# Synthesis of Highly Luminescent Organoboron Polymers Connected by Bifunctional 8-Aminoquinolate Linkers

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**ABSTRACT:** New organoboron aminoquinolate-based polymers linked by  $\pi$ -conjugated bridge were prepared by Sonogashira– Hagihara coupling of organoboron aminoquinolate-based bisiodo monomers bearing biphenyl or bithiophene moiety with 1,4-diethynylbenzene derivatives. Tetracoordination states of boron atoms in the obtained polymers were confirmed by <sup>11</sup>B NMR spectroscopy, and they were also characterized by <sup>1</sup>H NMR and IR spectroscopies and size-exclusion chromatography. Their optical properties were studied by UV–vis absorption and photoluminescence spectroscopies. In the region above 400 nm, the polymers prepared from 1,4-diethynyl-2,5-dioctyloxybenzene showed bathochromic shifts when compared with those prepared from 1.4-diethynyl-2-perfluorooctyl-5-trifluoromethylbenzene. The polymers with biphenyl moiety showed higher absolute fluorescence quantum yields ( $\Phi_F = 0.28$  and 0.65), whereas those with bithiophene moiety led to decreasing of the low quantum yields ( $\Phi_F = 0.19$  and 0.00). The density-functional theory (DFT) and time-dependent–DFT calculations of model compounds corresponding to the polymers were in good agreement with the results from UV–vis properties. The calculations revealed that the electronic structure of the polymer with bithiophene moiety is different from that with biphenyl moiety, and predicted the electron transfer from the bithiophene moiety to the  $\pi$ -extended quinoline moiety in transition state. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3693–3701, 2010

**KEYWORDS:** fluorescence; heteroatom-containing polymer; polycondensation

**INTRODUCTION** For a few decades, conjugated polymers have received much attention because of their extensive applications to electronic and photonic devices such as polymeric light-emitting diodes,<sup>1</sup> plastic lasers,<sup>2</sup> nonlinear optical materials,3 and polymer-based photovoltaic cells.4 The polymers have an advantage of low cost device fabrication via solution processing methods, including dip coating, spin casting, and ink-jet printing, when compared with inorganic or low molecular weight counterparts.<sup>5</sup> To control the physical properties of conjugated polymers from the view point of the molecular scale, various aromatic moieties and side chains have been incorporated into them.<sup>6-8</sup> One of the interesting approaches is an introduction of functional dyes into the conjugated polymer backbone.9-12 This method allows for increasing not only of the diversity of emission maxima available in the dyes, which were incorporated into the conjugated linkers, but also of stability of the dyes.

Many fluorescent organoboron dyes have been used as chemical probes, photosensitizers, and optical sensing due to high emission quantum yields.<sup>13–15</sup> Among them, organoboron quinolates such as 8-hydroxyquinoline biphenylboron  $(BPh_2q)^{16}$  turned out to be attractive as an alternative to tris(8-hydroxyquinoline)aluminum  $(Alq_3)^{17}$  for organic light-emitting diodes because of their good thermal stabilities and

the high emission quantum yields. They showed, however, lower molar absorption coefficient corresponding to the HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) transition relative to typical  $\pi$ conjugated molecules. This weak point has been improved by the synthesis of organoboron quinolate-containing conjugated polymers, in which *p*-phenylene-ethynylene units were embedded to boron atoms in the polymer backbones.18,19 These polymers gave strong green fluorescence, and an efficient energy migration from conjugated linkers with high molar absorption coefficient to boron quinolate moieties was observed. However, the linkage between boron atom and two p-phenylene-ethynylene moieties in the polymers prevented the phenylene-ethynylene linkers from  $\pi$ -conjugating to boron quinolate cores. Therefore, these polymers did not obviously change the absorption and emission maxima of boron quinolate moiety. Generally, the control of absorption and emission wavelength is as important as improvement of the molar absorption coefficient toward the application of actual device fabrication. Embedding the quinolato ligands in various main chains of conjugated polymers accomplished the efficient control by through-bond interaction between quinolato moiety and  $\pi$ -conjugated bridge. There are two types of polymer architecture fit for that qualification: (i)

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both the boron centers and the quinolato ligands are embedded in the main chain<sup>20</sup> and (ii) quinolate group is part of the polymer backbone with diphenylboron moieties as a pendant group.<sup>21</sup> The majority of polymers prepared by this procedure represented less emission quantum yield than BPh<sub>2</sub>q. However, we have previously reported organoboron 8-aminoquinolate–connected polymers with red-shifts of the emission maxima and higher absolute quantum yields when compared with BPh<sub>2</sub>q.<sup>22</sup> Herein, we report the synthesis and characterization of novel organoboron 8-aminoquinolate– connected polymers and discuss the relationship between the optical property and the structure of the polymer backbone in detail.

## **EXPERIMENTAL**

#### **General Procedures**

<sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), and <sup>11</sup>B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra used tetramethylsilane as an internal standard, <sup>11</sup>B NMR spectra were referenced externally to BF<sub>3</sub>OEt<sub>2</sub> (sealed capillary) in CDCl<sub>3</sub>. The number-average molecular weights  $(M_n)$  and molecular weight distribution [weight-average molecular weight/number-average molecular weight  $(M_w/M_n)$ ] values of all polymers were estimated by size-exclusion chromatography (SEC) with a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns [TOSOH gels:  $\alpha$ -4000,  $\alpha$ -3000, and  $\alpha$ -2500] and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with tetrahydrofuran (THF) as an eluent. Polystyrene standards were employed for calibration. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. FTIR spectra were obtained using a SHIMADZU IRPrestige-21 infrared spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University. All reactions were performed under nitrogen or argon atmosphere.

