Main-Chain-Type *N*,*N*′-Chelate Organoboron Aminoquinolate Polymers: Synthesis, Luminescence, and Energy Transfer Behavior

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ABSTRACT: A novel green luminescent compound, (κ^2-(*N*,*N* ′)-8-acetylaminoquinolate)diphenylborane (**1**) was synthesized and fully characterized. To incorporate into the polymer main-chain, (κ^2-(*N*,*N* ′)-8-acetylaminoquinolate)bis(4-iodophenyl)borane was also synthesized as a monomer. A new class of fluorescent main-chain type organoboron aminoquinolate polymers were prepared by means of the Sonogashira−Hagihara coupling reaction between diyne monomers and the aminoquinoline monomer. The obtained polymers were further investigated by UV−vis absorption and fluorescence spectroscopy. It was revealed that the fluorescent quantum efficiencies of the obtained polymers depended on the π-conjugated linker unit. In addition, an efficient energy transfer was observed and well π-extended linker units played a role in a light harvesting antenna for the organoboron aminoquinolate units.

1. Introduction

We have synthesized a wide variety of organoboron polymers including boron atoms in the main chain by means of hydroboration polymerization and transition metal coupling of organoboron monomers.[1–5] Because of their unique properties, they are expected to be a novel type of optical and electrical materials.[6,7] In our earlier studies, the polymers containing boron atoms as boron−nitrogen rings in their main chain like poly(cyclodiborazane)s[3] or poly(pyrazabole)s[4,5] showed not only efficient luminescence but also good stability with regard to the oxidative and hydrolytic degradation compared to other organoboron polymers.

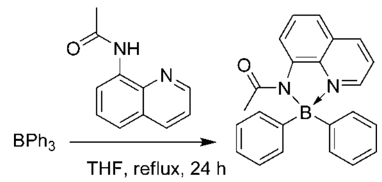
On the other hand, 8-hydroxyquinoline biphenylboron (BPh_2(q)) and their derivatives (Chart 1) attracted considerable attention as an alternative to tris(8-hydroxyquinoline)aluminum (Al(q)$_3$) for organic light emitting diodes (OLEDs) in recent years.[8–11] The side-chain-type organoboron quinolate polymers were also prepared by Jäkle et al.[12,13] and Weck et al.[14] to fabricate OLEDs using a low cost solution process. We have reported the first example of main-chain-type organoboron quinolate polymers.[15] The main-chain-type polymers showed strong green fluorescence and an efficient energy migration from conjugated linkers to boron quinolate moieties.

8-Aminoquinoline biphenylboron (BPh_2(aq)) has received some interest as a luminescent material. In 1969, Hohaus and Umland reported a bright green emission from the organoboron aminoquinolate modified with an ethoxycarbonyl group.[16] There is only one report regarding BPh_2(aq) as materials for OLEDs,[17] and detailed optical properties of BPh_2(aq) are still not clear. Considering our previous studies, BPh_2(aq) with the boron−nitrogen ring seems to be promising as more stable luminescent materials. We report here on the synthesis and properties of the low-molecular-mass organoboron aminoquinolate and incorporation of the organoboron aminoquinolate unit into polymer main-chain. These studies give an insight into the possibilities of new OLED materials based on organoboron aminoquinolate and should lead to the development of solution processable electron transport materials.

2. Results and Discussion

2.1. Synthesis. According to the previous reports,[16,17] fluorescence properties of the organoboron aminoquinolates were significantly influenced by the substituent on a chelating nitrogen atom. Especially, the alkylcarbonyl and alkoxycarbonyl modified organoboron aminoquinolates showed strong green emission. Therefore we chose 8-acetylaminoquinoline as a ligand for the simple example of the fluorescent organoboron aminoquinolate. (κ^2-(*N*,*N*′)-8-Acetylaminoquinolate)diphenylborane (**1**) was readily obtained by the reaction between triphenylborane and 8-acetylaminoquinoline (Scheme 1). Diiodo monomer **2** was also prepared in a similar manner as the analogue of the organoboron quinolate (Scheme 2).[15] The structures of compounds **1** and **2** were supported by ^{1}H, ^{13}C, and ^{11}B NMR, elemental analyses, and single-crystal X-ray diffraction analyses (Table 1). The boron centers coordinated with two nitrogen atoms in the compounds **1** and **2** display a typical tetrahedral geometry, as shown in Figures 1 and 2. The oxygen atoms on acetyl groups did not coordinate to the boron centers. The B−N and B−C bond lengths and angles are shown in Table 2 and they were similar to *N*,*N*′-chelate diphenylboron complexes previously reported.[18–20]

