 V) in THF. In addition, while the thiophene derivative **2** showed two-step reduction processes with an $E_{1/2}$ of −2.27 and −2.35 V, the bithiophene derivative **3** only showed one redox wave. These results suggest that the two boron moieties are electronically connected to each other by the short spacer compound **2**, but not by the longer bithiophene spacer derivative **3**, in which a two-electron reduction occurred at almost identical potentials.

Table 1. Photophysical and Electrochemical Data for **2** and **3**

	absorption[a]		fluorescence[a]		potential[c]	
compd	λ_{abs} [nm]	log ε [M^{-1} cm^{-1}]	λ_{em} [nm]	Φ_F[b]	$E_{1/2}^{ox}$ [V][d]	$E_{1/2}^{red}$ [V][a]
2	391	4.75	441	0.92	+0.90	−2.27 −2.35
3	418	4.76	482	0.25	+0.67	−2.27

[a] In THF. [b] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error. [c] With $Bu_4N^+PF_6^-$ (0.1 M) as an electrolyte at a scan rate of 0.1 V s^{-1}. Potentials vs ferrocene/ferrocenium. [d] In CH_2Cl_2.

To gain insight into the electronic structures of these compounds, we conducted theoretical calculations at the B3LYP/6-31G(d) level of theory (Figure S23).[16] The LUMOs of both **2** and **3** consist of the π* orbital of the π-spacer moieties and the vacant p orbitals of the B-atoms and are effectively delocalized over the molecules. Notably, these energy levels are almost comparable to each other (−1.95 eV for **2** and −2.00 eV for **3**). This result is consistent with the fact that **2** and **3** showed comparable first reduction potentials in the cyclic voltammograms. Yet, the HOMOs are mostly localized on the diphenylthiophene or diphenylbithiophene moiety. As the π-spacer moiety becomes longer, the energy level of the HOMO increases from −5.39 eV in **2** to −5.14 eV in **3**. These results suggest that the extension of the π-spacer moiety from thiophene to bithiophene mainly affects the energy level of the HOMO, whereas it does not effectively reduce the LUMO level.

We successfully obtained single crystals of **2** and **3** suitable for an X-ray crystallographic analysis by recrystallization using the vapor diffusion from chloroform/hexane. While compound **2** has a bow-shaped molecular structure due to the 2,5-thiophene linker, the entire molecular structure of the bithiophene derivative **3** is almost linear (Figure S21). Reflecting their molecular shapes, **2** and **3** have totally different packing structures from each other. The crystal structure of **2** consists of four crystallographically independent molecules, in which the dihedral angles between the thiophene and triphenylborane moieties vary from 8° to 52°. The molecules form a lattice-like packing structure with the CH$\cdots\pi$ interactions between the adjacent planarized triphenylborane moieties (Figure 2a). Accordingly, the crystal has large cavities with diameters of ca. 1 nm, which accommodate several solvent molecules. However, the bithiophene derivative **3** forms a slipped parallel molecular array (Figure 2b), in which the planarized triphenylborane moiety overlaps with the bithiophene moiety of the adjacent molecule. The closest distance between the B-atom of the planarized triphenylborane moiety and the C-atom of the adjacent bithiophene moiety is 3.48 Å, indicative of a certain intermolecular interaction. Indeed, the solubilities of **3** in common organic solvents were much lower (0.7 mg/mL in THF; 0.2 mg/mL in CH_2Cl_2) than those of **2** (19 mg/mL in THF; 30 mg/mL in CH_2Cl_2).

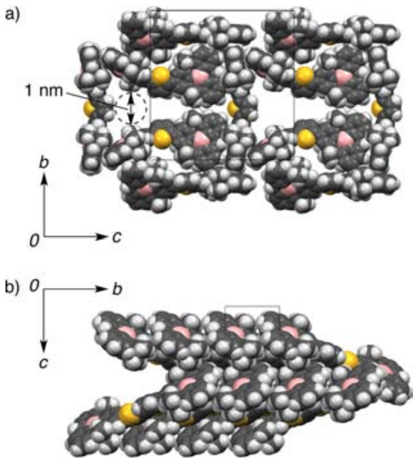

Figure 2. Packing structures of (a) **2** and (b) **3** determined by an X-ray crystallographic analysis.

