

Synthesis and Characterization of Organoboron Quinolate Polymers with Tunable Luminescence Properties

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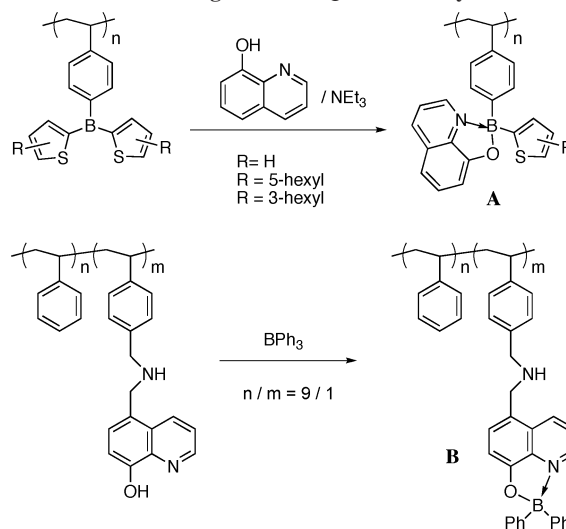
ABSTRACT: A modular one-pot approach for the synthesis of well-defined organoboron quinolate polymers and the tuning of their photoluminescence is reported. Highly selective borylation of poly(4-trimethylsilylstyrene) (**PSSiMe₃**) followed by replacement of one of the bromine substituents in the resulting reactive polymer **PSBBr₂** with *tert*-butylphenyl groups led to the common intermediate **PSBPhBr**. A series of organoboron quinolate polymers **PSBPhQ** were then obtained in high isolated yields (65–85%) by in situ treatment of **PSBPhBr** with differently substituted 8-hydroxyquinoline derivatives. All the quinolate polymers were fully characterized by multinuclear NMR spectroscopy, elemental analysis, gel permeation chromatography in-line with multiangle laser light scattering (GPC-MALLS), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). Luminescence measurements revealed distinct emission bands, ranging from the blue to the red region (486–615 nm), depending on the substitution pattern on the quinolate ligands.

Introduction

Polymeric light emitting device (PLED) materials have attracted much recent interest for their favorable solution processability,¹ such as ink-jet printing and roll-to-roll processing, a prerequisite for low-cost manufacturing and large area applications. Thus, conjugated semiconducting polymers and dendrimers have been extensively studied as electroactive materials in PLED devices.² An interesting alternative is to covalently link electro- and/or photoactive small molecules that are commonly used in small molecule organic light emitting devices (SMOLEDs) to a polymeric scaffold. The latter can be achieved either through polymerization of appropriately functionalized monomers or through polymer analogous reactions with suitable reagents. One of the major advantages of using a polymer scaffold is that well-defined polymers are easily prepared, for which the physical, optical and electronic properties can be fine-tuned. Moreover, through use of controlled polymerization techniques random and block copolymers are accessible, where multiple active components can be introduced into a single active display material. To this point, several studies on the attachment of aluminum tris(8-hydroxyquinolate) (AlQ₃), which is commonly used as electron conduction and emitting layer in OLEDs,^{3,4} to soluble polymeric scaffolds have been reported.^{5–9} Moreover, reports on polymeric analogs of platinum and iridium chelates have recently appeared in the literature.¹⁰

Molecular organoboron quinolates and related chelate complexes of boron have been shown to provide efficient luminescence and in some cases better stability over their aluminum counterparts.^{11–15} We are currently investigating the incorporation of electro- and photoactive organoboron moieties into polymers for the development of new solution processable device materials.^{16–19} In pursuit of this goal we have worked out a modular approach to well-defined organoboron quinolate polymers (**A**), which is based on the selective cleavage of di-(2-thienyl)boryl functionalized polystyrene derivatives with 8-hydroxyquinoline (Scheme 1).¹⁶ These fully functionalized organoboron quinolate polymers are readily prepared and fabricated into thin films, and they show bright green emission at ca. 508 nm ($\Phi = 12$ –14%) upon photoexcitation. In an