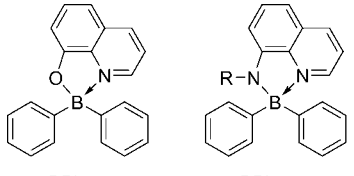
Scheme 1. Synthesis of Model Compound 1



1 (43%)

DFT calculation has been performed using the Gaussian 03 suit of programs[21] for further understanding of the behavior of the luminescence. The structures of BPh_2(q) and compound **1** were optimized using the B3LYP/6-31(d,p) method. The orbital diagrams were generated by using the GaussView program[22]

Chart 1



BPh_2(q) BPh_2(aq)

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10.1021/ma702873a CCC: $40.75

Scheme 2. Synthesis of Monomer 2

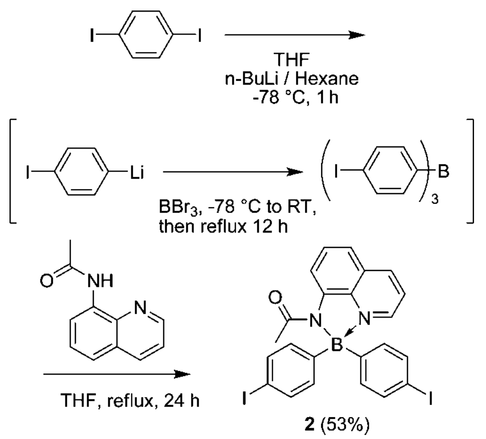

Table 1. Crystallographic Data of 1 and 2

compound	**1**	**2**·CH_2Cl_2
empirical formula	$C_{23}H_{19}BN_2O$	$C_{24}H_{19}BCl_2I_2N_2O$
formula weight	350.21	686.92
space group	$P\bar{1}$	*Pbca*
unit cell dimensions	$a = 10.127(3)$ Å $b = 12.996(4)$ Å $c = 14.471(6)$ Å $\alpha = 91.987(17)°$ $\beta = 100.256(17)°$ $\gamma = 107.122(14)°$	$a = 16.7466(3)$ Å $b = 20.0392(5)$ Å $c = 29.3774(6)$ Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
volume	1783.3(10) Å^3	9858.7(4) Å^3
Z	4	16
density (calculated)	1.304 g/cm^3	1.851 g/cm^3
absorption coefficient	0.080 mm $^{-1}$	2.789 mm $^{-1}$
θ range for data collection	3.15 to 27.48°	3.03 to 27.48°
no. of reflections collected	14747	87505
no. of independent reflections	7529 [$R_{int} = 0.0683$]	11250 [$R_{int} = 0.0936$]
max. and min. transmission	0.9613 and 0.9613	0.7679 and 0.4884
goodness-of-fit on F^2	1.01	0.973
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0618 wR2 = 0.1383	R1 = 0.0445, wR2 = 0.1150
R indices (all data)[a]	R1 = 0.1122 wR2 = 0.1585	R1 = 0.0761, wR2 = 0.1475

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

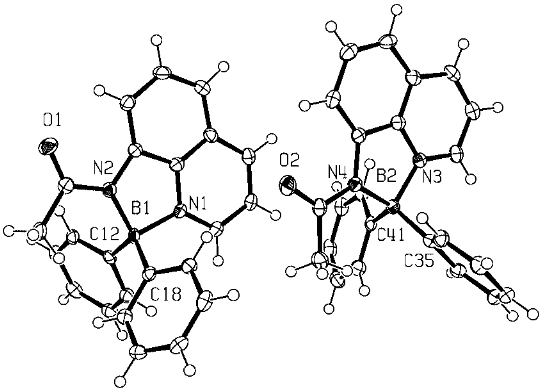

Figure 1. Structure of **1** with thermal ellipsoids drawn to the 50% probability level.

as shown in Figure 3. There was a good agreement between the geometry of the compound **1** optimized by DFT method and the structure determined by single-crystal X-ray diffraction. According to the previous reports for aluminum[23–26] and boron[27,28] quinolates, the highest occupied molecular orbital (HOMO) is mainly located on the phenolate side and the lowest unoccupied molecular orbital (LUMO) is mainly located on the pyridyl side as shown in Figure 3a. Also in the case of the compound **1**, the HOMO is mainly located on the electron-rich anilate and the acetyl group. The LUMO is mainly on the electron-deficient pyridyl ring. Compound **1** showed a lower LUMO level than that of BPh_2(q). This implies that the compound **1** is more promising as an electron transport material than BPh_2(q).