High-resolution mass spectra (HRMS) were obtained on a JEOL JMSSX102A spectrometer for electron ionization (EI) method and on a JEOL JMSHX110A for fast atom bombardment (FAB) method.

## **Preparation of the Compounds**

5-Iodo-8-aminoquinoline,<sup>22</sup> 4,4'-bis(dibromoboryl)biphenyl,<sup>23</sup> 2,2'-bis(dibromoboryl)bithiophene,<sup>23</sup> 1,4-diethynyl-2,5-dioctyloxybenzene,<sup>24</sup> and 1.4-diethynyl-2-perfluorooctyl-5-trifluoromethylbenzene<sup>25</sup> were prepared according to the literature. THF and triethylamine (Et<sub>3</sub>N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). Other reagents were commercially available and used as received.

# N-(5-Iodo-8-quinolyl)undecanamide (2)

5-Iodo-8-aminoquinoline (5.40 g, 20.0 mmol) and undecanoyl chloride (4.62 mL, 21.0 mmol) were dissolved in dichloromethane (90 mL), followed by addition of triethylamine (2.93 mL, 21.0 mmol). The resulting mixture was <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.81 (s, 1H, --N*H*--CO--), 8.77 (d, *J* = 4.1 Hz, 1H, Ar-*H*), 8.57 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 8.37 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 8.07 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 7.53 (dd, *J* = 8.3, 4.2 Hz, 1H, Ar-*H*), 2.55 (t, *J* = 7.6 Hz, 2H, --CO--CH<sub>2</sub>--), 1.81 (m, 2H, CO--CH<sub>2</sub>--CH<sub>2</sub>--), 1.43-1.26 (m, 14H, --CH<sub>2</sub>--), 0.87 (t, *J* = 6.6 Hz, 1H, --CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 7.13 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 171.98 (>*C*=-0), 148.64 (Ar), 140.72 (Ar), 138.94 (Ar), 138.30 (Ar), 135.47 (Ar), 129.55 (Ar), 123.09 (Ar), 117.76 (Ar), 88.98 (Ar-I), 38.28, 31.87, 29.56, 29.48, 29.38, 29.27, 25.57, 22.66.

## 4,4'-Bis(phenylbromoboryl)-biphenyl (3P)

Trimethyl(phenyl)tin (4.78 mL, 26.3 mmol) was added to a solution of 4,4'-bis(dibromoboryl)biphenyl (6.49 g, 13.2 mmol) in toluene (263 mL), and the mixture was stirred for 14 h. All volatile components were removed under a high vacuum, and the solid was washed with hexane to give a crude product (3.96 g), which was used without further purification.

## Monomer (4P)

The crude product **3P** (0.746 g), *N*-(5-iodo-8-quinolyl)undecanamide (1.75 g, 4.00 mmol), and triethylamine (0.43 mL, 3.1 mmol) were dissolved in toluene (30 mL). After the reaction mixture was refluxed for 12 h, the solvent was removed by rotary evaporation. The residue was treated with water, followed by extraction with diethyl ether, drying over MgSO<sub>4</sub>, and removal of the solvent under vacuum. The crude products were purified by silica gel (neutral) column chromatography eluted with hexane/dichloromethane. Recrystallization from hexane/dichloromethane gave a yellow solid in 50% yield (0.918 g, 0.763 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.77$  (d, I = 8.3 Hz, 2H, Ar-H), 8.47 (m, 4H, Ar-H), 8.23 (d, J = 8.3 Hz, 1H, Ar-H), 7.63 (dd, J = 8.4, 5.3 Hz, 2H, Ar-H), 7.52-7.44 (m, 12H, Ar-H), 7.28-7.25 (m, 6H, Ar-H), 2.18 (t, J = 7.6 Hz, 4H, -CO-CH<sub>2</sub>-), 1.23 (br, 8H, --CH<sub>2</sub>--), 1.15 (br, 8H, --CH<sub>2</sub>--), 1.09 (br, 8H, --CH<sub>2</sub>--), 0.96 (br, 8H, --CH<sub>2</sub>--), 0.83 (m, 6H, --CH<sub>3</sub>) ppm. <sup>11</sup>B NMR  $(CDCl_3): \delta = 6.74 \text{ ppm.}^{13}C \text{ NMR} (CDCl_3): \delta = 177.48$ (>C=0), 143.16 (Ar), 142.91 (Ar), 142.61 (Ar), 140.18 (Ar), 139.91 (Ar), 138.30 (Ar), 133.84 (Ar), 133.40 (Ar), 129.61 (Ar), 127.87 (Ar), 127.25 (Ar), 126.39 (Ar), 123.58 (Ar), 120.21 (Ar), 81.71 (Ar-I), 38.45 (-CO-CH2-), 31.84, 29.49, 29.38, 29.32, 29.24, 29.08, 25.20, 22.65, 14.11 (-CH<sub>3</sub>). IR (KBr): v = 3069, 3048, 3013, 2926, 2855, 1647 (C=0), 1574 (Ar-H), 1503, 1462, 1433, 1387, 1308, 1207, 1190, 1148, 1107, 1057, 1043, 1003, 961, 878, 841, 818, 781, 739, 708, 665, 644 cm<sup>-1</sup>. HRMS (FAB+): m/z: Calcd. for C<sub>60</sub>H<sub>70</sub>B<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: 1202.3774; found: 1202.3813 [M]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>70</sub>B<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.91; H, 5.87; N, 4.66. Found: C, 63.47; H, 5.81; N, 4.60.

