Synthesis of New Main-Chain-Type Organoboron Quinolate Polymer Linked on Quinolate Ligand

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Received October 22, 2007; Revised Manuscript Received November 24, 2007

ABSTRACT: A main-chain-type organoboron quinolate polymer was prepared by means of polymer reaction between the precursor polymer and triphenylborane. The precursor polymer was synthesized by the Sonogashira−Hagihara coupling reaction between diyne monomer and *tert*-butoxycarbonyl- (Boc-) protected dibromoquinolinol monomer. The polymer reactions we carried out were successfully achieved and the structures of the obtained polymers were confirmed by IR, ^{1}H NMR, and elemental analyses. The precursor polymers showed blue or green emissions. In contrast, the organoboron quinolate polymer exhibited dramatically red-shifted orange photoluminescence. The quantum yield of the organoboron quinolate polymer was not significantly high. However, the molar extinction coefficient of the polymer at the excitation wavelength was remarkably improved by incorporation of the quinolate structure into the conjugated polymer main-chain. It was suggested that the conjugated main-chain behaved as a light harvesting antenna for organoboron quinolate units.

1. Introduction

Aluminum quinolate (Alq$_3$) as a luminescent electron transport layer for organic light emitting diodes (OLEDs) was first reported by Tang and van Slyke[1] in 1987. Even now, Alq$_3$ is still an important material because of its excellent stability and electroluminescent properties. One of the demerits of Alq$_3$ is its two isomeric forms (the *fac* and *mer* isomers). The isomerization and the associated changes of luminescent properties are assumed to be an adverse affect for practical applications. As an alternative to Alq$_3$, the corresponding organoboron quinolinolates seem to be promising candidates because there are only one way the quinolinol ligand can coordinate to the boron center. Recently, Wang and coauthors revealed that boron quinolates (BPh$_2$q) and their derivatives showed efficient luminescence.[2−5] In addition, boron quinolates indicated a good stability due to the increased covalency of the boron−ligand bonds.[6] There have been some examples of the investigation on polymers that contain boron quinolilate derivatives. For example, Jäkle et al. reported the preparation of side-chain type organoboron quinolate polymers by utilizing poly(4-dibromoborylstyrene) as a reactive polymer[7] and Weck et al. reported the synthesis of poly(styrene)-supported organoboron quinolate via 8-hydroxyquinoline-functionalized polymers.[8]

Recently, we reported the first main-chain-type organoboron quinolate polymers and the obtained polymers exhibited intense green-blue photoluminescence and efficient energy migration.[9] These polymers kept the emission color of nonsubstituted BPh$_2$q and a red-shift or broadening in the emission spectra was not observed. On the other hand, various organoboron quinolates with π-extended quinolate ligands had been surveyed for luminescence tuning.[10−13] In such a case, their emission color was bathochromicly shifted by introduction of extended π-system on the phenolate ring side of the quinolinol ligand. In order to introduce a more extended π-system to organoboron quinolates, we have prepared a main-chain-type organoboron quinolate polymer linked on 5,7-position of quinolate moieties. In this paper, we discribe their synthesis and luminescent properties.

2. Results and Discussion

2.1. Synthesis. Iijima and Yamamoto have already reported main-chain-type quinolinol polymers using dibromo-8-(*tert*-butyldimethylsiloxy)quinoline and 1,4-didodecyloxy-2,5-diethynylbenzene as monomers.[14] Their obtained polymers showed low solubility and they had to decrease the content of quinolinol units to improve solubility. In that paper, they removed *tert*-butyldimethylsilyl group by tributylammonium fluoride (TBAF). However, TBAF also acts as a strong base and sometimes causes undesired side reaction. TBAF might react with quinolinol. Therefore, we adopted a much milder procedure. Montes and coauthors reported the *tert*-butoxycarbonyl- (Boc-) protecting/piperidine-deprotecting system to prepare 5-substituted-8-hydoroxyquinoline.[15] We protected the hydroxyl group of 5,7-dibromoquinolin-8-ol by Boc group before transition metal-catalyzed polymerization. After the reaction, the crude product was recrystallized from hexane, which gave single crystals of monomer **1** in good yield. The crystal structures of monomer **1** have been determined by single-crystal X-ray diffraction analysis (Figure 1). It showed that bromo groups as reactive points were not hindered, in spite of modification by bulky Boc group.