Scheme 1. Organoboron Quinolate Polymers



alternative approach, Weck and co-workers recently reported the copolymerization of 8-hydroxyquinoline functionalized styrene via free radical polymerization.⁷ The resulting styrene copolymer serves as a versatile scaffold for polymeric metal-quinolates through complexation with boron (**B**, Scheme 1), aluminum, or other metal salts. Emission maxima of 497 nm ($\Phi = 10\%$) and 498 nm ($\Phi = 20\%$) were reported for copolymers **B** featuring 33% and 10% loading with the photoactive groups, respectively.

The major advantage of our methodology is that the chemical, physical, and photophysical properties of the boron quinolate polymers can readily be fine-tuned by varying the substitution pattern of the chelating ligand. However, we found that the long-term oxidative stability of polymers **A** was moderate, presumably due to the electron-rich character of the thiophene moieties. Moreover, the initial attachment of a thienyl group, which later is cleaved off again was undesirable. We report in here a new and highly versatile method that addresses these issues and describe the preparation of a series of new luminescent polymers with tunable emission color.

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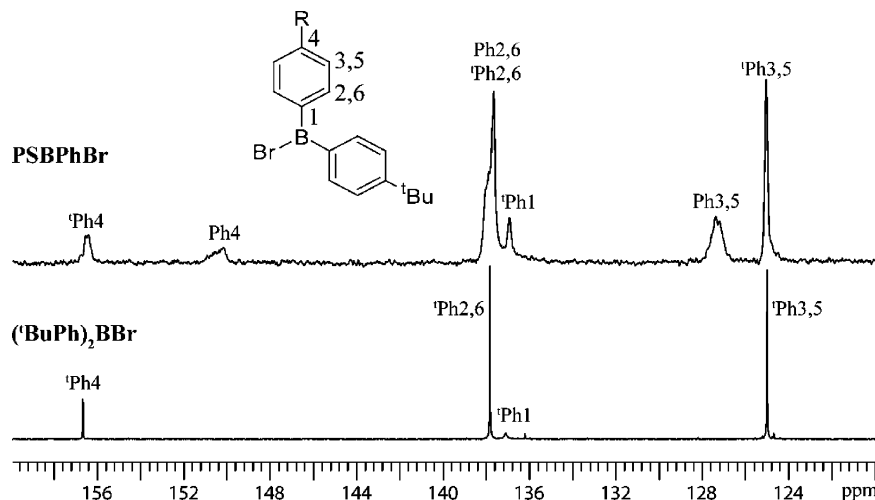
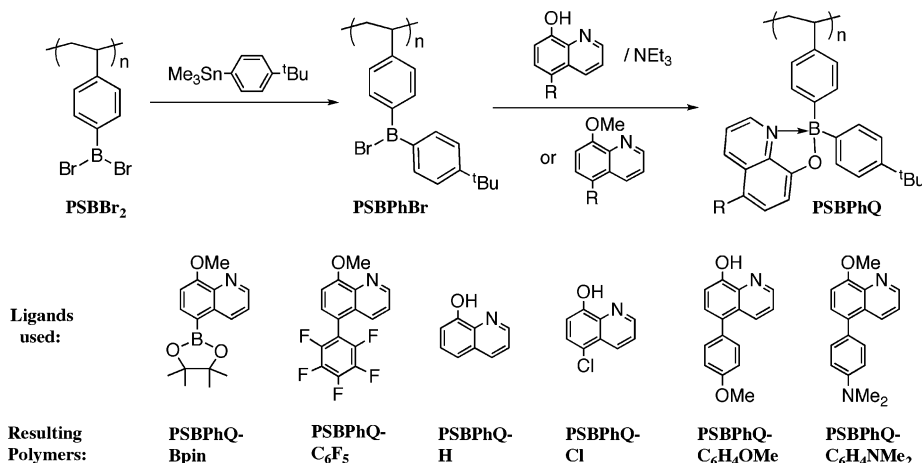


Figure 1. Aromatic region of the ^{13}C NMR spectra of **PSBPhBr** (R = polymer backbone) and $(t\text{BuPh})_2\text{BBR}$ (R = $t\text{Bu}$). Ph and $t\text{Ph}$ refer to phenyl groups attached to the polymer backbone and *tert*-butyl phenyl groups, respectively.