# 2,2'-Bis(phenylbromoboryl)-5,5'-bithiophene (3T)

A solution of 2,2'-bis(dibromoboryl)-5,5'-bithiophene (1.50 g, 3.00 mmol) in toluene (90 mL) was cooled to -78 °C and then trimethyl(phenyl)tin was added. The reaction mixture was slowly allowed to warm up to room temperature and left stirring for 16 h. All volatile components were removed under a high vacuum, and the solid was washed with CH<sub>2</sub>Cl<sub>2</sub> and hexane to give a crude product (1.08 g), which was used without further purification.

# Monomer (4T)

The crude product **3T** (0.750 g), *N*-(5-iodo-8-quinolyl)undecanamide (1.45 g, 3.30 mmol), and triethylamine (0.42 mL, 3.0 mmol) were dissolved in toluene (30 mL). After the reaction mixture was refluxed for 12 h, water was added, followed by extraction with ethyl ether, drying over MgSO<sub>4</sub>, and removal of the solvent under vacuum. The crude products were purified by silica gel (neutral) column chromatography eluted with dichloromethane. Recrystallization from hexane/ dichloromethane gave a yellow solid in 47% yield (0.856 g, 0.705 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.73$  (dd, I = 8.3, 4.2 Hz, 2H, Ar-H), 8.49 (d, J = 8.3 Hz, 2H, Ar-H), 8.42 (d, J = 4.9 Hz, 2H, Ar-H), 8.23 (dd, J = 8.4, 3.1 Hz, 2H, Ar-H), 7.64 (m, 2H, Ar-H), 7.54 (d, J = 3.9 Hz, 4H, Ar-H), 7.26 (m, 6H, Ar-H), 7.08 (m, 4H, Ar-H), 2.26 (m, 4H, -CO-CH<sub>2</sub>-), 1.35-0.98 (br, 32H, -CH<sub>2</sub>-), 0.85 (m, 6H, -CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 4.40 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 177.31$  (>C=0), 143.37 (Ar), 142.57 (Ar), 142.41 (Ar), 140.63 (Ar), 130.18 (Ar), 137.73 (Ar), 133.02 (Ar), 132.81 (Ar), 132.49 (Ar), 132.24 (Ar), 129.61 (Ar), 127.95 (Ar), 127.61 (Ar), 124.18 (Ar), 123.94 (Ar), 123.66 (Ar), 123.45 (Ar), 120.22 (Ar), 81.93 (Ar-I), 38.27 (-CO-CH<sub>2</sub>-), 31.85, 29.48, 29.36, 29.25, 29.07, 25.18, 22.65, 14.12 (-*C*H<sub>3</sub>). IR (KBr): v = 3071, 3049, 3005, 2924, 2852, 1653 (C=O), 1591, 1574 (Ar-H), 1501, 1460, 1433, 1412, 1387, 1371, 1308, 1283, 1211, 1148, 1103, 1057, 1043, 961, 885, 841, 804, 781, 725, 706, 669, 648 cm<sup>-1</sup>. HRMS (FAB+): m/z: Calcd. for C<sub>60</sub>H<sub>60</sub>B<sub>2</sub>I<sub>2</sub>N<sub>6</sub>O<sub>4</sub>: 1214.2903; found: 1214.2869 [M]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>66</sub>B<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 59.32; H, 5.48; N, 4.61. Found: C, 59.12; H, 5.35; N, 4.53.

# Polymer (6PO)

A typical procedure is shown as follows: triethylamine (0.70 mL) was added to a solution of 4 (0.168 g, 0.14 mmol), 1,4diethynyl-2,5-dioctyloxybenzene (0.054 g, 0.140 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (8.10 mg, 7.00  $\mu$ mol), CuI (1.30 mg, 7.00  $\mu$ mol) in THF (1.40 mL) at room temperature. After the mixture was stirred at 40 °C for 48 h, a small amount of CHCl<sub>3</sub> was added and poured into a large excess of methanol to precipitate the polymer. The polymer was purified by repeated precipitations from a small amount of CHCl<sub>3</sub> into a large excess of methanol and hexane, respectively, to give a red solid in 91% yield (0.169 g, 0.127 mmol);  $M_n = 34,000$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.96$  (4H, Ar-*H*), 8.49 (2H, Ar-*H*), 8.00 (2H, Ar-H), 7.59 (2H, Ar-*H*), 7.51 (12H, Ar-H), 7.28 (4H, Ar-*H*), 7.24 (2H, Ar-*H*), 7.09 (2H, Ar-*H*), 4.10 (4H,  $-0CH_2-$ ), 2.21 (4H,  $-CO-CH_2-$ ), 1.90 (4H,  $-CH_2-$ ), 1.53 (4H,