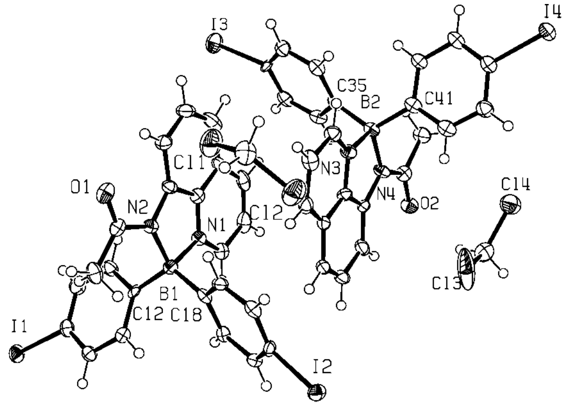

Figure 2. Structure of monomer **2** with thermal ellipsoids drawn to the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

		1 (X-ray)	
B(1)−N(1)	1.619(3)	N(2)−B(1)−C(12)	113.37(19)
B(1)−N(2)	1.587(3)	N(2)−B(1)−C(18)	115.8(2)
B(1)−C(12)	1.606(4)	C(12)−B(1)−C(18)	114.9(2)
B(1)−C(18)	1.611(4)	N(2)−B(1)−N(1)	96.07(18)
		C(12)−B(1)−N(1)	106.65(18)
		C(18)−B(1)−N(1)	107.68(17)
		1 (DFT)	
B(1)−N(1)	1.6367	N(2)−B(1)−C(12)	113.4
B(1)−N(2)	1.5984	N(2)−B(1)−C(18)	113.0
B(1)−C(12)	1.6243	C(12)−B(1)−C(18)	117.6
B(1)−C(18)	1.6248	N(2)−B(1)−N(1)	96.2
		C(12)−B(1)−N(1)	105.9
		C(18)−B(1)−N(1)	108.1
		2 (X-ray)	
B(1)−N(1)	1.615(8)	N(2)−B(1)−C(12)	112.3(5)
B(1)−N(2)	1.588(8)	N(2)−B(1)−C(18)	112.4(5)
B(1)−C(12)	1.600(9)	C(12)−B(1)−C(18)	118.7(5)
B(1)−C(18)	1.607(9)	N(2)−B(1)−N(1)	95.8(4)
		C(12)−B(1)−N(1)	107.8(5)
		C(18)−B(1)−N(1)	107.1(4)

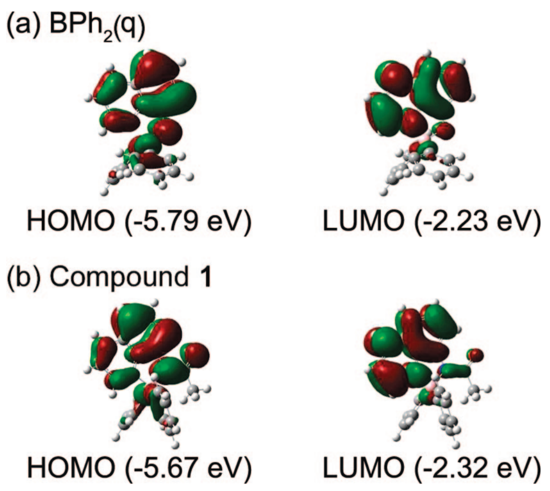

Figure 3. HOMO and LUMO diagrams of BPh_2(q) and the compound **1**. The scaling radius is 75% and molecular orbital surface isovalue is 0.02.