We applied the Sonogashira−Hagihara coupling reaction to prepare the precursor polymer **3**. Coupling reactions utilizing Pd and Cu catalysts between the Boc-protected dibromoquinolinol monomer **1** and 1,4-diethynyl-2,5-dihexadecyloxybenzene (**2**) gave the corresponding polymer as described in Scheme 1. The GPC measurement was carried out for the precursor polymer **3**. The number-average molecular weight was 5600 g/mol and the weight-average molecular weight was 11000 g/mol. The IR spectrum showed absorption peaks at 1766 and 2210 cm^{-1} due to the stretching of the carbonyl group of Boc and the carbon−carbon triple bond in the main-chain, respectively.

For the synthesis of the precursor polymer **4**, Boc group was deprotected using piperidine. The structure of polymer **4** was confirmed by IR and ^{1}H NMR spectra. After the reaction, strong

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10.1021/ma702346j CCC: $40.75

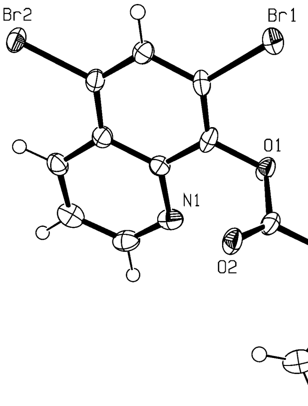


Figure 1. Structure of monomer **1** with thermal ellipsoids drawn to the 50% probability level.

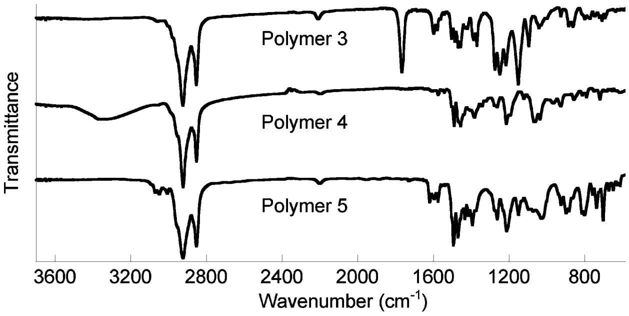
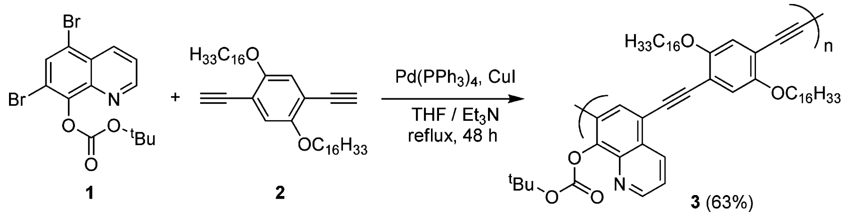


Figure 2. IR spectra of polymers **3**, **4**, and **5**.