-CH<sub>2</sub>—), 1.34 (4H, -CH<sub>2</sub>—), 1.22-1.08 (36H, -CH<sub>2</sub>—), 0.96 (8H, -CH<sub>2</sub>—), 0.81 (12H, -CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 2.93 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 177.57 (>C=0), 153.62 (Ar), 142.28 (Ar), 139.92 (Ar), 137.60 (Ar), 133.94 (Ar), 133.44 (Ar), 128.21 (Ar), 127.87 (Ar), 127.25 (Ar), 126.39 (Ar), 122.73 (Ar), 118.44 (Ar), 115.69 (Ar), 113.48 (Ar), 111.33 (Ar), 91.51 (-C=C—), 91.13 (-C=C—), 69.32 (-OCH<sub>2</sub>—), 38.53 (-CO-CH<sub>2</sub>—), 31.87, 31.74, 29.51, 29.40, 29.25, 26.02, 25.28, 22.66, 22.60, 14.12 (-CH<sub>3</sub>), 14.06 (-CH<sub>3</sub>) ppm. IR (KBr):  $\nu$  = 3069, 3049, 3010, 2930, 2909, 2845, 2197 (C=C), 1653 (C=0), 1570 (Ar-H), 1499, 1476, 1431, 1395, 1373, 1310, 1273, 1215, 1190, 1144, 1067, 1001, 876, 847, 818, 783, 737, 706, 683, 654 cm<sup>-1</sup>. Anal. Calcd. for C<sub>90</sub>H<sub>106</sub>B<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C, 81.31; H, 8.04; N, 4.21. Found: C, 79.38; H, 7.98; N, 4.03.

# Polymer (6PF)

Similarly to the preparation of **6PO**, polymer **6PF** was prepared from monomer **4P** (0.144 g, 0.120 mmol) and 1.4diethynyl-2-perfluorooctyl-5-trifluoromethylbenzene (0.0735 g, 0.120 mmol) in 85% yield as a yellow solid;  $M_{\rm n} = 15,400$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.98$  (2H, Ar-*H*), 8.80 (2H, Ar-*H*), 8.52 (2H, Ar-H), 8.09 (3H, Ar-*H*), 7.98 (1H, Ar-H), 7.71 (1H, Ar-*H*), 7.64 (1H, Ar-*H*), 7.52 (12H, Ar-*H*), 7.28 (4H, Ar-H), 7.24 (1H, Ar-H), 7.09 (1H, Ar-*H*), 2.22 (4H,  $-\text{CO}-\text{CH}_2-$ ), 1.24–1.08 (24H,  $-\text{CH}_2-$ ), 0.96 (8H,  $-\text{CH}_2-$ ), 0.83 (6H,  $-\text{CH}_3$ ) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta = 5.18$  ppm. IR (KBr): v = 3071, 3049, 3011, 2928, 2855, 2203 (C=C), 1663 (C=O), 1614, 1572 (Ar-H), 1499, 1476, 1433, 1395, 1379, 1310, 1240, 1213, 1202, 1148, 1117, 1088, 1053, 1016, 1003, 978, 878, 851, 820, 783, 737, 706, 677, 656 cm<sup>-1</sup>. Anal. Calcd. for C<sub>83</sub>H<sub>72</sub>B<sub>2</sub>F<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.94; H, 4.65; N, 3.59. Found: C, 63.13; H, 4.62; N, 3.56.

# Polymer (6TO)

Similarly to the preparation of **6PO**, polymer **6TO** was prepared from monomer **4T** (0.122 g, 0.100 mmol) and 1,4-diethynyl-2,5-dioctyloxybenzene (0.0383 g, 0.100 mmol) in 88% yield as a red solid;  $M_{\rm n} = 27,900$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.98 (2H, Ar-*H*), 8.80 (2H, Ar-*H*), 8.52 (2H, Ar-H), 8.09 (3H, Ar-H), 7.98 (1H, Ar-H), 7.71 (1H, Ar-H), 7.64 (1H, Ar-H), 7.52 (12H, Ar-H), 7.28 (4H, Ar-H), 7.24 (1H, Ar-H), 7.09 (1H, Ar-H), 2.22 (4H, -CO-CH2-), 1.24-1.08 (24H, --CH<sub>2</sub>--), 0.96 (8H, --CH<sub>2</sub>--), 0.83 (6H, --CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta = 2.15$  ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta =$ 177.40 (>C=0), 153.63 (Ar), 148.21 (Ar), 145.55 (Ar), 141.81 (Ar), 140.50 (Ar), 140.24 (Ar), 139.09 (Ar), 137.08 (Ar), 135.93 (Ar), 134.55 (Ar), 132.97 (Ar), 132.39 (Ar), 128.22 (Ar), 127.96 (Ar), 127.61 (Ar), 124.14 (Ar), 122.71 (Ar), 118.45 (Ar), 115.75 (Ar), 113.50 (Ar), 111.52 (Ar), 91.61 (-C≡C-), 91.04 (-C≡C-), 69.33 (-OCH<sub>2</sub>-), 38.36  $(-CO-CH_2-)$ , 31.88, 31.74, 29.58, 29.51, 29.40, 29.32, 29.26, 29.11, 26.02, 25.26, 22.68, 22.60, 14.14 (-CH<sub>3</sub>), 14.07  $(-CH_3)$ . IR (KBr): v = 3070, 3051, 3005, 2924, 2853, 2199(C≡C), 1653 (C=O), 1570 (Ar-H), 1499, 1468, 1431, 1395, 1375, 1312, 1271, 1217, 1190, 1146, 1113, 1067, 1051, 1024, 912, 885, 849, 804, 783, 758, 739, 704, 655 cm<sup>-1</sup>.



Anal. Calcd. for  $C_{86}H_{102}B_2N_4O_4S_2$ : C, 77.00; H, 7.66; N, 4.18. Found: C, 75.67; H, 7.41; N, 4.00.

