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Synthesis of Methyl-Substituted Main-Chain-Type Organoboron Quinolate Polymers and Their Emission Color Tuning

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ABSTRACT: Highly fluorescent main-chain-type organoboron quinolate polymers were prepared by means of Sonogashira−Hagihara coupling reaction between diyne monomers and methyl-substituted diiodo-organoboron quinolates. By combining methyl substitution of quinolinol ligands and incorporation of organoboron quinolate into polymer main chain, more efficiently luminescent materials with blue-shifted emission were successfully synthesized.

Introduction

Tang and VanSlyke reported efficient green electroluminescence by utilizing tris(8-hydroxyquinoline)aluminum (Alq$_3$) as an electron-transport and luminescent layer in 1987. After the great discovery, numerous numbers of electron-transport materials were reported for more efficient organic light-emitting diodes (OLEDs). Even two decades later, Alq$_3$ is still regarded as the most promising material for an electron-transport layer because of their thermal stability and excellent electron-transporting ability. Therefore, functionalized Alq$_3$ or other metal quinolates were extensively studied for more efficient OLEDs materials.

Recently, Wang and co-workers reported that organoboron quinolates showed efficient luminescence and good stability.[1–5] Functionalizations of organoboron quinolates for emission color tuning were also reported. Jäkle and co-workers introduced electron-donating or electron-withdrawing moieties on the 5-position of quinolate ligands,[6] and Anderson and co-workers introduced a methyl group on 2−7-positions.[7] Especially, the introduction of a methyl group on the 2- or 4-position leads to more efficient and hypsochromic-shifted fluorescent emission.

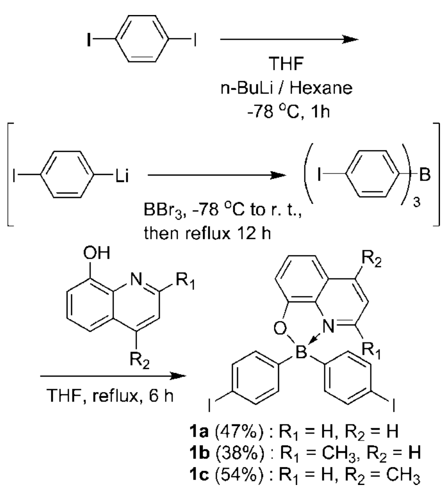
In addition, organoboron quinolates containing polymers were also reported to fabricate OLEDs by a solution process. For example, Jäkle et al. reported the preparation of side-chain-type organoboron quinolate polymers by utilizing poly(4-dibromoborylstyrene) as a reactive polymer,[8,9] and Weck et al. reported the synthesis of polystyrene-supported organoboron quinolate via 8-hydroxyquinoline-functionalized polymers.[10] On the other hand, we have recently synthesized and reported main-chain-type organoboron quinolate polymers.[11] These polymers showed strong green fluorescence, and an efficient energy migration from conjugated linkers to boron quinolate moieties was observed.

Generally, wet processable and blue emissive electron-transporting materials are strongly desired for the development of OLEDs. We report here on the synthesis and properties of the methyl-substituted organoboron quinolate polymers with tunable emission color and improved quantum efficiency.

Results and Discussion

Synthesis. The key monomers, bis(iodophenyl)boron quinolates **1a-c**, were prepared according to Scheme 1. In our previous report, the scheme and conditions for synthesis of monomer **1a** were revealed. Monomers **1b** and **1c** were easily obtained by using 2- or 4-methyl-8-hydroxyquinoline instead of nonsubstituted 8-hydroxyquinoline. These monomers were purified by recrystallization from dichloromethane and hexane. Monomer **1c** gave single crystals including accurately 0.5 equiv of dichloromethane. This complex **1c** $(CH_2Cl_2)_{0.5}$ was quite stable, and the included solvent could not be removed at even 100 °C under reduced pressure. Therefore, **1c** $(CH_2Cl_2)_{0.5}$ was used as a monomer without removing the solvent.

Scheme 1. Synthesis of Diiodoboron Quinolate Monomers 1a−c



The crystal structures of monomers **1b** and **1c** were determined by single-crystal X-ray diffraction measurements. The boron center showed a typical tetrahedral geometry, as shown in Figures 1 and 2. The methyl-substituted quinoline ligands are chelated to the boron in the same manner to form a five-membered ring despite the introduction of a methyl group. The B−N, B−O, and B−C bond lengths and angles are similar to those reported previously,[1,3] as shown in Table 2.

