

Development of Organic Electronic Devices Using Boronate Esters and Related Heterocycles

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New oligomers containing tricoordinated boron atoms were prepared, and OFET devices based on these compounds were fabricated. These are first examples of OFET devices based on compounds containing tricoordinated boron atoms.

Organic semiconductors have attracted much attention for electronic and optical applications such as organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs), which have advantages of low cost, lightness, mechanical flexibility and disposability. Many OFETs based on acenes such as pentacene or oligomers such as oligothiophenes have been reported, and some of these materials show high hole or electron mobilities comparable to amorphous Si ($\approx 1.0 \text{ cm}^2/\text{Vs}$).¹⁻⁸ However, development of new materials is still important to enhance the FET performance as well as to investigate the mechanism of carrier transportation. In this context, boron-containing π -conjugated compounds are attractive since the boron atom has a planar geometry with a vacant 2p orbital. This leads to Lewis acid characteristics and electron-accepting properties. Boron-containing materials have been developed for chemical sensors, electroluminescence, nonlinear optics, and hole or electron carrier transport.⁹⁻¹² However, compounds with tricoordinated borons have not been used for OFETs, to our best knowledge, although tetracoordinated boron-containing compounds showed FET properties.¹³ This is considered to be due to the following reasons. Tricoordinated boron-containing π -conjugated molecules are generally unstable and need bulky substituents like a mesityl (Mes) unit around the boron center for steric protection to enhance the stability. These molecules have weak intermolecular interactions and are unfavorable for FETs since carrier transportation requires strong intermolecular interactions. As stable boron-containing compounds with planar structures, we have paid attention to boronates and their analogues.¹⁴ Although boronic acids and esters are well-known reagents for the Suzuki–Miyaura coupling reaction, they have never been used as semiconductors for OFETs. We have now prepared arylboronates and related compounds with extended π conjugation and examined their physical properties and structures. The FET devices based on them were successfully fabricated here for the first time.

Compounds **1–3** (Chart 1) were synthesized by reaction of the corresponding boronic acids with catechol, 1,2-dihydroxynaphthalene and 2,5-diamino-1,4-benzenedithiol dihydrochloride in the presence of *p*-toluenesulfonic acid in toluene in 5–34% yields. Compound **3** was designed because the nitrogen and sulfur atoms were expected to enhance the stability of the boron-containing heterocycle by conjugation. The reaction products were purified by sublimation. Their structures were deter-

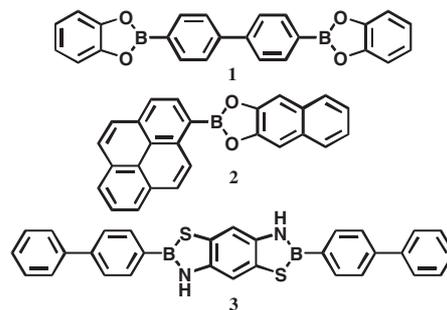


Chart 1.

Table 1. Optical properties and redox potentials of **1–3**

Compound	$\lambda_{\text{abc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$E_{\text{ox}}/\text{V}^{\text{c}}$	$E_{\text{red}}/\text{V}^{\text{c}}$
1	291 ^a	337 ^a	+1.10	−1.36
2	268, 278, 332 347, 376 ^b	277, 389, 409 ^b	+1.22	−0.85
3	270, 341 ^b	443 ^b	+0.95	

^aIn CH_2Cl_2 . ^bIn DMF. ^c0.1 M *n*-Bu₄NPF₆ in DMF, Pt electrode, scan rate 100 mV/s, V vs. SCE.

mined by the spectral data along with elemental analysis.

The optical properties and redox potentials of **1–3** are shown in Table 1. They have no absorptions in the visible region and their transparent films could be formed. They showed efficient fluorescence even in the solid state. The fluorescence spectrum of **3** in the solid state is shown in Figure S1.¹⁵ The emission is blue with a maximum at 446 nm, and the fluorescence quantum yield was 20% in the solid state. Compounds **1** and **2** showed both the oxidation and reduction potentials, whereas compound **3** showed only the oxidation potential. The observation of the reduction potentials can be attributed to the presence of the electron-deficient boron atoms.

