1,3-Diketone-Based Organoboron Polymers: Emission by Extending π-Conjugation along a Polymeric Ligand

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Torrential effort has been devoted to the design and synthesis of boron-containing polymers and oligomers because these polymers and oligomers are potential use in catalysis, sensor applications, and material science.[1] Main synthetic techniques for them are the incorporation of boron moieties into the backbone and the connection in side groups of polymeric structures (e. g., poly(*p*-phenylene−borane)s,[2] poly(cyclodiborazane)s,[2a,3] polyborole,[4] poly(bora-acetylene)s,[5] boron-containing polymeric acids,[6] poly(boronate)s,[7] arylboroxine-functionalized poly(styrene-*co*-vinylpyridine),[8] etc.). Recently, with the aid to dye chemistry, the incorporation of boron-chelating dyes into polymer main chain or side chain is particularly attractive for applications such as electroluminescent devices, organic field-effect transistors, photovoltaics, and so on.[9] The incorporation of organoboron quinolate as an electroluminescent chromophore, possessing efficient luminescence and good stability,[10] into the polymer side chain has been some of the intriguing research topics. For example, Jäkle et al. have demonstrated that novel well-defined organoboron quinolate polymers were prepared by the polymeric reaction of 8-hydroxyquinoline and thienyl-substituted poly(borylstyrene)[11] and have succeeded in the emission color-tunings of the organoboron quinolate polymers from blue to red regions by treatment with substituted 8-hydroxyquinoline derivatives.[12] Subsequently, Weck et al. have also reported the synthesis of polystyrene-supported organoboron quinolate through 8-hydroxyquinoline-functionalized polymers to fabricate organic light-emitting diodes (OLEDs) using a low-cost solution process.[13] In contrast, we reported the synthesis of the π-conjugated polymers integrated organoboron quinolate, i.e., main-chain-type organoboron quinolate polymers, into polymer backbone[14] and further main-chain-type organoboron aminoquinolate polymers.[15] Their polymers possess analogous properties, that is, strong fluorescence and an efficient energy migration to boron-chelating moieties by extending π-conjugation along the polymer backbones.

Boron diketonate is also one of boron-chelating dyes and has attracted attention as fluorophores owing to large molar absorption coefficients and large fluorescence quantum yields (Φ_F).[16] Conjugation of boron diketonate arises due to inhibition of nonradiative dissipation through O−H stretching modes from tautomerization between ketone and enol structures by forming stable six-membered boron-chelating ring, and boron complex has no loss of the unique characteristics of the diketonate fluorophore such as high fluorescence quantum yield, high photostability in contrast with heavy-metal complex. Recently, Fraser et al. have reported that difluoroboron dibenzoylmethane having a hydroxyl group (BF_2dpmOH), which showed most high Φ_F (ca. 0.95), was prepared and was employed as an initiator in the ring-opening polymerization of DL-lactide to give BF_2dpm end-functionalized polylactide with high Φ_F and interesting phosphorescence.[17] More recently, we have also proposed the synthesis of novel diarylboron diketonates possessing large molar absorption coefficients and high Φ_F.[18] Their emission behaviors depended on the electronic structures of boron atoms; that is, although boron complex **2** having strong electron-withdrawing C_6F_5 groups showed high fluorescence, no emission of **1** having diphenyl groups was observed because the highest occupied molecular orbital (HOMO) of **1** is not localized on the diketonate moiety (Figure 1). Herein, we anticipate that the emission of diphenyl diketonate moiety is restored by extending π-conjugation along the polymer linker; i.e., the HOMO of diphenylboron moiety is delocalized on the whole of polymeric diketone ligand. In this Communication we describe here the synthesis of a novel 1,3-diketonate-based polymeric ligand, and luminescent properties of main-chain-type diarylboron diketonate polymers obtained by chelating the polymeric ligand with boron compounds.