We applied the Sonogashira−Hagihara coupling reaction to prepare the polymers as reported before.[11] In the previous work, we employed 1,4-diethynyl-2,5-dihexyloxybenzene and 1,4-diethynyl-2,5-didodecyloxybenzene as comonomers for the organoboron quinolate monomer. The solubilities of the obtained polymers were not sufficient, and the degrees of polymerization were limited by their solubility. Therefore, we adopted 1,4-diethynyl-2,5-dihexadecyloxybenzene for improvement of solubility of the polymers. In addition, the reaction temperature was set to ambient temperature to prevent undesired side reactions and gelation. Instead, the reaction time was elongated to 96 h. After the reaction, the emerged salts were filtered off and the

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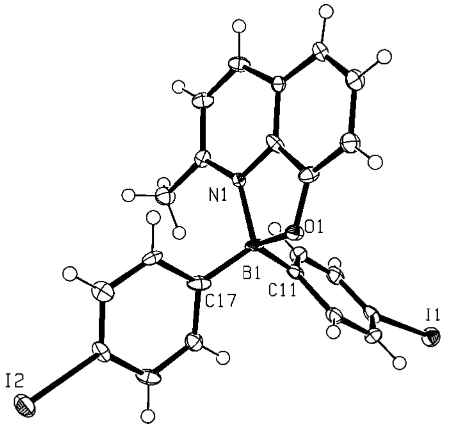


Figure 1. X-ray crystal structure of **1b** with thermal ellipsoids drawn to the 50% probability level.

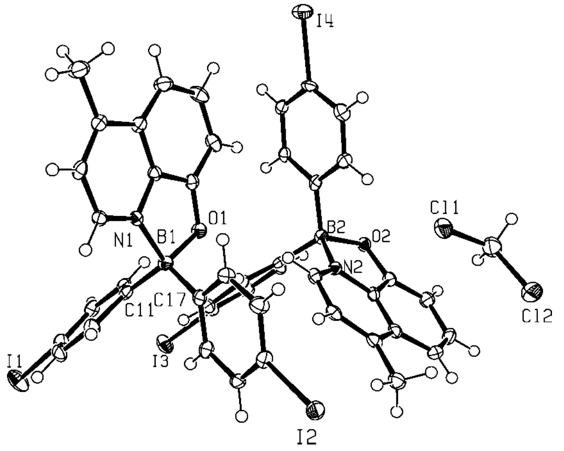


Figure 2. X-ray crystal structure of **1c** with thermal ellipsoids drawn to the 50% probability level.

Table 1. Crystallographic Data of 1b and 1c

compound	**1b**	**1c**
empirical formula	$C_{22}H_{16}BI_2NO$	$C_{45}H_{34}B_2Cl_2I_4N_2O_2$
formula weight	574.97	1234.86
space group	$P2_1/c$	$P2_1/n$
unit cell dimensions	a = 10.946(3) Å b = 14.726(3) Å c = 12.5476(17) Å α = 90° γ = 95.614(16)° β = 90°	a = 12.0045(15) Å b = 21.615(2) Å c = 17.3932(13) Å α = 90° γ = 102.415(5)° β = 90°
volume	2012.8(7) Å^3	4407.7(8) Å^3
Z	4	4
density (calculated)	1.897 g/cm^3	1.861 g/cm^3
absorption coefficient	3.136 mm^{-1}	2.989 mm^{-1}
θ range for data collection	3.21°−27.48°	3.05°−27.48°
reflections collected	16955	41898
independent reflections	4532 (R_{int} = 0.0655)	10069 (R_{int} = 0.0786)
completeness to θ = 27.48°	98.00%	99.50%
max and min transmission	0.7444 and 0.4530	0.7543 and 0.4675
goodness-of-fit on F^2	1.154	1.072
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0457, wR2 = 0.1508	R1 = 0.0386, wR2 = 0.0778
R indices (all data)[a]	R1 = 0.0692, wR2 = 0.2390	R1 = 0.0604, wR2 = 0.0834