## Polymer (6TF)

Similarly to the preparation of **6PO**, polymer **6TF** was prepared from monomer **4T** (0.146 g, 0.120 mmol) and 1.4diethynyl-2-perfluorooctyl-5-trifluoromethylbenzene (0.0735 g, 0.120 mmol) in 89% yield as a yellow solid;  $M_n = 12,600$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.94$  (2H, Ar-*H*), 8.83–8.74 (2H, Ar-*H*), 8.49 (2H, Ar-H), 8.11–7.98 (4H, Ar-*H*), 7.72–7.55 (6H, Ar-H), 7.28 (6H, Ar-H), 7.10 (4H, Ar-H), 2.30 (4H,  $-CO-CH_2-$ ), 1.16–1.10 (24H,  $-CH_2-$ ), 1.00 (8H,  $-CH_2-$ ), 0.84 (6H,  $-CH_3$ ) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta = 3.52$  ppm. IR (KBr): v =3073, 3051, 2926, 2855, 2203 (C=C), 1663 (C=O), 1570 (Ar-H), 1501, 1474, 1433, 1395, 1379, 1312, 1240, 1213, 1200, 1170, 1146, 1117, 1070, 1053, 910, 851, 810, 783, 743, 704, 656 cm<sup>-1</sup>. Anal. Calcd. for C<sub>83</sub>H<sub>72</sub>B<sub>2</sub>F<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.94; H, 4.65; N, 3.59. Found: C, 63.13; H, 4.62; N, 3.56.

# *N*-(5-Iodo-8-quinolyl)-*N*-(diphenylboryl)undecanamide (7) Triphenylborane (0.969 g, 4.00 mmol) and *N*-(8-quinolyl)undecanamide (1.75 g, 4.00 mmol) were dissolved in toluene (24 mL). After the reaction mixture was refluxed for 12 h,

the solvent was removed under vacuum. The crude product was purified by precipitation from a small amount of  $CH_2Cl_2$  into a large excess of hexane, followed by precipitation from a small amount of  $CHCl_3$  into a large excess of methanol to give a yellow solid in 57% yield (1.37 g, 2.27 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.76 (d, J = 8.4 Hz, 1H, Ar-H), 8.48 (d, J = 8.4 Hz, 1H, Ar-H), 8.44 (d, J = 4.8 Hz, 1H, Ar-H), 8.23 (d, J = 8.4 Hz, 1H, Ar-H), 7.63 (dd, J = 8.4, 5.2 Hz, 1H, Ar-H), 7.45 (m, 4H, Ar-H), 7.29–7.25 (m, 6H, Ar-H), 2.16 (t, J = 7.6 Hz, 2H,  $-CO-CH_2-$ ), 1.26–1.09 (m, 12H,  $-CH_2-$ ), 0.96 (m, 4H,  $-CH_2-$ ), 0.87 (t, J = 8.0 Hz,  $-CH_3$ ) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 6.45 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 177.47 (>C=0), 143.12 (Ar), 142.94 (Ar), 142.59 (Ar), 140.15 (Ar), 138.30 (Ar), 133.41 (Ar), 129.58 (Ar), 127.84 (Ar), 127.21

SCHEME 1 Synthesis of ligand 2.

(Ar), 123.55 (Ar), 120.19 (Ar), 81.65 (Ar-I), 38.41 (-CO- $CH_2$ -), 31.88, 29.50, 29.37, 29.27, 29.03, 25.16, 22.66, 14.11 (- $CH_3$ ) ppm. IR (KBr):  $\nu$  = 3071, 3048, 3005, 2924, 2853, 1645 (C=O), 1576 (Ar-H), 1504, 1460, 1433, 1412, 1387, 1368, 1337, 1308, 1227, 1209, 1190, 1146, 1113, 1055, 1043, 961, 895, 878, 835, 781, 741, 704, 642 cm<sup>-1</sup>. HRMS (EI): m/z: Calcd. for C<sub>32</sub>H<sub>36</sub>BIN<sub>2</sub>O: 602.1965; found: 602.1955 [M]<sup>+</sup>. Anal. Calcd. for C<sub>32</sub>H<sub>36</sub>BIN<sub>2</sub>O: C, 63.81; H, 6.02; N, 4.65. Found: C, 63.63; H, 5.98; N, 4.69.