Scheme 2. Synthesis of Organoboron Quinolates Polymers



Results and Discussion

Polymer Synthesis. The silyl-functionalized polymer poly(4-trimethylsilyl styrene) (**PSSiMe₃**) with $M_w = 59\,540$ and $\text{PDI} = 1.12$ was prepared by atom transfer radical polymerization (ATRP)²⁰ and quantitatively converted to poly(4-dibromoboryl styrene), **PSBBR₂**, with a slight excess of BBr_3 as previously described.²¹ The reactive polymer **PSBBR₂** was then treated in situ with a slight excess of 1-trimethylstannyl-4-*tert*-butylbenzene at $-20\text{ }^\circ\text{C}$ in CH_2Cl_2 . Under these conditions, selective replacement of only one of the boron-bound bromine substituents by the *tert*-butylphenyl group led to the formation of **PSBPhBr** (Scheme 2).²² For characterization purposes **PSBPhBr** was isolated by precipitation into hexanes and freeze-dried from benzene. Transfer of a single phenyl group to the boron moieties was evident from multinuclear NMR spectroscopy and further confirmed by comparison of the polymer data with those of the corresponding molecular compound $(t\text{BuPh})_2\text{BBR}$.²² Integration of the ^1H NMR spectrum of **PSBPhBr** was consistent with the presence of one *tert*-butylphenyl group per repeat unit of the polymer. The aromatic region of the ^{13}C NMR spectrum of the polymer is shown in Figure 1 in comparison to that of $(t\text{BuPh})_2\text{BBR}$. The signals for the pendent *tert*-butylphenyl groups of the polymer and those of $(t\text{BuPh})_2\text{BBR}$ occur at essentially the same chemical shifts, while the signals for the phenyl groups attached to the polymer backbone are slightly shifted and broadened due to the atactic nature of the polystyrene. The close resemblance of the polymer and $(t\text{BuPh})_2\text{BBR}$

spectra and the absence of signals for the starting material (**PSBBR₂**) confirm the monosubstitution pattern and suggest a high degree of functionalization.

As shown in Scheme 2, **PSBPhBr** was reacted in situ with 8-hydroxyquinoline or methyl-protected 8-hydroxyquinoline derivatives to give the corresponding boron quinolate polymers. In all reactions, in which the 8-hydroxy substituted ligands were employed, a large excess of triethylamine was added to remove the byproduct HBr ; with methoxy-protected ligands, the O-Me bond was readily cleaved under formation of the boron quinolate moiety and MeBr .²³ A distinct color change and spontaneous appearance of luminescence upon addition of the ligands indicated a rapid reaction. The transformations proceeded to completion within 12 h, and the resulting polymers were isolated in good yields (65–85%) by repeated precipitation into methanol and dried under high vacuum.