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

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

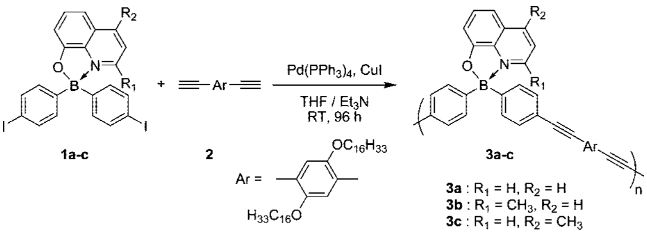
		1a	
B(1)−N(1)	1.629(6)	O(1)−B(1)−C(11)	110.4(4)
B(1)−O(1)	1.524(7)	O(1)−B(1)−C(16)	109.8(4)
B(1)−C(11)	1.598(8)	C(11)−B(1)−C(16)	116.9(4)
B(1)−C(16)	1.591(7)	O(1)−B(1)−N(1)	99.9(4)
		C(11)−B(1)−N(1)	110.7(4)
		C(16)−B(1)−N(1)	107.7(4)
		1b	
B(1)−N(1)	1.627(10)	O(1)−B(1)−C(11)	106.1(6)
B(1)−O(1)	1.537(10)	O(1)−B(1)−C(17)	110.0(6)
B(1)−C(11)	1.616(12)	C(11)−B(1)−C(17)	116.7(6)
B(1)−C(17)	1.605(11)	O(1)−B(1)−N(1)	99.3(5)
		C(11)−B(1)−N(1)	109.4(6)
		C(17)−B(1)−N(1)	113.6(6)
		1c	
B(1)−N(1)	1.625(5)	O(1)−B(1)−C(11)	111.7(3)
B(1)−O(1)	1.526(5)	O(1)−B(1)−C(17)	110.4(3)
B(1)−C(11)	1.603(6)	C(11)−B(1)−C(17)	115.5(3)
B(1)−C(17)	1.613(6)	O(1)−B(1)−N(1)	98.8(3)
		C(11)−B(1)−N(1)	109.7(3)
		C(17)−B(1)−N(1)	109.4(3)

Table 3. Polymerization Results

	yield (%)[a]	M_w[b]	M_n[b]	PDI[b]	DP_n[c]
3a	77	15 100	6600	2.3	7.2
3b	74	15 400	6600	2.3	7.2
3c	82	10 500	5200	2.0	5.6

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

Scheme 2. Polymerization of Monomers 1a−c with Diyne Monomer 2

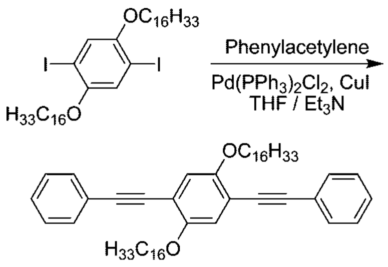


filtrates were evaporated under vacuum. The residues were reprecipitated into methanol and washed with methanol repeatedly. The molecular weights of polymers **3a−c** were estimated by GPC measurements. The number-average molecular weights (M_n) were in the range of 5200–6600 g/mol with a molecular weight distribution (M_w/M_n) of 2.0–2.3 with polystyrene standards. In addition, the degrees of polymerization (PDI) were 5.6–7.2. The results are summarized in Table 3. These values were not so high, however, enough to fabricate a thin film by a spin-coating method. The structures of the obtained polymers were supported by ^1H NMR, ^{11}B NMR, and elemental analyses. The end groups of the polymers should be iodophenyl or acetylene groups. In the ^1H NMR spectrum of polymer **3c**, a small peak of acetylene groups at 3.32 ppm was observed, and there were no peaks of acetylene groups in the spectra of polymers **3a** and **3b**. While the peaks of iodophenyl groups were submerged with other aromatic peaks, the results of elemental analyses were reasonable with containing iodophenyl groups as their end groups. On the basis of the iodine content from elemental analyses, the degrees of polymerizations (DP_n) were estimated to be approximately 10−20 (see Supporting Information). The iodines on the end groups might be partially eliminated, and the DP_n may be overestimated compared with the DP_n from GPC measurements.

Model compound **4** was synthesized as the model structure for the conjugated linker of the polymers (Scheme 3). The structure of the model compound **4** was confirmed by ^1H NMR, ^{13}C NMR, and elemental analysis.