absorption peak at 1766 cm^{-1} due to Boc group disappeared completely in the IR spectra (Figure 2). Instead, a broad peak of a hydroxyl group on the quinolinol was emerged at 3366 cm^{-1}. In the ^1H NMR spectrum, a shape peak of the *tert*-butyl group around 1.6 ppm also disappeared. These spectra supported the deprotecting reaction proceeded entirely. The yielded polymer showed good solubility in common organic solvents like chloroform, dichloromethane, and THF. Finally, the reaction between the precursor polymer **4** and triphenylborane was carried out. An excess amount (five equivalents per units) of triphenylborane was used to introduce the diphenylboron group into all quinolinol units. The IR spectrum of polymer **5** showed a complete disappearance of the assignable peak to from hydroxyl groups. On the basis of the integral ratio in the ^1H NMR, the conversion from quinolinol unit to organoboron quinolate was also completely achieved. The ^{11}B NMR was also performed and a broad peak was observed at 8.99 ppm. This value suggested the presence of diphenylboron quinolate structure in polymer **5**. The ^1H NMR spectra of these polymers showed no terminal acetylene peaks. Some small peaks were observed in aromatic region probably due to the quinoline rings in their end groups. However, their degree of polymerization were not determined because of the peaks overlapping. Elemental analyses were also performed for polymers **3**, **4**, and **5**, which were in good agreement with the expected data assuming quinoline end groups. On the basis of the results of elemental analyses, their degree of polymerization were estimated to be ca. 4 using least-squares method. This calculated value was reasonable with the results of GPC measurement.

2.2. Optical Properties. The optical properties of the obtained polymers were investigated by UV−vis absorption and photoluminescence spectroscopies. The results are summarized in Table 1. The absorption spectra of polymers **3** and **4** were almost same (Figure 3). In contrast to that the spectrum of polymer **5** was significantly broadened and red-shifted. This bathochromic shift should be caused by a formation of organoboron quinolate structures. Polymers **3** and **4** showed blue and green fluorescence, respectively (Figure 4). On the other hand, polymer **5** exhibited orange emission. This dramatic bathochromic shift of polymer **5** could be explained by molecular orbitals of qunolate compounds. According to the previous reports for aluminum[15−18] and boron[12,19] quinolates, the HOMO is mainly located on the phenolate side and the LUMO is mainly located on the pyridyl side. Substitution on the phenolate side (i.e., 5,7-

Scheme 1. Synthesis of the Precursor Polymer 3



Scheme 2. Synthesis of the Precursor Polymer 4 and the Organoboron Quinolate Polymer 5

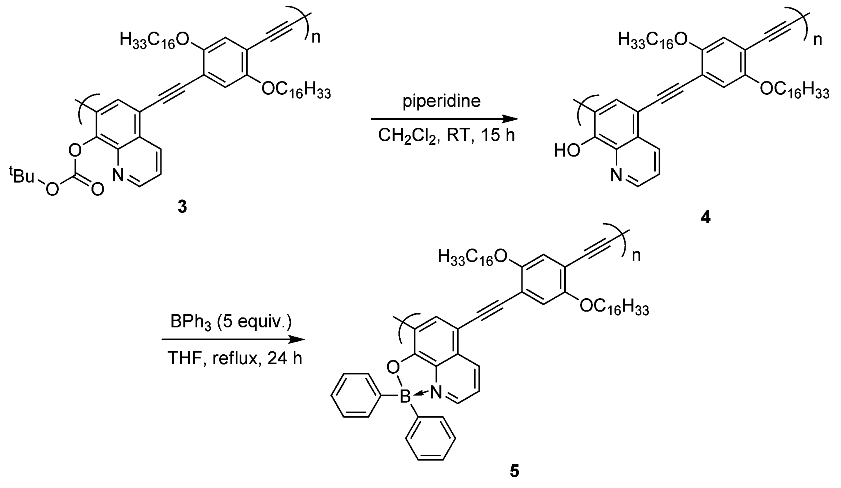


Table 1. Optical Properties of Polymers 3, 4, and 5

compound[a]	UV−vis[b] (λ_{max}, nm)	excitation[c] (λ_{ex}, nm)	emission[c] (λ_{em}, nm)	quantum yield[d] (Φ, %)
polymer **3**	231, 318, 402	400	449	13
polymer **4**	318, 403	397	480	1.8
polymer **5**	283, 319, 398	398	562	0.29
BPh_2q[10]	242, 264, 396	395	504	30

[a] Refer to Scheme 2 for polymer structures. [b] 50 μM solutions in dichloromethane were used. [c] 0.1 μM (polymer **3** and **4**) or 1 μM (polymer **5**) solutions in dichloromethane were used. [d] Relative to 9,10-diphenylanthracene in cyclohexane at room temperature.