In order to test our hypothesis, **1m** and **2m** were initially designed as the model compounds of diarylboron diketonate polymers by using the Gaussian 03 suit of programs,[19] and their electronic states were investigated by theoretical calculations using density-functional theory (DFT) method at the B3LYP/6-31G (d, p)//B3LYP/6-31G (d, p) level of theory (Figure 2). The HOMO and the lowest unoccupied molecular orbital (LUMO) of **2m** are mainly located on the phenylacetylene and 1,3-diketone ligand. As expected, although the HOMO of **1** is almost localized on the diphenylboron group, that of **1m** is inverted on the ligand and the π-orbital of 1,3-diketone moiety in the ligand lies on the LUMO, resulting from the extended π-conjugation of 1,3-diketone moiety along phenylacetylene groups having electron-donating groups (−OMe). From these data, we expect that π-conjugation of poly(*p*-phenylene−ethynylene) alternatively connected with 1,3-diketone moiety is extended by attaching boron and the uprising of the HOMO level of diphenylboron diketonate moiety leads to the larger red shift in the UV−vis and emission spectra of the polymer by the electron-donating group, implying the emissive potentiality of diphenylboron moiety in the polymer.

With these DFT results in mind, we selected the Sonogashira−Hagihara coupling reaction to give the diarylboron diketonate polymer based on *p*-phenylene−ethynylene structure, as shown in Scheme 1. At first, *tert*-butoxycarbonyl diiododiketone monomer **3**, which was synthesized by the reaction of di-*tert*-

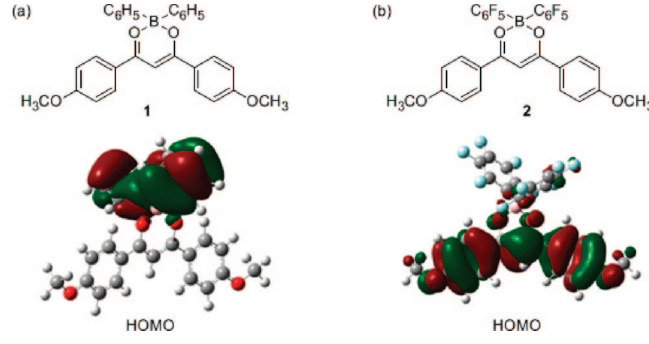

Figure 1. Structure and molecular orbital diagram for the HOMO (B3LYP/6-31G (d, p)//B3LYP/6-31G (d, p)) of **1** (a) and **2** (b).