## Model Compound (8)

Triethylamine (2.0 mL) was added to a solution of *N*-(5-iodo-8-quinolyl)-*N*-(diphenylboryl)undecanamide (0.482 g, 0.800 mmol), 1,4-diethynyl-2,5-dioctyloxybenzene (0.153 g, 0.400 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (23.1 mg, 20.0  $\mu$ mol), CuI (3.80 mg, 20.0  $\mu$ mol) in THF (4.0 mL) at room temperature. After the mixture was stirred at 40 °C for 24 h, the solvent was removed under vacuum. The crude was precipitated from a small amount of CHCl<sub>3</sub> into a large excess of methanol twice. The precipitate was purified by recrystallization from hexane/dichloromethane to give a red solid in 68% (0.359 g, 0.273 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.01 (d, J = 8.4 Hz, 2H, Ar-H), 8.95 (d, J = 8.0 Hz, 2H, Ar-H), 8.48 (d, J = 4.4 Hz, 2H, Ar-H), 8.00 (d, J = 8.4 Hz, 2H, Ar-H), 7.61 (dd, J = 8.0, 5.6 Hz, 2H, Ar-H), 7.49 (m, 8H, Ar-H), 7.29 (m, 10H, Ar-H), 7.10 (s, 2H, Ar-H), 4.11 (t, J = 6.8 Hz, 4H,  $-\text{OCH}_2-$ ), 2.19 (t, J = 7.6 Hz, 4H,  $-\text{CO}-\text{CH}_2-$ ), 1.93 (m, 4H,  $-\text{CH}_2-$ ), 1.53 (m, 4H,  $-\text{CH}_2-$ ), 1.36 (m, 4H,  $-\text{CH}_2-$ ), 1.23–1.12 (m, 36H,  $-\text{CH}_2-$ ), 0.97 (m, 8H,  $-\text{CH}_2-$ ), 0.87 (t, J = 7.2 Hz, 12H,  $-\text{CH}_3$ ), 0.82 (t, J = 6.8 Hz, 6H,  $-\text{CH}_3$ ) ppm. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 6.26 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 177.56 (>C=0), 153.64 (Ar), 142.33 (Ar), 140.05 (Ar), 138.78 (Ar), 137.60 (Ar), 135.93 (Ar), 133.46 (Ar), 128.19 (Ar), 127.84 (Ar), 127.19 (Ar), 122.72 (Ar), 118.38 (Ar), 115.80 (Ar), 113.54 (Ar), 111.28 (Ar), 91.47 (-C=C-), 91.11 (-C=C-), 69.37 ( $-\text{OCH}_2-$ ), 38.48 ( $-\text{CO}-\text{CH}_2-$ ), 31.89, 31.73, 29.57, 29.51, 29.40, 29.28,



**SCHEME 2** Synthesis of monomers.



SCHEME 3 Synthesis of polymers.

29.24, 29.06, 26.03, 25.23, 22.67, 22.58, 14.11 ( $-CH_3$ ), 14.03 ( $-CH_3$ ) ppm. IR (KBr):  $\nu = 3071$ , 3049, 3005, 2924, 2853, 2201 ( $-C\equiv C-$ ), 1653 (C=O), 1570 (Ar-H), 1499, 1476, 1429, 1395, 1377, 1312, 1275, 1217, 1190, 1144, 1051, 877, 847, 820, 785, 760, 739, 704, 644 cm<sup>-1</sup>. HRMS (FAB+): m/z: Calcd. for C<sub>90</sub>H<sub>108</sub>B<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: 1330.8557; found: 1330.8547 [M]<sup>+</sup>. Anal. Calcd. for C<sub>90</sub>H<sub>108</sub>B<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C, 81.19; H, 8.18; N, 4.21. Found: C, 81.12; H, 8.18; N, 4.23.

#### **RESULTS AND DISCUSSION**

## Synthesis

Initially, the ligand N-(5-iodo-8-quinolyl)undecanamide (2) was synthesized from 8-aminoquinoline as a starting compound according to Scheme 1. The other precursors for organoboron monomers, 4,4'-bis(phenylbromoboryl)biphenyl 3P and bithiophene 3T were obtained via tin-boron exchange from 4,4'-bis(dibromoboryl)biphenyl<sup>23</sup> and 2,2'-bis(dibromoboryl)thiophene<sup>23</sup> on reaction with trimethyl(phenyl)tin. **3P** and **3T** were not absolutely purified due to their high reactivities. The reaction of these bis(phehylbromoboryl)-functionalized compounds with the ligand 2 produced organoboron aminoquinolate-based monomers 4P and 4T bearing bisiodo groups as yellow powders (Scheme 2). These monomers possess good solubility in various organic solvents due to the long alkyl chains attached by amide linkages. The tetracoordination state of the boron atoms in 4P and 4T was confirmed by the <sup>11</sup>B NMR spectroscopy in  $\text{CDCl}_3$  [**4P**:  $\delta_{\text{B}} =$ 6.74 ppm, **4T**:  $\delta_{\rm B}$  = 4.40 ppm]. Strong electron-donating nature of the bithiophene unit moved chemical shift  $\delta_B$  of  $\mathbf{4T}$ 

**TABLE 1** Polymerization Results

Polymer	Yield <sup>a</sup> (%)	$M_{n}^{b}$	$M_{\rm w}{}^{\rm b}$	$M_{\rm w}/M_{\rm n}^{\rm b}$	DPc
6PO	91	34,000	100,300	3.0	25.6
6PF	85	15,400	29,800	1.9	9.9
6TO	88	28,000	102,000	3.7	20.9
6TF	89	12,600	23,200	1.8	8.0

<sup>a</sup> Isolated yields after reprecipitation.

<sup>b</sup> Estimated by SEC based on polystyrene standards in THF.

<sup>c</sup> Degree of polymerization estimated by number-average molecular weight.

to the upfield relative to that of 4P. The basic structures of 4P and 4T were also characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, ELEM ANAL, and mass spectroscopies. Connecting of the aminoquinolate generates a stereogenic center at boron. However, the stereoconformation might be not significantly responsible for emission behavior, so that the stereoisomers were not separated here.<sup>20,26</sup> Sonogashira-Hagihara coupling polymerizations of 4P or 4T were conducted with 1,4-diethynyl-2,5-dioctyloxybenzene<sup>24</sup> or 1,4-diethynyl-2-(perfluorooctyl)-5-(trifluoromethyl)benzene<sup>25</sup> in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI in the mixed solvent of THF and triethylamine (Et<sub>3</sub>N) at 40 °C for 48 h (Scheme 3). The obtained polymers 6PO and 6TO were collected as red solids, while 6PF and 6TF were collected as yellow solids. The polymers were soluble in THF, CH2Cl2, and CHCl3. The <sup>11</sup>B NMR spectra of the obtained polymers were observed at  $\delta_{\rm B} = 5.18$ –2.15 ppm assignable to the tetracoordination state of the boron atoms in each polymer, indicating that the polymerization proceeded without any damage to the structure in the organoboron quinolate moiety. The IR spectra of the polymers showed the weak absorption peaks at 2203-2197 cm<sup>-1</sup> and the strong absorption peaks at 1663-1653 cm<sup>-1</sup>, which are attributable to stretching of the C=C bond and the C=O



SCHEME 4 Synthesis of model 8.