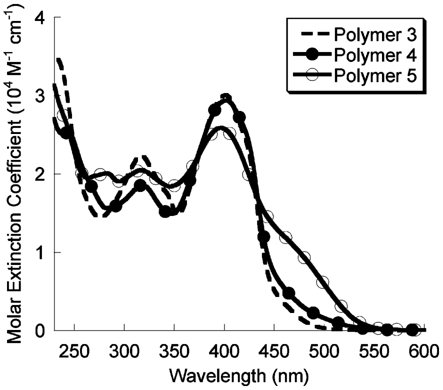


Figure 3. UV−vis absorption spectra of polymers **3**, **4**, and **5** (per units) in dichloromethane at room temperature.

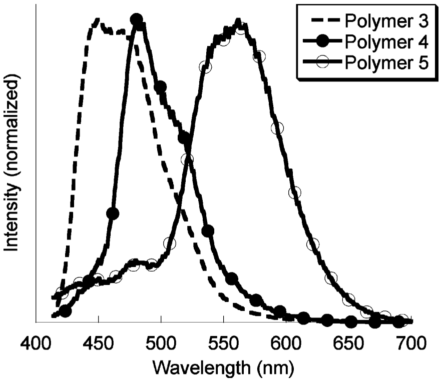


Figure 4. Photoluminescence spectra of polymers **3**, **4**, and **5** in dichloromethane at room temperature.

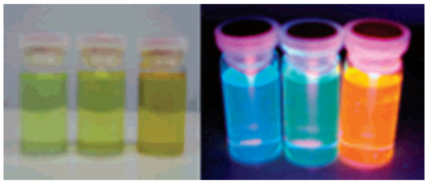


Figure 5. Photographs of dichloromethane solutions of polymers (from left to right, polymer **3**, **4**, and **5**). Left: under ambient light. Right: under UV light at 365 nm.

position) with π -extended aromatic group should lead to elevated HOMO levels and smaller HOMO−LUMO gaps, thus resulting in a red-shift. The quantum yields of the polymers were not remarkable comparing with BPh_2q. However, since the molar extinction coefficient of polymer **5** at the excitation wavelength ($\epsilon = 25\,900$ per units) was eight times higher than non-substituted BPh_2q ($\epsilon = 3200$),[2] the appearance of luminescence was comparable to BPh_2q. From these results, it seemed that the conjugated main-chain acted as a light harvesting antenna for boron quinolate units.

3. Conclusion

The synthesis, characterizations, and optical properties of the main-chain-type organoboron quinolate polymer linked on qunolate ligand were demonstrated. The organoboron quinolate polymer thus obtained showed significantly red-shifted emission. The appearance of luminescence was comparable to BPh_2q in spite of their relatively low quantum yield due to the huge molar extinction coefficient at the excitation wavelength. Further investigations on the relationship between substitutents on comonomers and their luminescent properties will be performed.

4. Experimental Section

General Data. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL JNM-EX400 instrument. The chemical shift values were expressed relative to Me_4Si (^1H and ^{13}C NMR) as an internal standard and $BF_3{\cdot}OEt_2$ (^{11}B NMR) as an external standard. UV−vis spectra were obtained on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8020 (TOSOH TSK-GEL α−3000 column) using THF as an eluent after calibration with standard polystyrenes. Elemental analysis was performed at the Microanalytical Center of Kyoto University. All procedures were performed under argon atmosphere. X-ray diffractions were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR.[20] The analysis was carried out with direct methods (SHELX-97[21] or SIR92[22]) using Yadokari-XG.[23] The program ORTEP3[24] was used to generate the X-ray structural diagrams.