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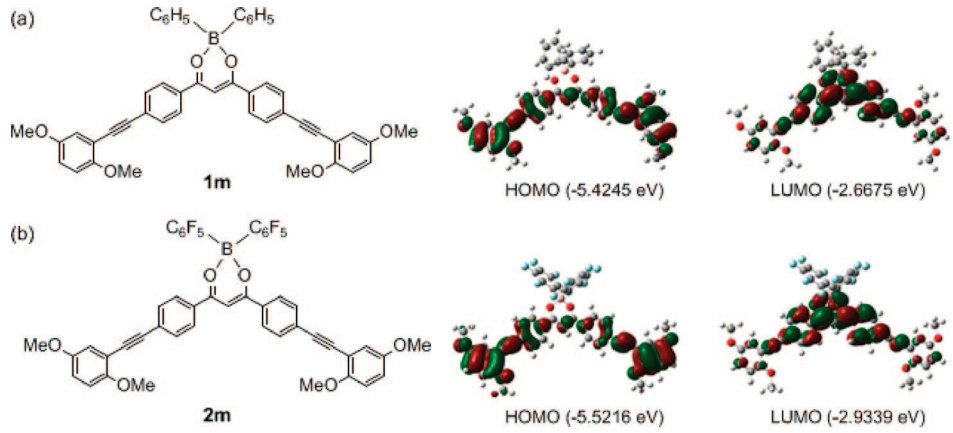
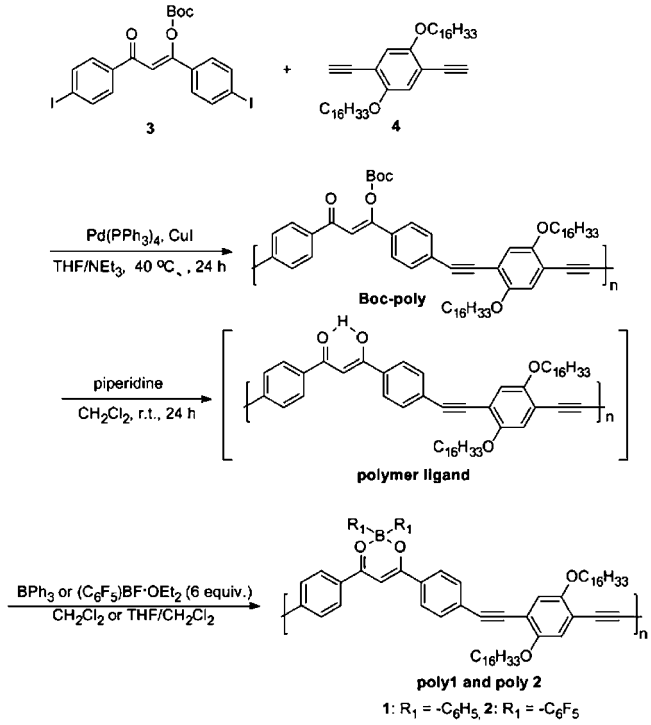


Figure 2. Structure and molecular orbital diagram for the LUMO and HOMO of **1m** (a) and **2m** (b) (B3LYP/6-31G (d, p)//B3LYP/6-31G (d, p)).

Scheme 1. Synthesis of Boc-poly and Boron Chelating Polymers (poly1 and poly2)



butyl dicarbonate and 1,3-bis(4-iodophenyl)propane-1,3-dione in the presence of *N*,*N*-dimethylaminopyridine, was polymerized using 1,4-diethynyl-2,5-dihexadecyloxybenzene (**4**) in the presence of $Pd(PPh_3)_4$ and CuI as catalysts to obtain the corresponding polymer **Boc-poly**. The polymer was obtained as a yellow solid after the precipitation into methanol, and the polymer yield was 84%. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n), measured by size-exclusion chromatography (SEC) in THF, were 5100 and 3.56, respectively. The degree of polymerization (DP) estimated by M_n from SEC was 5.5. The IR spectrum showed the absorption peaks at around 1766 and 2202 cm^{-1} assignable to stretching of the Boc group and the carbon−carbon triple bond in the backbone, respectively, indicating that the coupling reaction between **3** and **4** proceeded without any damage on the Boc group in spite of a weak bond between enol and Boc groups. Next, the deprotecting reaction of Boc group in the **Boc-poly** was carried out using piperidine in CH_2Cl_2 for 24 h. Although the reaction proceeded remaining homogeneous, the obtained polymer was unexpectedly insoluble in common solvents such as CH_2Cl_2, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and so on after the precipitation into methanol, presumably due to intermolecular cross-linking reaction by hydrogen bonding between hydroxyl proton of enol moiety and oxygen atom of ketone moiety. Accordingly, it is impossible to isolate and purify the polymer ligand. Therefore, the reaction was newly conducted without isolation and purification. After 24 h, a strong IR absorption at 1766 cm^{-1} assigned to Boc group disappeared completely, and a new broad absorption assignable to a hydroxyl group on the enol moiety was observed at around 3500 cm^{-1} in CH_2Cl_2 (Figure S1). These observations might support the complete deprotecting reaction for Boc group. Continuously, an excess amount of triphenylborane (BPh_3) or fluorobis(pentafluorophenyl)borane diethyl etherate ($(C_6F_5)BF\cdot OEt_2$) was employed to afford the corresponding boron-chelating polymers. The yields of the obtained polymers were high enough (**poly1**: 94%; **poly2**: 88%), and the molecular weights of **poly1** and **poly2** were M_n = 5400 and 6300, respectively, which were expectedly higher than that of **Boc-poly** and were in good agreement with the theoretical values (M_n = 5500 and 6400) calculated from the DP of Boc-polymer (5.5) and the formula weight of each expected polymer repeating unit. The molecular weight distributions of the resulting polymers maintained unimodel peaks (Figure S2), clearly indicating no side reaction during the chelating reaction. In addition, the chelating percentages of the obtained polymers were high enough (**poly1**: ≈ 94%; **poly2**: ≈ 92%), which was calculated from DP of **Boc-poly** and M_n [chelating ratio = (M_n − 5.5 × formula weight of polymer repeating unit)/5.5 × formula weight of $-BR_2$]. The obtained polymers were characterized by ^1H NMR, ^{11}B NMR, and IR spectrocopies. No IR absorption assignable to hydroxyl group on the enol moiety in each polymer was observed (Figure S1). The characteristic structures of the obtained polymers were supported by ^1H NMR spectroscopy, and the tetracoordination states of the boron atoms were confirmed by the ^{11}B NMR spectroscopy (**poly1**: δ_B = 2.15 ppm; **poly2**: δ_B = 3.71 ppm). These results indicate that the chelations of boron compounds into **Boc-poly** proceeded efficiently.