SYNTHESIS OF LUMINESCENT ORGANOBORON POLYMERS, TOKORO, NAGAI, AND CHUJO



FIGURE 1 UV–Vis spectra of polymers and model compounds in CHCl<sub>3</sub> (1.0  $\times$  10 $^{-5}$  M).

bond, respectively. Table 1 summarizes the polymerization results. The number-average molecular weights  $(M_n)$  and the molecular weight distributions  $(M_w/M_n)$  of the polymers, measured by SEC in THF toward polystyrene standards, were 12,600-34,000 and 1.4-3.0, respectively. The low reactivity of the monomer 5F with electronegative substituent for Sonogashira-Hagihara coupling resulted in the low molecular weight polymers 6PF and 6TF when compared with the polymers 6PO and 6TO. To evaluate the optical properties of the polymers, a model compound (8) for the polymer 6PO was also prepared from boron aminoquinolate bearing mono-iodo group (7) and 1,4-diethynyl-2,5-dioctyloxybenzene under the similar condition to the polymerization (Scheme 4). After the purification by the reprecipitation, the model compound 8 was collected as a solid, which is similar color to the polymer 6PO.

## **Optical Properties**

The optical properties of the obtained polymers and the model compound were investigated by UV-vis absorption



FIGURE 2 Normalized emission spectra of polymers and model compounds in CHCl<sub>3</sub> (1.0  $\times$  10<sup>-5</sup> M).



FIGURE 3 UV-Vis spectra of polymers and model compounds in film state.

and photoluminescence experiments. Figure 1 illustrates UVvis absorption spectra of the polymers and the model compound in CHCl<sub>3</sub> solution ( $c = 1.0 \times 10^{-5}$  M). The spectra of the polymer 6PO and its model compound 8 overlapped in the region of the wavelength between 300 and 550 nm, obviously indicating that the polymer 6PO consists of the scaffold of the model compound 8, and their absorption bands in this region were probably assigned to the absorption of the unit composed of two quinoline rings and diethynylbenzene (qAr<sub>2</sub>q unit). In the region of the wavelength above 400 nm, the polymers having the same side chain at  $Ar_2$  give the same absorption peaks. The absorption bands of the polymers with octyloxy group (6PO and 6TO) were bathochromically shifted in comparison with those of the polymers with perfluoroalkyl group (6PF and 6TF). This would mean that the absorption maximum of the polymer with any Ar<sub>1</sub> unit depends on Ar<sub>2</sub> unit, i.e., the diethynyl-functionalized monomer in Scheme 3, and the bathochromic shift is related to the electron-donating nature of Ar<sub>2</sub> unit in that region. All the polymers and the model compounds strongly absorb the visible light at longer wavelength in comparison with typical organoboron quinolates and aminoquinolates, meaning



FIGURE 4 Normalized emission spectra of polymers and model compounds in film state.

Compound	$\lambda_{abs,max}$ (nm) <sup>a</sup>	$\varepsilon (M^{-1} \ cm^{-1})^{b}$	Ex (nm) <sup>c</sup>	$\lambda_{em,max} \; (nm)^{d}$	$\Phi_{\rm F}{}^{\rm e}$
6PO	272, 356, 376, 471	35,800	471	555	0.28
6PF	273, 389, 457	53,800	457	519	0.65
6ТО	263, 353, 471	33,900	471	558	0.19
6TF	271, 331, 388, 455	54,000	455	531	0.00
8	268, 356, 376, 470	35,200	470	550	0.29

TABLE 2 UV–Vis Absorption and Photoluminescence Properties in Solution State

 $^{a}$  Absorption maxima:  $CHCl_{3}$  (1.0  $\times$  10  $^{-5}$  M).

<sup>b</sup> Molar extinction coefficients at the longest absorption maxima.

<sup>c</sup> Excited wavelength.

coplanarity and extended  $\pi$ -conjugation of quinoline rings through Ar<sub>2</sub> unit.