Materials. Tetrahydrofuran (THF) and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 1,4-Diethynyl-2,5-dihexadecyloxybenzene (**2**) was prepared according to the literature.[25] All other reagents were commercially available and used as received.

5,7-Dibromo-8-*tert*-butoxycarbonyloxyquinoline (1). *N*,*N*-Dimethyl-4-aminopyridine (136 mg, 1.12 mmol) was added at room temperature to a stirred suspension of 5,7-dibromoquinolin-8-ol (6.76 g, 22.32 mmol) and di-*tert*-butyl dicarbonate (4.87 g, 22.32 mmol) in hexane (500 mL). The mixture was stirred for 12 h at room temperature, filtered using paper filter and the filtrate was concentrated in vacuum to provide a crude product as yellowish solid. The product was crystallized from 100 mL hexane to yield 7.43 g (83%) of white crystals. ^1H NMR ($CDCl_3$, δ, ppm): 8.93 (1H, dd, *J* = 4.40, 1.46 Hz, Q2-H), 8.41 (1H, dd, *J* = 8.77, 1.46 Hz, Q4-*H*), 8.00 (1H, s, Q5-*H*), 7.51 (1H, dd, *J* = 8.77, 4.40 Hz, Q3-*H*), 1.60 (9H, s, $-^tBu$). ^{13}C NMR ($CDCl_3$, δ, ppm): 151.61, 150.23, 145.08, 142.31, 135.53, 132.85, 127.50, 122.81, 118.94, 116.43, 84.34, 27.50. Anal. Calcd for $C_{14}H_{13}Br_2NO_3$ (mol wt 403.07): C, 41.72; H, 3.25; Br, 39.65; N, 3.48; O, 11.91 Found: C, 41.70; H, 3.31; Br, 39.52; N, 3.49.

Polymer 3. A mixture of 5,7-dibromo-8-*tert*-butoxycarbonyloxyquinoline **1** (1.01 g, 2.50 mmol), 1,4-diethynyl-2,5-dihexadecyloxybenzene **2** (1.52 g, 2.50 mmol), 289 mg of $Pd(PPh_3)_4$, 48 mg of CuI, 50 mL of THF, and 25 mL of Et_3N was placed in a 200 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The reaction mixture was refluxed for 48 h with stirring under argon atmosphere. After the reaction mixture was cooled, the precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and the residue was dissolved in a small amount of $CHCl_3$ and poured into methanol to precipitate the polymer. The resulting polymer was filtered, washed with methanol, and dried in vacuo to give 1.33 g (1.57 mmol, 63%) as an yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 9.03−8.99 (1H, m, Q2-*H*), 8.93−8.87 (1H, m, Q4-*H*), 7.98 (0.3H, s, end group of Q2-*H*), 7.94 (0.3H, s, end group of Q4-*H*), 7.66 (1H, s, Q5-*H*), 7.53 (1H, s, Q3-*H*), 7.20−7.08 (2H, m, Ar−*H*), 4.12 (4H, br s, −OC*H*$_2$−), 1.97 (4H, br s, −OCH$_2$−C*H*$_2$−), 1.63−1.60 (9H, m, −^{t}Bu), 1.41 (4H, br s, −OCH$_2$−CH$_2$−C*H*$_2$−), 1.24 (48H, br s, −C*H*$_2$−), 0.87 (6H, s, −C*H*$_3$). IR (NaCl, λ^{-1}, cm^{-1}): 2924 (s, ν(CH$_2$)), 2853 (s, ν(CH$_2$)), 2210 (m, ν(C≡C)), 1766 (s, ν(C=O)). Anal. Calcd for $C_{239}H_{338}Br_2N_4O_{23}$ (mol wt 3795.06): C, 75.64; H, 8.98; Br, 4.21; N, 1.48; O, 9.70 Found: C, 75.55; H, 9.15; N, 1.56.