The optical properties of the obtained polymers were investigated with UV−vis absorbance and fluorescence spectroscopies. The absorption peaks of **Boc-poly** and **polymer ligand** containing piperidine were observed at 414 and 426 nm, respectively (Figure S3). The peaks of **poly1** and **poly2** were significantly broadened to bathochromic side, resulting from the extended π-conjugation by formation of boron diketonate

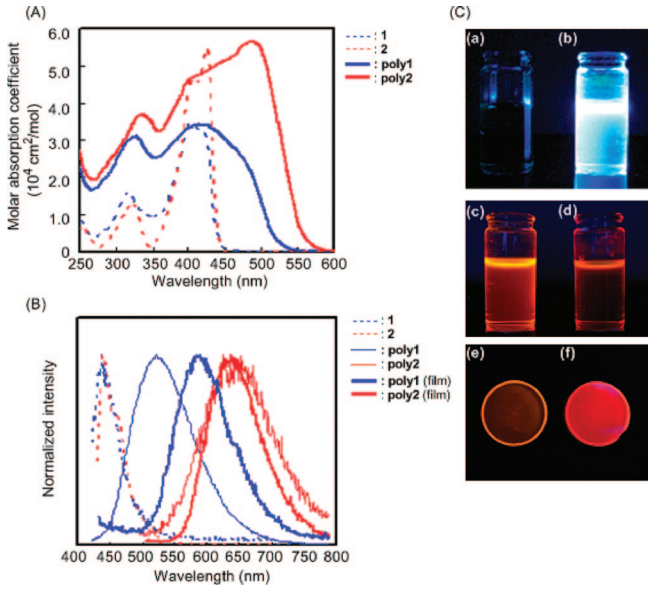


Figure 3. (A) UV−vis spectra of **1**, **2**, **poly1**, and **poly2** in CH_2Cl_2 (1.0×10^{-5} mol/L). (B) Normalized emission spectra of **1**, **2**, **poly1**, and **poly2** in CH_2Cl_2 (1.0×10^{-5} mol/L) and **poly1** and **poly2** in the film states. (C) Photographs of (a) **1** in CH_2Cl_2 solution, (b) **2** in CH_2Cl_2 solution, (c) **poly1** in CH_2Cl_2 solution, (d) **poly2** in CH_2Cl_2 solution, (e) **poly1** in the film state, and (f) **poly2** in the film state.