Scheme 3. Synthesis of Polymers 4a−c

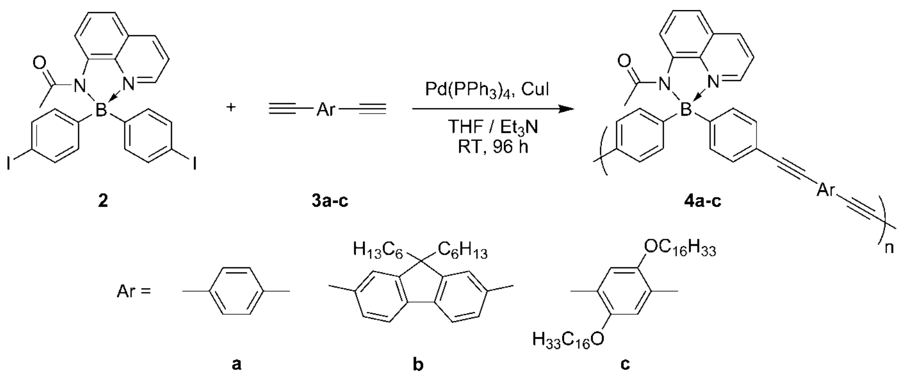

Table 3. Polymerization Results

	yield (%)[a]	M_w[b]	M_n[b]	PDI[b]	DP_n[c]
4a	40	5100	2100	2.5	4.4
4b	51	32600	11200	2.9	15.3
4c	49	39700	18100	2.2	18.9

[a] Isolated yields after reprecipitation. [b] Measured by GPC (THF), PSt standards. [c] Degree of polymerization estimated by number-average molecular weight from GPC measurement.

We carried out TD-DFT calculations to obtain further insight into the origin of the electronic transitions for $BPh_2(q)$ and the compound **1**. The calculation revealed that both compounds of the lowest energy transition correspond to promotion of electrons from the HOMO to the LUMO levels. The calculated excitation wavelength of the compound **1** was 450 nm with 0.0732 of the oscillator strength f. This excitation wavelength was red-shifted compared to that of $BPh_2(q)$ (420 nm, $f = 0.0637$) and the direction of the absorption shift was in good agreement with their absorption spectra we report in the later section.

We applied the Sonogashira−Hagihara coupling reaction to prepare the polymers as reported using the organoboron quinolate monomer.[15] Coupling reactions utilizing Pd and Cu catalysts between aminoquinolate monomer **2** and diyne monomers **3a−c** gave the corresponding polymers as described in Scheme 3. The crude products were reprecipitated into MeOH and washed with MeOH repeatedly until the supernatants were clear. The polymerization results are summarized in Table 3. Comparing the molecular weights of polymers **3a−c**, the degree of polymerization of polymer **3a** was smaller than those of polymers **3b** and **3c**. It is due to the difference of solubility which depends on the alkyl side chain. Polymer **3a** showed poor solubility and it took long time to dissolve into THF, chloroform and dichloromethane. However, polymers **3b** and **3c** were soluble in various organic solvents because of their long alkyl chains. The structures of the obtained polymers were supported by ^{1}H NMR, ^{11} B NMR, and elemental analyses. In the ^{1}H NMR spectrum of the polymer **3a**, a small peak of acetylene groups at 3.23 ppm was observed and there was no peak of acetylene groups in the spectra of the polymers **3b** and **3c**. While the peaks of iodophenyl groups were submerged by other aromatic peaks, the results of elemental analyses were reasonable with containing iodophenyl groups as their end-groups.

2.2. Optical Properties. The optical properties of the obtained polymers were investigated by UV−vis absorption and fluorescence emission spectroscopy. The absorptions of compound **1** and the polymers **4a−c** are shown in Figure 4. The compound **1** showed the weak absorption peak at 401 nm ($\varepsilon = 4100$). This absorption peak should be caused by the HOMO−LUMO transition on the acetylaminoquinoline ligand from the DFT calculation. The polymers **4a−c** showed the strong absorption peaks in the region of 300−400 nm (ε = 36900, 80800, and 47000 per unit, respectively). These peaks should be due to the π-conjugated linkers connecting the aminoquinolate units each other. Figure 5 shows the fluorescence spectra of the compound **1** and the polymers **4a−c** in dichloromethane when excited at their absorption maxima. This means that compound **1** was excited at the aminoquinoline ligand and polymers **4a−c** were mainly excited at the π-conjugated linkers. The emission spectra of the polymers were completely same as that of the compound **1** in spite of the excitation of the π-conjugated linkers. This phenomenon was very similar to the emission behavior of the π-extended organoboron quinolate polymers.[15,29] It could be explained by the energy transfer from the π-conjugated linkers in the main-chain to the acetylaminoquinoline ligands on the boron centers.