Notably, **2** and **3** were stable enough to prepare thin films by the vacuum vapor deposition process despite the absence of the steric protection of the boron moiety. The OLED devices employing **2** and **3** as the electron-transporting layer were fabricated, the device structure of

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(16) Frisch, M. J.; et al. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004. See the SI for full reference.

which is shown in Figure 3a. *N*,*N*′-Di-(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD), tris(8-hydroxyquinoline)aluminum(III) (Alq_3), 8-hydroxyquinolinatolithium (Liq), and aluminum (Al) were employed as the hole-transporting, emission, electron-injection, and cathode materials, respectively (Figure S26). Hereafter, the devices employing **2** and **3** are abbreviated [**2**(15)] and [**3**(15)], respectively, in which the thickness of the borane layers is shown in parentheses. The dependence on the thickness of each layer is described in the SI. A device, [Alq_3], that employed only Alq_3 (thickness of 70 nm) as the emissive electron-transporting layer was also fabricated for comparison.

We measured the ionization potential of the deposited film made from each material by photoelectron spectroscopy in the air (AC-3, RIKEN KEIKI Co., Ltd.) (Figure 3b). It is noteworthy that the ionization potential of **2** (6.20 eV) was higher than that of Alq_3 (6.01 eV), indicative of the role of **2** as a hole-blocking layer. We also estimated the electron affinities from the ionization potentials and optical band gaps. The electron affinities of **2** and **3** were estimated to be 3.45 and 3.43 eV, respectively, which are comparable to that of Alq_3 (3.47 eV). These results suggested the suitable electronic structures of **2** and **3** for effective electron transport from these compounds to Alq_3. Indeed, all the devices that we fabricated showed a green emission from Alq_3 in their electroluminescence spectra (Figure S27d). These results confirmed that both **2** and **3** act as the electron-transporting material in the OLED devices.

The *J*−*V*−*L* characteristics of the three devices are shown in Figure 4. The applied voltage *V* to gain the luminance of 1000 cd/m^2 was 7.6 V for [**3**(15)]. This value is lower than that of [**2**(15)] (9.4 V) and is comparable to that of [Alq_3] (7.2 V). Thus, the performance of the bithiophene derivative **3** as the electron-transporting material is higher than that of **2** in the OLED devices. This result may reflect their different crystal packing structures, although the structure in the crystalline state is not directly relevant to the device performance in the noncrystalline state. On the basis of the calculation by the ADF program (PW91/DZP level of theory),[17,18] the slipped array structure of **3** in the crystal showed a large transfer integral t_{LUMO} of 57 meV in the stacking direction, although the t_{LUMO} between the adjacent arrays was small (2.2 meV).

In summary, we have synthesized two planarized triphenylborane derivatives **2** and **3** with thiophene or bithiophene spacers by the Suzuki−Miyaura coupling of a Br-substituted precursor. A notable finding is that both compounds have sufficient thermal stabilities that allow the thin film preparation by the vacuum vapor deposition despite the absence of the steric protection of the boron moieties. Our preliminary experiments for the device fabrication revealed that these compounds indeed act as the electron-transporting material for OLEDs. **3** exhibited performance comparable to that of the widely used Alq_3. These results demonstrated the high potential of the planarized triphenylboranes as a building unit for the organic electronic materials.

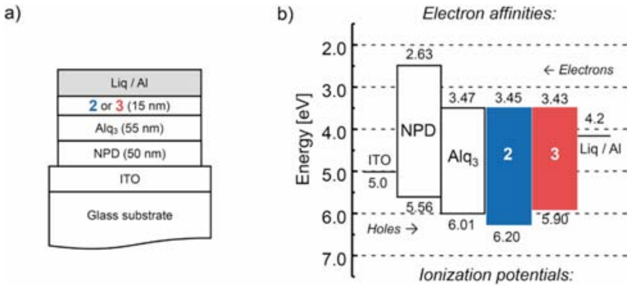

Figure 3. (a) Device structure. (b) Electronic structures of NPD, Alq_3, **2**, and **3**. Ionization potentials were measured by photoelectron spectroscopy in the air.

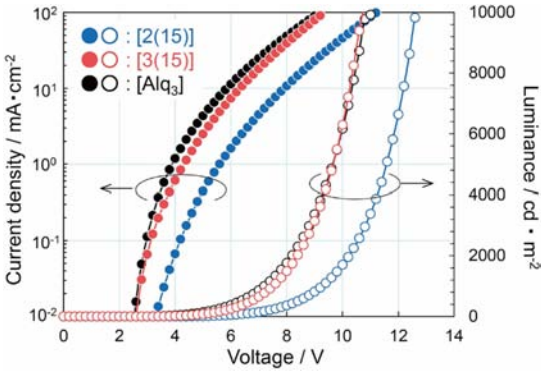

Figure 4. *J*−*V*−*L* characteristics of [Alq_3], [**2**(15)], and [**3**(15)].

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Supporting Information Available. Experimental procedures, photophysical properties, cyclic voltammograms, results of theoretical calculations, details of the OLED devices, and the crystallographic information files (CIFs) for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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