structures (Figure 3A). Previously, we have shown that **1** and **2** (Figure 1) display photoluminescence spectra in CH_2Cl_2 solution (**1**: 421 nm; **2**: 441 nm) when excited at their absorption maxima (**1**: 385 nm; **2**: 425 nm), and their absolute fluorescence quantum yields (Φ_F) in CH_2Cl_2 solution were 0.06 and 0.86, respectively.[18] The absorption peaks of **poly1** and **poly2** were drastically broadened and red-shifted as compared with those of **1** and **2**; i.e., **poly1**is from 385 to 412 nm, and **poly2** is from 425 to 487 nm (Figure 3A). These bathochromic shifts should be caused by the nature of the substituents on ligands of boron diketonate, which is consistent with previous reports that the emissive behaviors in the organoboron 1,3-diketone derivatives are significantly altered by the electron-donating nature of the substituents on diketone ligands.[16a,18] The emission color of **poly2** changed from blue or blue-green to red region in comparison with **2** or **polymer ligand** (from 441 or 515 to 652 nm), and **poly1** showed orange fluorescence (535 nm) although **1** was no emissive, indicating the inversion of HOMO orbital to the ligand side by extending π-conjugation along the *p*-phenylene−ethynylene-based polymeric ligand as we hypothesized (Figures 3B,C and S3). The molar absorption coefficients of both polymers (**poly1**: $\varepsilon = 3.4 \times 10^4$ M^{-1} cm^{-1}; **poly2**: $\varepsilon = 5.7 \times 10^4$ M^{-1} cm^{-1}) were barely higher than those of **1** and **2** (**1**: $\varepsilon = 2.7 \times 10^4$ M^{-1} cm^{-1}; **2**: $\varepsilon = 5.5 \times 10^4$ M^{-1} cm^{-1}). However, the quantum yields of the polymers (**poly1**: $\Phi_F = 0.04$; **poly2**: $\Phi_F = 0.02$) were low comparing with those of **1**, **2**, **Boc-poly** ($\Phi_F = 0.23$), and **polymer ligand** ($\Phi_F = 0.47$) because of their large Stokes shifts (**poly1**: 123 nm; **poly2**: 165 nm).[12] In a film state, the emission spectra of **poly1** was dramatically red-shifted to 591 nm compared with that in a solution state due to a higher degree of ordering in the polymer as shown in Figure 2B. In contrast, no bathochromic shift of **poly2** was observed. At this point, the reason is not obvious. Further, the emission colors of **poly1** and **poly2** became clearly bright in comparison with those in solution state ((e) and (f) in Figure 3C). However, both quantum yields of them in the film states were very low (<0.01), originating from collisional quenching of the excited state by $\pi-\pi$ stacking.[20]

In conclusion, we have prepared the first main-chain-type organoboron 1,3-diketonate polymers by chelating reaction of 1,3-diketone-based *p*-phenylene−ethynylene derivative as a polymeric ligand with arylboron compounds. Especially, designing the polymeric structure under theoretical calculations using density-functional theory (DFT) method led to emission of diphenylboron diketonate polymer (**poly1**) by extending π-conjugation along a polymeric ligand. The obtained polymers showed significantly red-shifted emission, and their molar absorption coefficients were slightly higher than those of the model complexes **1** and **2**. However, the absolute quantum yields of **poly1** and **poly2** were lower than those of the model boron complexes and **polymer ligand** due to their large Stokes shifts. Future work will focus on the fine-tuning of the emission colors via redesigns of polymeric ligands having several substituents and entail further research on potential device applications as electron-conducting materials or organic light-emitting diodes.

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Supporting Information Available: Text giving typical experimental procedures data for all new compounds, Figure S1 showing IR spectra of **Boc-poly**, deprotected polymer, **poly1**, and **poly2**, Figure S2 showing SEC traces of **Boc-poly**, **poly1**, and **poly2**, and Figure S3 showing the UV−vis absorption and fluorescence spectra of **Boc-poly** and **polymer ligand**. This material is available free of change via the Internet at http://pubs.acs.org.

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