NMR Characterization. The organoboron quinolate polymers were fully characterized by ^1H , ^{13}C , and ^{11}B NMR spectroscopy. Sharp signals in the ^{11}B NMR spectra at ca. 7 ppm ($w_{1/2} = 350\text{--}570\text{ Hz}$) confirm the tetracoordinated nature of the boron centers. The ^1H NMR data of the polymers provide very little information due to signal overlap, but a comparison of the ^{13}C NMR spectra with those of the corresponding molecular compounds, $(t\text{BuPh})_2\text{BQ}$,²² confirms the polymer structure as illustrated in Figure 2. The carbon resonances for the quinolate and the pendent *tert*-butylphenyl groups are virtually unchanged in the polymer relative to those of

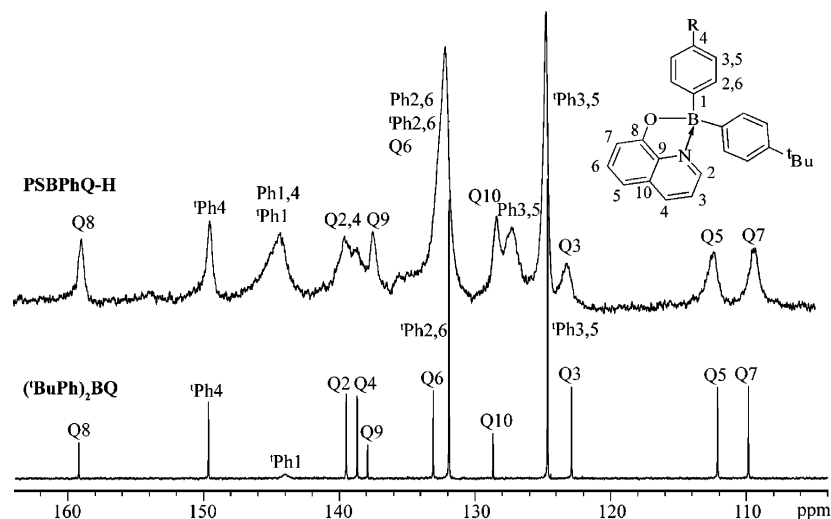


Figure 2. Aromatic region of the ^{13}C NMR spectra of **PSBPhQ-H** (R = polymer backbone) and **(*t*BuPh) $_2$ BQ** (R = *t*Bu). Ph, ^iPh and Q represent phenyl groups attached to the polymer backbone, *tert*-butylphenyl, and quinolone groups, respectively.

Table 1. Data from Gel Permeation Chromatography Analysis in Line with Multiangle Laser Light Scattering (GPC-MALLS)

polymers ^a	M_w^b	DP ^d	PDI ^e	dn/dc (mL/g) ^f	R_H (nm) ^g
PSSiMe$_3$	59 540	338	1.12	0.148	2
PSBPhQ-Bpin	172 700	334	1.15	0.177	7
PSBPhQ-C$_6$F$_5$	189 200	339	1.18	0.163	7
PSBPhQ-H	135 700	347	1.14	0.194	6
PSBPhQ-Cl	144 100	338	1.13	0.190	7
PSBPhQ-C$_6$H$_4$OMe	169 800	341	1.13	0.208	7
PSBPhQ-C$_6$H$_4$NMe$_2$^c	178 900	350	1.11	0.229	7

^a See Scheme 2 for polymer abbreviations. ^b Measurements were performed in THF (1 mL/min). ^c Measurements were performed with 0.2% (w/w) [Bu $_4$ N]Br in THF (1 mL/min). ^d The average number of repeat units (DP) was calculated from M_w and molecular weights of the repeating units. ^e Polydispersity index. ^f Refractive index increment (dn/dc). ^g Hydrodynamic radii (R_H) were derived from QELSBatch software (Wyatt) using cumulant analysis.

(*t*BuPh) $_2$ BQ. The signals for the phenyl groups attached to the polymer backbone, on the other hand, are slightly shifted and strongly broadened due to the atactic nature of the polymer. The close similarity of the spectra between the polymer and the molecular compound, and the absence of signals for the starting material suggest a high degree of functionalization.