Optical Properties. The optical properties of the obtained polymers were investigated by UV–vis absorption and fluores-

Scheme 3. Synthesis of Model Compound 4



Model compond **4** (73%)

cence emission spectroscopy. The absorption spectra of the monomers **1a**−**c**, polymers **3a**−**c**, and model compound **4** are shown in Figure 3. Monomers **1a**−**c** showed the weak absorption peaks around 390 nm (ϵ = 2700–4200) arising from the quinolinol ligand. On the other hand, polymers **3a**−**c** showed strong absorption peaks in the range of 300–400 nm (ϵ = 39 700–43 200 per unit). On the basis of the spectrum of model compound **4**, these strong peaks should be due to the conjugated linker in the main chain.

The fluorescence emission spectra of the monomers, the polymers, and the model compound are shown in Figure 4. The excitation wavelengths were set to the absorption maxima from the UV–vis absorption spectra. In other words, the monomers were excited at the quinolinol rings and the polymers were excited at the conjugated linker moieties in the main chain. The emission spectra of the monomers were successfully blue-shifted by introducing the methyl groups. According to the previous report,[7] the highest occupied molecular orbital (HOMO) is located mainly on the electron-rich phenoxide ring of the quinolinol ligands and the lowest unoccupied molecular orbital (LUMO) is mainly on the electron-deficient pyridyl ring. Electron donation into the LUMO raises the energy of the LUMO, resulting in a wide band gap. Therefore, methyl group (electron donating) in positions 2 and 4 on the quinolinol ligands results in blue shift in the emission spectra. The emission spectra of the polymers were completely different from model compound **4**. In contrast to that, the emission spectra of the polymers and the monomers having same quinolinol ligands were almost same, and the emission wavelength was also blue-shifted. It could be explained that the energy transfer from the conjugated linker moieties to the quinolinol ligands as Wang[3] and our group[11] pointed previously.

The results of these measurements are summarized in Table 4. The quantum yield of monomer **1a** was different from our previous report;[11] however, the difference was small, and the value we reported here was a reproducible result. Comparing diiodo monomers **1a**−**c** and nonsubstituted analogues reported by Anderson and co-workers,[7] there was no significant difference on the optical properties. This supports that fluorescent emissions occurred from quinolinol ligands and are not influenced by iodo atoms introduced on the phenyl groups. The quantum yields (Φ_F) of the polymers **3a**−**c** were 20%, 20%, and 29%, respectively. The quantum yield of polymer **3c**, which is methyl-substituted on the 4-position of quinolinol ligands, was improved to 1.5 times higher than that of nonsubstituted polymer **3a**. In addition, the molar extinction coefficient of the polymers at the excitation wavelengths was almost 10 times higher than that of the monomers. It seemed that the conjugated linkers in the main chain played a role in a light-harvesting antenna for boron quinolate units.

Photographs of photoluminescence of the polymers solutions and the Commission Internationale de L'Eclairage (CIE) 1931 (x,y) chromaticity diagram are shown in Figure 5. The obtained polymers **3a**−**c** showed intense green, green-blue, and blue

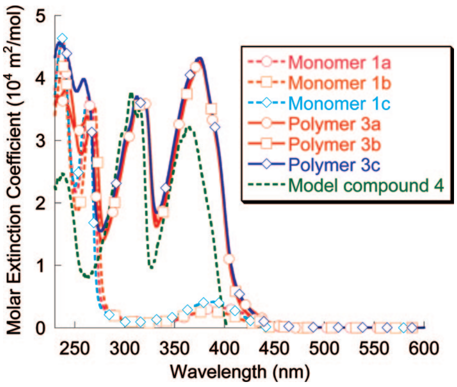


Figure 3. UV–vis spectra of monomers **1a**−**c**, polymers **3a**−**c**, and model compound **4** in CH_2Cl_2.

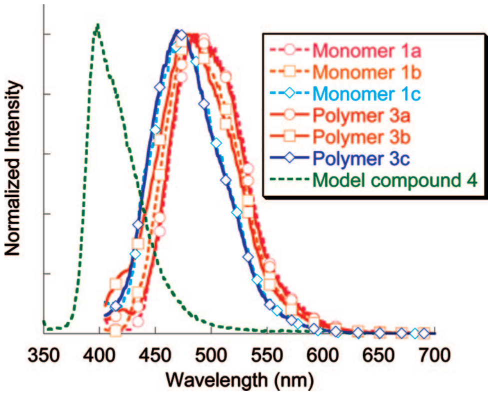


Figure 4. Fluorescence spectra of monomers **1a**−**c**, polymers **3a**−**c**, and model compound **4** in CH_2Cl_2.