Emission spectra of the polymers and the model compound in CHCl<sub>3</sub> solution ( $c = 1.0 \times 10^{-5}$  M) are represented in Figure 2. All the emission data given here were obtained after exciting at the longest wavelength of the absorption peaks, i.e., absorption maxima corresponding to qAr<sub>2</sub>q unit. The emission bands of the polymers with octyloxy group (6P0 and 6TO) were red-shifted in comparison with those with perfluoroalkyl group (6PF and 6TF). Moreover, the spectrum of the polymer 6PO coincided with that of the model compound (8). Based on these results, it can be concluded that the polymers emit the light from qAr2q unit, and its wavelength is mainly controlled by electron-donating Ar<sub>2</sub> unit like the visible light absorption of the polymers. In the case that the polymers have the same Ar<sub>2</sub> group, the emission band of the polymer with bithiophene moiety (6TO or 6TF) appeared in the region of longer wavelength than that with biphenyl moiety (6PO or 6PF). On the contrary,  $Ar_1$  unit shifted the emission band while that had no relation with the absorption band in the region above 400 nm. This would mean that Ar<sub>1</sub> affects the electronic structure of qAr<sub>2</sub>q unit not in the ground state but in the excited state. Absolute fluorescence quantum yields  $(\Phi_F)$  of the polymers and the model compound in CHCl<sub>3</sub> were measured by integrating sphere method. The quantum yields of the polymers with bithiophene moiety (6TO, 6TF) were lower than those with biphenyl moiety (6PO or 6PF), and especially, the polymer with strong electron-withdrawing substituent (6TF) gave  $\Phi_{\rm F}$ = 0.00. It seems to be that electron-donating ability of the bithiophene moiety is very strong, so that electron transfer from bithiophene moiety to quinoline ring leads to decreasing of the quantum yield.

UV-vis absorption and photoluminescence experiments in spin-coated film state were also carried out (Figs. 3 and 4). All the polymers and the model compound in film state showed bathochromic shift of the absorption and photoluminescence spectra (7–29 nm) when compared with those in solution state due to intermolecular stacking interaction of  $\pi$ -conjugated main chain. Moreover, the polymers with perfluoroalkyl chains (**6PF** and **6TF**) represented smaller bathochromic shift than those with alkoxy chains (**6PO** and **6TO**),

 $^{d}$  Fluorescence maxima: CHCl\_3 (1.0  $\times$  10  $^{-5}$  M).

<sup>e</sup> Absolute quantum yield.

indicating that repulsion between highly electronegative surfaces of perfluoroalkyl chains inhibits the stabilization by the stacking of  $\pi$ -conjugated main chain. In the normalized fluorescence spectra, the film state disappears in the difference between the polymers with biphenyl moiety and those with bithiophene moiety as shown in the solution state (Fig. 2). This is probably due to no solvation of the transition state from charge transfer in the film of **6TO** and **6TF** (Tables 2 and 3).

## **Molecular Orbital Calculations**

To further understand the nature of optical properties, we have carried out theoretical calculation for model compounds **9PO** and **9TF** using density-functional theory (DFT) method at the B3LYP/6-31G(d), and also using time-dependent-DFT (TD-DFT) at the B3LYP/6-31G(d,p).<sup>27</sup> Figure 5(A,B) exhibit HOMO and LUMO of 9PO and 9TF, respectively, and the molecular orbitals around frontier orbitals separate well into qAr<sub>2</sub>q and Ar<sub>1</sub> units. The HOMO and LUMO of **9PO** are located predominantly on qAr2q unit, and the oscillator strength (f) mainly responsible for HOMO-LUMO transition of **9PO** was large (f = 1.1089). These results indicate that the  $\pi$ -conjugation is extended through Ar<sub>2</sub> moiety, and that the HOMO-LUMO transition at qAr<sub>2</sub>q unit results in the absorption band of the polymer  $6P0 \sim 470$  nm as mentioned above. In contrast, the HOMO of 9TF is localized on bithiophene moiety, and the LUMO is on qAr2q unit. TD-DFT

TABLE 3
UV-Vis
Absorption
and
Photoluminescence
Properties
in
Film
State
Sta

Compound	$\lambda_{abs,max} (nm)^a$	Ex (nm) <sup>b</sup>	λ <sub>em,max</sub> (nm) <sup>c</sup>
6PO	369, 489	489	580
6PF	467	467	537
6TO	362, 490	490	586
6TF	468	468	538
8	367, 497	497	579

<sup>a</sup> Absorption maxima.

<sup>b</sup> Excited wavelength.

<sup>c</sup> Fluorescence maxima.



FIGURE 5 Molecular orbital diagrams for the HOMO and LUMO of (A) 9PO and (B) 9TF (B3LYP/6-31G(d)// B3LYP/6-31G(d)).

calculation revealed that HOMO-LUMO transition hardly occurs ( $f \sim 0.01$ ), whereas transition from HOMO-2 on qAr<sub>2</sub>q unit to LUMO easily occurs (f = 1.5044) corresponding to the absorption band of the polymer **6TF** ~455 nm (Fig. 1). The order of the oscillator strength was consistent with that of the molar extinction coefficient. From the result of **9TF**, it can be said that the electron transition from HOMO-2 to LUMO provides a hole at HOMO-2 on qAr<sub>2</sub>q unit and that an electron localized on the bithiophene moiety transfers from HOMO to HOMO-2 to stabilize the transition state leading to the nonradiative relaxation.

## **CONCLUSIONS**

We have successfully synthesized the novel organoboron aminoquinolate-based polymers with high molecular weight by Sonogashira–Hagihara coupling in good yields. The color and the emission intensity of the polymers can be tuned by diethynyl and diiodo monomers, respectively. The absorption and emission bands in the region above 400 nm predominantly depended on the backbone structure composed of two quinoline rings and diethynylbenzene. The polymers with biphenyl group exhibited the high fluorescence absolute quantum yields, while no emission of the polymers with the bithiophene moiety and the perfluoroalkyl chain was observed. This result and the DFT calculations on the molecular model systems of the polymers suggest that the electron transfer easily occurs from bithiophene moiety to the  $\pi$ -extended quinoline moiety in transition state.

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