Polymer 4. Piperidine (0.24 mL, 1.8 mmol) was added to a stirred solution of polymer **3** (255 mg, 0.30 mmol) in dry dichloromethane (80 mL) at room temperature and the mixture was stirred for 15 h at the same temperature. The reaction mixture was concentrated under vacuum and the residue was washed with 100 mL of boiling methanol repeatedly until the supernatant was clear (3 times). The resulting polymer was filtered and dried in vacuo to give 0.112 g (0.15 mmol, 50%) as an orange powder. ^{1}H NMR (CDCl$_3$, δ, ppm): 8.87 (2H, br s, Q2-*H* and Q4-*H*), 7.88 (1H, br s, Q5-*H*), 7.55 (1H, br s, Q3-*H*), 7.10 (2H, br s, Ar-*H*), 4.12 (4H, br s, −OC*H*$_2$−), 1.96 (4H, br s, −OCH$_2$−C*H*$_2$−), 1.40 (4H, br s, −OCH$_2$−CH$_2$−C*H*$_2$−), 1.23 (48H, br s, −C*H*$_2$−), 0.85 (6H, br s, −C*H*$_3$). IR (NaCl, λ^{-1}, cm^{-1}): 3366 (m, ν(O−H)), 2923 (s, ν(CH$_2$)), 2853 (s, ν(CH$_2$)), 2198 (m, ν(C≡C)). Anal. Calcd for $C_{229}H_{322}Br_2N_4O_{19}$ (mol wt 3594.83): C, 76.51; H, 9.03; Br, 4.45; N, 1.56; O, 8.46 Found: C, 77.41; H, 9.30; N, 1.65.

Polymer 5. Triphenylborane in tetrahydrofuran 0.25 M (2.0 mL, 0.50 mmol) was added to a stirred solution of polymer **4** (75 mg, 0.10 mmol) in dry tetrahydrofuran (200 mL) at room temperature and the mixture was refluxed for 24 h. The reaction mixture was concentrated under vacuum and the residue was dissolved in a small amount of CHCl $_3$ and precipitated into 50 mL of methanol and then precipitated into 50 mL of hexane. The resulting polymer (**3a**) was filtered and dried in vacuo to give 0.30 mg (0.032 mmol, 32%) as an orange powder. ^{1}H NMR (CD$_2$Cl$_2$): 8.91 (1H, br s, Q2-*H*), 8.62 (1H, br s, Q4-*H*), 7.92 (1H, br s, Q3-*H*), 7.70 (1H, br s, Q5-*H*), 7.36−7.32 (4H, m, Ph−*H*), 7.18 (6H, br s, Ph−*H*), 7.10−7.05 (2H, m, Ar−*H*), 4.03 (4H, br s, −OC*H*$_2$−), 1.84 (4H, br s, −OCH$_2$−C*H*$_2$−), 1.30 (4H, br s, −OCH$_2$−CH$_2$−C*H*$_2$−), 1.14 (48H, br s, −C*H*$_2$−), 0.77 (6H, br s, −C*H*$_3$). IR (NaCl, λ^{-1}, cm^{-1}): 3049 (w, ν(Ph−H)), 2923 (s, ν(CH$_2$)), 2853 (s, ν(CH$_2$)), 2200 (m, ν(C≡C)). Anal. Calcd for $C_{253}H_{340}B_2Br_2N_4O_{19}$ (mol wt 3922.85): C, 77.46; H, 8.74; B, 0.55; Br, 4.07; N, 1.43; O, 7.75 Found: C, 78.63; H, 8.78; N, 1.48.

Supporting Information Available: Crystallographic data for monomer **1** in CIF format and figures showing the structures of polymers **3**, **4**, and **5** and the estimation of the degree of polymerization from elemental analyses for polymers **3**, **4** and **5**. This information is available free of charge via the Internet at http://pubs.acs.org.

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MA702346J