These results are summarized in Table 4. Compound **1** showed slightly red-shifted intense green emission compared to $BPh_2(q)$ as predicted by DFT calculations. The quantum yield of the compound **1** was a little lower than that of $BPh_2(q)$. In a comparison between compound **1** and polymers **4a−c**, the

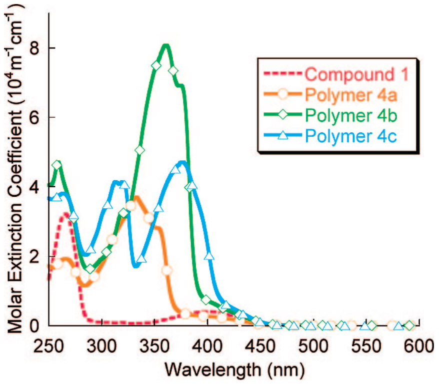

Figure 4. UV−vis spectra of the model compound **1** and the polymers **4a−c** in CH_2Cl_2.

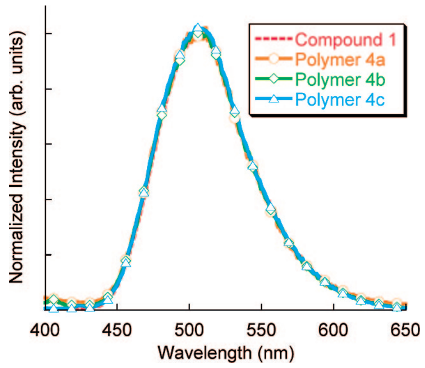

Figure 5. Fluorescence spectra of the model compound **1** and the polymers **4a−c** in CH_2Cl_2.

Table 4. UV−Vis Absorption and Fluorescence Properties

compound	λ_{max} (nm) [a]	$\varepsilon_{\lambda_{max}}$ (M^{-1} cm^{-1})[a]	em (nm)[b]	Φ_F (%)[b,d]
Al(q)$_3$[30]	387	7000	526	17
BPh$_2$(q)[29]	395	3200	496	30
1	401	4100	504	26
4a	333	36900	500	14
4b	361[c]	80800[c]	502	17
4c	376	47000	503	23

[a] UV−vis: CH_2Cl_2 (5.0×10^{-5} M). [b] Fluorescence: CH_2Cl_2 (1.0×10^{-7} M). [c] UV−vis: CH_2Cl_2 (1.0×10^{-5} M). [d] Relative to 9,10-diphenylanthracene in cyclohexane at room temperature.[31]

polymers showed lower quantum yields than that of the compound **1**. The value of the quantum yield of the polymer divided by that of compound **1** roughly represents the energy transition efficiency. In the case of polymer **4c**, the energy transition efficiency was achieved to ca. 88%. The probability of Förster energy transfer depends on the angular and distance relationship between energy donor and energy acceptor and spectral overlap integral between donor emission band and acceptor absorption band.[32] In these polymers, the angular and distance relationship between donor linker units and acceptor aminoquinolate units should be almost same because the structures of the polymers were quite similar. Presumably, there are some differences of the spectral overlap integrals in these polymers. The absorption maxima of the polymers were closely related to their quantum yields and this supports the existence of the differences of the spectral overlap integrals. In addition, the molar extinction coefficients of the polymers per unit at the excitation wavelengths were significantly higher than that of the compound **1**. In particular, the polymer **4b** exhibited a huge molar extinction coefficient (ε = 80800 per unit), retaining enough quantum efficiency because of the highly π-extended linkers containing fluorene units. These results tell us that the π-conjugated linkers in the main-chain played a role in a light harvesting antenna for aminoquinolate dye units.

3. Conclusion

In conclusion, a low-molecular-mass organoboron aminoquinolate compound and a new series of organoboron polymers containing organoboron aminoquinolate structures in the main chain were successfully prepared and characterized. These compounds exhibited intense green photoluminescence and the polymers showed an efficient energy transfer from conjugated linkers to aminoquinolate units. Efforts are underway to fabricate and evaluate OLEDs utilizing the compound **1** and the polymers **4a**−**c**.

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 CH_2Cl_2 at room temperature. Fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in CH_2Cl_2 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.[33] The analysis was carried out with direct methods (SHELX-97[34] or SIR92)[35] using Yadokari-XG.[36] The program ORTEP3[37] 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). 8-Acetylaminoquinoline,[38] 2,7-diethynyl-9,9-dihexylfluorene (**3b**),[39] and 1,4-diethynyl-2,5-dihexadecyloxybenzene (**3c**)[40] were prepared according to the literatures. All other reagents were commercially available and used as received.