Table 4. UV–vis Absorption and Fluorescence Properties

compound[e]	λ_{max}[a]	$\epsilon_{\lambda_{max}}$ (M^{-1} cm^{-1})[a]	Ex (nm)[b]	Em (nm)[b]	Φ_F[b,d]
AlQ_3[12]	387	7000		526	17
BPh_2Q[3]	395	3200		496	30
1a	395	3200	395	490	31
1b	385	2700	385	481	36
1c	389	4200	389	477	64
3a	376	43200	376	484	20
3a (film)			381	488	
3b	375	42300	375	478	20
3b (film)			380	482	
3c	375	39700	375[c]	472[c]	29[c]
3c (film)			382	471	
4	365	32200	365[d]	404[d]	74[d]

[a] UV–vis: CH_2Cl_2 (5.0×10^{-5} M). [b] Fluorescence: CH_2Cl_2 (1.0×10^{-7} M). [c] Fluorescence: CH_2Cl_2 (5.0×10^{-8} M). [d] Fluorescence: CH_2Cl_2 (1.0×10^{-8} M). [e] Relative to 9,10-diphenylanthracene in cyclohexane at room temperature.[13]

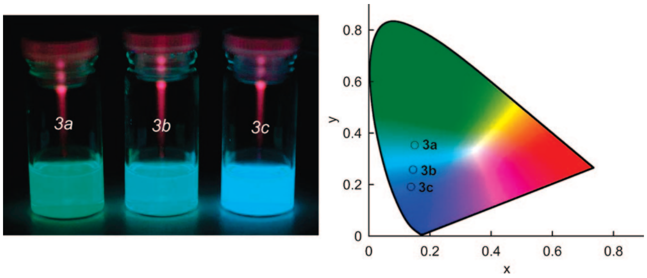


Figure 5. Left: photographs of dichloromethane solutions of polymers (from left to right, polymers **3a**, **3b**, and **3c**) under UV light at 365 nm. Right: CIE 1931 (x,y) chromaticity diagram of polymers **3a**−**c** converted from fluorescence spectra.

photoluminescence with the CIE coordinates of (0.1502, 0.3532), (0.1450, 0.2579), and (0.1383, 0.1914), respectively. The emission color of the main-chain-type organoboron quinolate polymers were blue-shifted in a successful manner by introducing a methyl group.

Conclusion

In conclusion, a new series of organoboron polymers containing methyl-substituted organoboron quinolate structures in the main chain were prepared by the Sonogashira−Hagihara coupling. These polymers exhibited intense green, green-blue, and blue photoluminescence. Moreover, the quantum yield of polymer **3c** which is methyl-substituted on the 4-position was elevated up to 1.5 times higher than that of nonsubstituted polymer **3a**, and the efficient energy transfer from π-conjugated linker in the main chain to quinoline rings has been indicated. By combining methyl substitution of quinolinol ligands and incorporation of organoboron quinolate into polymer main chain, more luminescent materials with hypsochromic-shifted emission were successfully produced. Efforts are underway to fabricate and evaluate OLEDs utilizing polymers **3a**−**c**.

Experimental Section

Materials and Instruments. Tetrahydrofuran (THF) and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 instrument. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane. Chemical shifts for ^{11}B NMR were measured in ppm relative to external BF_3OEt_2 (sealed capillary) in $CDCl_3$. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with polystyrene standards. UV–vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. B(4-iodophenyl)$_2$-q (**1a**),[11] 4-methyl-8-quinolinol,[14] 1,4-diiodo-2,5-dihexadecyloxybenzene, and 1,4-diethynyl-2,5-dihexadecyloxybenzene (**2**)[15] were prepared according to the literature. Other reagents were commercially available. All reactions were performed under an argon atmosphere using standard Schlenk techniques.