The single crystals of **1–3** suitable for the X-ray structure analysis were obtained by sublimation.¹⁶ All of the molecules were found to be almost planar as expected. In molecule **1**, the dihedral angles between the phenyl and boronate rings are 8.9 and 9.4°, and the angle in the biphenyl unit is 0.4°. This molecule forms a π -stacking structure, where the electron-donating benzene ring is overlapped with the electron-deficient boron atom (Figure S2). In the crystal of **2**, there exist two crystallographically independent molecules. These also form a π -stacking structure (Figure S3). The dihedral angle between the pyrene and boronate rings is 8.1° (molecule I) and 10.9° (molecule II). In molecule **3**, the dihedral angles between the phenyl and heterocyclic rings are 6.3 and 5.3°, and the angle between the

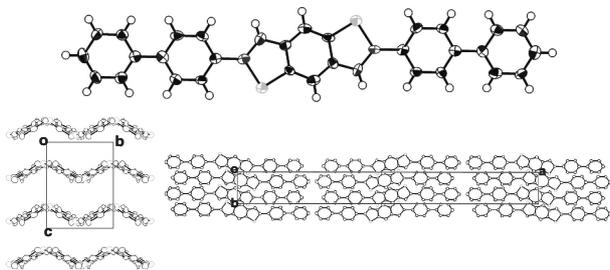


Figure 1. Structure and packing view of **3**.

Table 2. Field-effect characteristics of **2** and **3**^a

Compound	SiO ₂ treatment	T _{sub} /°C	Mobility /cm ² V ⁻¹ s ⁻¹	On/off ratio	Threshold /V
2 ^b	HMDS	rt	2.4 × 10 ⁻⁷	20	-45
3 ^c	bare	rt	2.1 × 10 ⁻⁷	72	-49
	HMDS	rt	1.8 × 10 ⁻³	10 ⁴	-66

^aElectrode: Cr/Au = 10/20 nm, SiO₂/Si substrates, SiO₂: 300 nm. ^bL/W = 5/38000 μm. ^cL/W = 25/294000 μm, interdigital electrode.

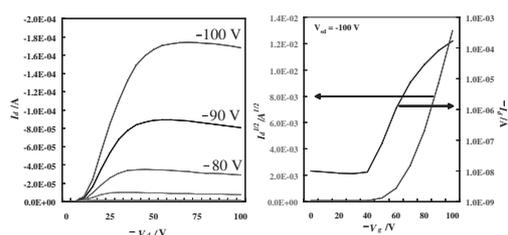


Figure 2. Output and transfer characteristics of **3**.

phenyl groups in the biphenyl unit is 2.1°. It should be noted here that molecule **3** is packed in a herringbone manner in contrast to **1** and **2** (Figure 1). This result may be attributed to the difference in the electron affinity of the boron atoms. Thus, in the case of boronates **1** and **2**, the intermolecular interaction between the aromatic π electron and the vacant p orbital of the boron can lead to the stacking structure. On the other hand, such an interaction is considered to be weak in **3** since the nitrogen lone-pair electrons flow to the boron p orbital to reduce the electron-accepting property.

The FET devices were fabricated by a vapor-deposition method with bottom contact geometry on bare or HMDS-treated SiO₂ substrates. The FET measurements were carried out at room temperature in a high-vacuum chamber (10⁻⁵ Pa). The device of **1** did not exhibit typical FET characteristics. Instead, it showed a very unusual varistor-like I - V curve (Figure S4), where the current nonlinearly increased on the high source-drain voltages. This detail is still puzzling and under investigation. On the other hand, the devices based on **2** and **3** exhibited p-type FET behavior. The transfer and output characteristics of **2** and **3** on the HMDS-treated SiO₂ substrates are shown in Figures S5 and 2, respectively. The FET characteristics are summarized in Table 2. The device of **2** is the first example of FETs based on boronates. The device of **3** showed higher performance. The hole mobility and on/off ratio of **3** were 1.8 × 10⁻³ cm²/Vs and 10⁴, respectively. The high threshold voltage (-66 V) may be attributed to the low HOMO level since the ionization potential of

the thin film of **3** was 5.8 eV, which was measured in air by PES. The value is significantly higher than the work function of Au electrodes (5.1 eV). The device of **3** did not show atmospheric stability although it has a high ionization potential.

To investigate the thin film structure of **3**, XRD measurement was carried out. As shown in Figure S6, the peaks are sharper on the HMDS substrate than on the bare one, indicating that the crystallinity in the film increases by the substrate treatment. This result is consistent with the better FET performance on the HMDS-treated substrate. The d spacing obtained from the first reflection peak is 2.69 nm ($2\theta = 3.28^\circ$). Since the molecular length is 2.64 nm, the molecules are considered to be arranged nearly perpendicularly to the substrate. The film of **3** was also investigated by atomic force microscope (AFM) (Figure S7). Many small grains were observed, and the surface of the thin film is rather rough. Large space between grains may result in the atmospheric instability of the device.

In summary, we have developed new π -conjugated systems containing tricoordinated boron atoms. The introduction of boron atoms was effective to increase intermolecular donor-acceptor interactions. The device of boronate ester **1** showed unusual varistor-like behavior. The devices using compound **2** and **3** showed p-type FET behavior, which are first examples of OFETs based on compounds containing tricoordinated boron atoms.

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- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-694950, 694951, and 694902.