(κ^2-(*N,N′*)-8-Acetylaminoquinolate)diphenylborane, 1. A 10 mL aliquot of of triphenylborane solution in THF (0.25 M, 2.5 mmol) was added to a solution of 8-acetylaminoquinoline (0.47 g, 2.5 mmol) in 10 mL of THF and refluxed for 24 h. After the reaction, the solvents were removed under vacuum. The residue was put in a small vial and then dissolved in CH_2Cl_2, on which hexane was slowly laid. The phase separated solution was allowed to stand for 1 week for diffusion, which gave yellow crystals of **1** in 43% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.93 (1H, dd, J = 7.80, 0.73 Hz), 8.41 (1H, dd, J = 5.24, 1.10 Hz), 8.37 (1H, dd, J = 8.28, 0.97 Hz), 7.79 (1H, t, J = 8.04 Hz), 7.54−7.46 (6H, m), 7.31−7.24 (6H, m), 1.92 (3H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 174.24, 146.44, 141.94, 139.48, 138.99, 137.50, 133.44, 132.51, 127.74, 127.47, 127.05, 122.33, 118.59, 116.98, 26.66. ^{11}B NMR ($CDCl_3$, δ, ppm): 6.11. Anal. Calcd for $C_{23}H_{19}BN_2O$ (mol wt 350.22): C, 78.88; H, 5.47; B, 3.09; N, 8.00; O, 4.57. Found: C, 78.78; H, 5.37; N, 7.96.

(κ^2-(*N,N′*)-8-Acetylaminoquinolate)bis(4-iodophenyl)borane, 2. To a solution of 1,4-diiodobenzene (10.56 g, 32.0 mmol) in 160 mL of THF was added 20.0 mL of *n*-BuLi (1.6 M, 32.0 mmol) slowly at −78 °C and the mixture was stirred at −78 °C for 1 h. BBr_3 (0.99 mL, 10.7 mmol) was added to the reaction mixture at −78 °C, which was then allowed to warm room temperature and then refluxed for 12 h. 8-Acetylaminoquinoline (1.99 g, 10.7 mmol) dissolved in 50 mL of THF in a separate flask was added to the reaction mixture, then refluxed for 24 h. The solvents were removed under vacuum. The residue was dissolved in 200 mL of MeOH and placed in a −20 °C freezer for 12 h. The yellow crystals formed were collected by filtration and washed with 100 mL of cold MeOH. The yellow crystals thus obtained were vacuum-dried to yield 3.40 g (53%) of the product. For X-ray diffractions, single crystals were prepared by the same method as above. ^1H NMR ($CDCl_3$, δ, ppm): 8.91 (1H, d, J = 7.80 Hz), 8.44 (1H, d, J = 8.28 Hz), 8.33 (1H, d, J = 5.12 Hz), 7.80 (1H, dd, J = 7.80, 8.28 Hz), 7.61 (4H, d, J = 8.04 Hz), 7.57 (1H, dd, J = 8.28, 5.12 Hz), 7.52 (1H, d, J = 8.28 Hz), 7.18 (4H, d, J = 8.04 Hz), 1.89 (3H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 173.79, 145.33, 141.65, 139.54, 139.31, 137.41, 136.93, 135.30, 132.77, 127.57, 122.48, 118.93, 117.29, 93.76, 26.62. ^{11}B NMR ($CDCl_3$, δ, ppm): 5.72. Anal. Calcd for $C_{23}H_{17}BI_2N_2O$ (mol wt 602.01): C, 45.89; H, 2.85; B, 1.80; I, 42.16; N, 4.65; O, 2.66. Found: C, 45.70; H, 2.94; I, 42.02; N, 4.60.