Synthesis of B(4-iodophenyl)$_2$-2-methyl-q (1b). To the solution of 1,4-diiodobenzene (6.60 g, 20 mmol) in 100 mL of THF was added 12.5 mL (1.6 M, 20 mmol) of *n*-BuLi slowly at −78 °C, and the mixture was stirred at −78 °C for 1 h. BBr_3 (0.67 mL, 6.7 mmol) was added to the reaction mixture at −78 °C and then allowed to room temperature and refluxed for 12 h. 2-Methyl-8-hydroxyquinoline (1.06 g, 6.7 mmol) dissolved in 30 mL of THF in a separate flask was added to the reaction mixture and then refluxed for 6 h. The solvents were removed under vacuum. The residue was dissolved in 100 mL of CH_2Cl_2, and the insoluble salt was removed from the solution by filtration. The solvent was removed under vacuum. The remaining yellow oil was purified by dissolving in a small amount of CH_2Cl_2 and reprecipitating with 100 mL of ice-cooled methanol, giving a yellow solid. The crude product 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 24 h for diffusion, which gave yellow single crystals of (**1b**) in 38% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.33 (1H, d, J = 8.53 Hz), 7.60–7.58 (5H, m), 7.39 (1H, d, J = 8.28 Hz), 7.23 (1H, d, J = 8.28 Hz), 7.10–7.08 (5H, m), 2.50 (3H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.00, 153.18, 143.08, 139.45, 137.46, 136.56, 135.17, 131.67, 126.66, 125.25, 112.62, 109.87, 93.61, 21.33. ^{11}B NMR ($CDCl_3$, δ, ppm): 11.53. Anal. Calcd for $C_{22}H_{16}BI_2NO$ (mol wt 574.94): C, 45.95; H, 2.80; I, 44.14; N, 2.44. Found: C, 46.01; H, 2.90; I, 44.16; N, 2.29.

Synthesis of B(4-iodophenyl)$_2$-4-methyl-q $(CH_2Cl_2)_{0.5}$ (1c·$(CH_2Cl_2)_{0.5}$. The reaction was carried out by following the procedure described above, except with the use of 4-methyl-8-hydroxyquinoline (1.06 g, 6.7 mmol) as a ligand. The crude product 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 24 h for diffusion, which gave yellow single crystals of (**1c**) containing dichloromethane as an included solvent in 54% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.35 (1H, d, J = 5.36 Hz), 7.66 (1H, dd, J = 8.53, 7.80 Hz), 7.58 (4H, d, J = 8.28 Hz), 7.45 (1H, d, J = 5.36 Hz), 7.29 (1H, d, J = 8.53 Hz), 7.15 (1H, d, J = 7.80 Hz), 7.13 (4H, d, J = 8.28 Hz), 5.30 (1H, s), 2.79 (3H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.59, 150.79, 146.11, 138.55, 136.94, 136.60, 133.95, 132.50, 128.32, 123.23, 109.87, 109.78, 93.45, 53.41, 18.79. ^{11}B NMR ($CDCl_3$, δ, ppm): 10.56. Anal. Calcd for $C_{22}H_{16}BI_2NO(CH_2Cl_2)_{0.5}$ (mol wt 616.92): C, 43.77; H, 2.78; N, 2.27. Found: C, 43.61; H, 2.84; N, 2.39.

Synthesis of Polymer 3a. A mixture of B(4-iodophenyl)$_2$q (**1a**) (0.22 g, 0.40 mmol), 1,4-diethynyl-2,5-dihexadecyloxybenzene (**2**) (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 under an 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 (**3a**) was filtered, washed with MeOH, and dried in vacuo to give 0.28 g (77%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.56 (1H, d, J = 4.39 Hz), 8.44 (1H, d, J = 8.53 Hz), 7.70–7.64 (2H, m), 7.44 (4H, d, J = 8.28 Hz), 7.40 (4H, d, J = 8.28 Hz), 7.27 (1H, d, J = 7.80 Hz), 7.20 (1H, d, J = 7.80 Hz), 6.96 (2H, s), 3.98 (4H, t, J = 6.46 Hz), 1.83–1.76 (4H, m), 1.52–1.45 (4H, m), 1.35–1.15 (48H, m), 0.86 (6H, t, J = 6.70 Hz). ^{11}B NMR ($CDCl_3$, δ, ppm): 7.42. Calcd for $(C_{63}H_{82}BNO_3)_n$: C, 82.96; H, 9.06; N, 1.54. Found: C, 80.70; H, 8.94; N, 1.26; I, 0.93.

Synthesis of Polymer 3b. The reaction was carried out by following the procedure described above. The polymerization between 0.23 g (0.40 mmol) of **1b** and 0.24 g (0.40 mmol) of **2** gave the corresponding polymer **3b** 0.27 g (74%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.34 (1H, d, J = 8.53 Hz), 7.60 (1H, dd, J = 7.80, 8.28 Hz), 7.45 (4H, d, J = 8.04 Hz), 7.41 (1H, d, J = 8.53 Hz), 7.36 (4H, d, J = 8.04 Hz), 7.24 (1H, d, J = 8.28 Hz), 7.12 (1H, d, J = 7.80 Hz), 6.98 (2H, s), 3.99 (4H, t, J = 6.33 Hz), 2.52 (3H, s), 1.84–1.78 (4H, m), 1.53–1.46 (4H, m), 1.35–1.17 (48H, m), 0.87 (6H, t, J = 6.70 Hz). ^{11}B NMR ($CDCl_3$, δ, ppm): 7.33. Calcd for $(C_{64}H_{84}BNO_3)_n$: C, 83.00; H, 9.14; N, 1.51. Found: C, 80.19; H, 8.87; N, 1.20; I, 1.35.

Synthesis of Polymer 3c. The reaction was carried out by following the procedure described above. The polymerization between 0.25 g (0.40 mmol) of **1c**·$(CH_2Cl_2)_{0.5}$ and 0.24 g (0.40 mmol) of **2** gave the corresponding polymer **3c** 0.32 g (82%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.42 (1H, d, J = 5.12 Hz), 7.67 (1H, dd, J = 8.53, 7.80 Hz), 7.46 (1H, d, J = 5.12 Hz), 7.43 (4H, d, J = 8.28 Hz), 7.39 (4H, d, J = 8.28 Hz), 7.28 (1H, d, J = 8.53 Hz), 7.18 (1H, d, J = 7.80 Hz), 6.96 (2H, s), 3.98 (4H, t, J = 6.46 Hz), 2.79 (3H, s), 1.83–1.76 (4H, m), 1.52–1.45 (4H, m), 1.35–1.18 (48H, m), 0.87 (6H, t, J = 6.70 Hz). ^{11}B NMR ($CDCl_3$, δ, ppm): 7.48. Calcd for $(C_{64}H_{84}BNO_3)_n$: C, 83.00; H, 9.14; N, 1.51. Found: C, 79.01; H, 8.77; N, 1.33; I, 2.89.

Synthesis of Model Compound 4. A mixture of phenylacetylene (0.45 g, 4.4 mmol), 1,4-diiodo-2,5-dihexadecyloxybenzene (**2**) (1.62 g, 2.00 mmol), 70 mg of $Pd(PPh_3)_2Cl_2$, 19 mg of CuI, 40 mL of THF, and 20 mL of Et_3N was placed in a 200 mL flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The reaction mixture was refluxed for 12 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 washed with 100 mL of MeOH twice. The crude product was recrystallized from 100 mL of $CHCl_3$/EtOH (v/v = 1/1). The resulting crystals were filtered, washed with MeOH, and dried in vacuo to give 1.10 g (73%) as yellow needles. ^1H NMR ($CDCl_3$, δ, ppm): 7.55–7.52 (4H, m), 7.37–7.32 (6H, m), 7.02 (2H, s), 4.03 (4H, t, J = 6.46 Hz), 1.88–1.81 (4H, m), 1.58–1.50 (4H, m), 1.41–1.21 (48H, m), 0.88 (6H, t, $J = 6.82$ Hz). ^{13}C NMR ($CDCl_3$, δ, ppm): 153.66, 131.58, 128.29, 128.22, 123.50, 117.00, 114.01, 94.82, 85.97, 69.66, 31.92, 29.70 (4 carbons are overlapped), 29.68, 29.66 (2 carbons are overlapped), 29.63, 29.45, 29.38, 29.36, 26.09, 22.69, 14.11. Calcd for $C_{54}H_{78}O_2$ (mol wt 759.20): C, 85.43; H, 10.36; O, 4.21 Found: C, 85.48; H, 10.44; O, 4.08.

X-ray Crystallography Analyses. Single-crystals of **1b** and **1c** were obtained from CH_2Cl_2/hexane solution and were mounted in the loop. The data were collected on a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation operating at 50 kV and 30 mA at −180 °C with an imaging plate. Data were processed with direct methods SHELX-97[16] and SIR97.[17] Empirical absorption correction was applied to all crystals.[18] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

Supporting Information Available: Crystallographic data for monomers **1a**−**c** in CIF format and the relationships between the iodine contents from elemental analyses and the degree of polymerizations for polymers **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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