Polymer 4a. A mixture of monomer (**2**) (0.54 g, 0.90 mmol), 1,4-diethynylbenzene (**3a**) (0.11 g, 0.90 mmol), 104 mg of $Pd(PPh_3)_4$, 17 mg of CuI, 36 mL of THF, and 18 mL of Et_3N was placed in a 100 mL vial equipped with a magnetic stirring bar in a glovebox of argon atmosphere. The reaction was carried out at room temperature for 96 h with stirring. After the reaction, a yellow solid was precipitated as a film which stuck to the wall of the vial. The solid was filtered and washed with 100 mL of MeOH. The obtained solid was dissolved in 30 mL of THF and filtered to remove insoluble part. The filtrate was poured into 100 mL of MeOH to precipitate the polymer. The resulting polymer (**4a**) was filtered, washed with MeOH repeatedly, and dried in vacuo to give 0.17 g (40%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.94 (1H, d, J = 7.80 Hz), 8.45 (1H, d, J = 8.53 Hz), 8.40 (1H, d, J = 5.12 Hz), 7.82 (1H, dd, J = 8.53, 7.80 Hz), 7.59 (1H, dd, J = 8.53, 5.12 Hz), 7.53 (1H, d, J = 8.53 Hz), 7.46 (12H, s), 1.92 (3H, s). ^{11}B NMR ($CDCl_3$, δ, ppm): 2.44. Anal. Calcd for $C_{33}H_{21}BN_2O$ (mol wt 472.34 per unit): C, 83.91; H, 4.48; B, 2.29; N, 5.93; O, 3.39. Found: C, 79.22; H, 4.40; N, 5.33; I, 1.64.

Polymer 4b. A mixture of monomer (**2**) (0.36 g, 0.60 mmol), 2,7-diethynyl-9,9-dihexylfluorene (**3b**) (0.23 g, 0.60 mmol), 69 mg of $Pd(PPh_3)_4$, 11 mg of CuI, 24 mL of THF, and 12 mL of Et_3N was placed in a 50 mL vial equipped with a magnetic stirring bar in a glovebox of argon atmosphere. The reaction was carried out at room temperature for 96 h with stirring. After the reaction, the precipitated ammonium salts were filtered off and washed with a small amount of THF. The filtrate was concentrated and the residue was dissolved in 5 mL of $CHCl_3$ and poured into 100 mL of MeOH to precipitate the polymer. The resulting polymer (**4b**) was filtered, washed with MeOH repeatedly, and dried in vacuo to give 0.22 g (51%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.97−8.95 (1H, m), 8.49−8.39 (2H, m), 7.87−7.78 (1H, m), 7.73−7.57 (4H, m), 7.50 (12H, br s), 2.05−1.85 (7H, m), 1.16−0.92 (12H, m), 0.75 (6H, s), 0.60 (4H, s). ^{11}B NMR ($CDCl_3$, δ, ppm): 2.98. Anal. Calcd for $C_{52}H_{49}BN_2O$ (mol wt 728.77 per unit): C, 85.70; H, 6.78; B, 1.48; N, 3.84; O, 2.20. Found: C, 83.44; H, 6.78; N, 3.61; I, 1.10.

Polymer 4c. A mixture of monomer (**2**) (0.24 g, 0.40 mmol), 1,4-diethynyl-2,5-dihexadecyloxybenzene (**3c**) (0.24 g, 0.40 mmol), 46 mg of $Pd(PPh_3)_4$, 8 mg of CuI, 16 mL of THF and 8 mL of Et_3N was placed in a 50 mL vial equipped with a magnetic stirring bar in a glovebox of argon atmosphere. The reaction was carried out at room temperature for 96 h with stirring. After the reaction, the precipitated ammonium salts were filtered off and washed with a small amount of THF. The filtrate was concentrated and the residue was dissolved in 2 mL of $CHCl_3$ and poured into 50 mL of MeOH to precipitate the polymer. The resulting polymer (**4c**) was filtered, washed with MeOH repeatedly, and dried in vacuo to give 0.18 g (49%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.95 (1H, d, J = 8.04 Hz), 8.44 (1H, d, J = 8.04 Hz), 8.39 (1H, d, J = 5.12 Hz), 7.82 (1H, dd, J = 8.04, 8.04 Hz), 7.58 (1H, dd, J = 8.28, 5.12 Hz), 7.52 (1H, d, J = 8.28 Hz), 7.46 (8H, s), 6.97 (2H, s), 3.99 (4H, t, J = 6.46 Hz), 1.92 (3H, s), 1.85−1.78 (4H, m), 1.53−1.46 (5H, m), 1.38−1.15 (52H, m), 0.86 (6H, t, J = 6.82 Hz). ^{11}B NMR ($CDCl_3$, δ, ppm): 2.69. Anal. Calcd for $(C_{65}H_{85}BN_2O)_n$ (mol wt 921.19 per unit): C, 81.90; H, 8.99; B, 1.13; N, 2.94; O, 5.04. Found: C, 79.96; H, 8.79; N, 2.76; I, 0.73.

Supporting Information Available: Crystallographic data for compound **1** and monomer **2** in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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