Molecular Weight Determination. The new quinolone polymers were subjected to gel permeation chromatography (GPC) analysis in THF for determination of the molecular weights using refractive index (RI) and multiangle laser light scattering (MALLS) detectors (Table 1). Monomodal elution profiles with narrow polydispersities (PDI = 1.11–1.18) were observed for all polymers except for **PSBPhQ-C $_6$ H $_4$ NMe $_2$** . The latter did not elute from the columns, presumably due to strong interactions between the amino groups and the column material. A small amount of [Bu $_4$ N]Br (0.2 wt %) was added to the solvent to effectively prevent polymer aggregation and interaction with the column material, while keeping the change of the solvent refractive index negligible. Under these conditions, a monomodal trace was obtained also for **PSBPhQ-C $_6$ H $_4$ NMe $_2$** . However, the molecular weights determined by GPC–RI detection vs polystyrene standards were generally considerably lower than expected. This is likely a result of deviation from the calibration curve derived from linear polystyrene standards due to significant structural and conformational differences between the quinolone polymers and polystyrene.

We turned to in-line GPC-MALLS (multiangle laser light scattering) detection for the determination of absolute molecular

weights. The molecular weights of all the polymers calculated from MALLS are listed in Table 1. As expected, the organoboron quinolone polymers experience a significant molecular weight increase relative to the starting material, **PSSiMe $_3$** . However, the average number of repeat units (DP) for the quinolone polymers is almost unchanged. Moreover, the polydispersity index (PDI) of the quinolone polymers remains narrow and comparable to that of **PSSiMe $_3$** . Thus, the synthesis of the quinolone polymers, which includes borylation, aryl group transfer, and introduction of the quinolone ligand, occurs without cleavage of the polymer backbone or significant cross-linking.

Thermal Properties and Polymer Stability. Diphenyl-8-hydroxyquinoloneborane (Ph $_2$ BQ) was shown by Wang et al. to possess good stability under ambient conditions.¹¹ However, we found that the long-term environmental stability of thienyl-substituted organoboron quinolone polymers (Scheme 1, **A**) is somewhat limited, as oxidative degradation was observed after prolonged storage under ambient conditions (several weeks). In contrast, when we monitored the ^1H NMR spectra of the *tert*-butylphenyl-substituted quinolone polymers both in wet and oxygenated solvents and as solids in air, no sign of decomposition was found for at least 4 weeks, and the GPC traces were virtually identical to those of the freshly prepared polymer samples. Thus, the stability of the quinolone polymers with phenyl groups on boron is significantly improved relative to those containing electron-rich thiophene groups, and the polymers can easily be handled under ambient conditions for extended periods of time.

The thermal properties of the quinolone polymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 2). DSC analysis revealed high glass transition temperatures (ranging from 210 to 275 $^{\circ}\text{C}$) for the quinolone polymers, and the TGA plots confirmed high thermal stability with decomposition temperatures over 300 $^{\circ}\text{C}$. After the polymers were heated under nitrogen to 800 $^{\circ}\text{C}$, significant amounts of residual material (up to 30%) were observed for all polymers, presumably due to formation of boron-containing ceramic materials, which may also possibly explain the relatively low nitrogen and carbon contents from the elemental analyses of the polymers.²⁴

Luminescence. We have shown previously that the thiophene substituted boron quinolone polymers (**A**, Scheme 1) display green luminescence in solution (~ 508 nm) when excited at their absorption maxima (~ 393 nm).¹⁶ Replacement of the pendent

Table 2. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) Data for the Boron Quinolate Polymers

	PSBPhQ-Bpin	PSBPhQ-C ₆ F ₅	PSBPhQ-H	PSBPhQ-Cl	PSBPhQ-C ₆ H ₄ OMe	PSBPhQ-C ₆ H ₄ NMe ₂
T_g (°C) ^a	275	245	240	238	220	230
T_{dec} (°C) ^b	420	350	385	305	465	375
wt loss (%) ^c	75	85	90	85	72	76

^a Glass transition temperature, onset, second heating curve, 20 °C/min. ^b Decomposition temperature, onset. ^c Total weight loss at 800 °C from thermogravimetric analysis at 20 °C/min.

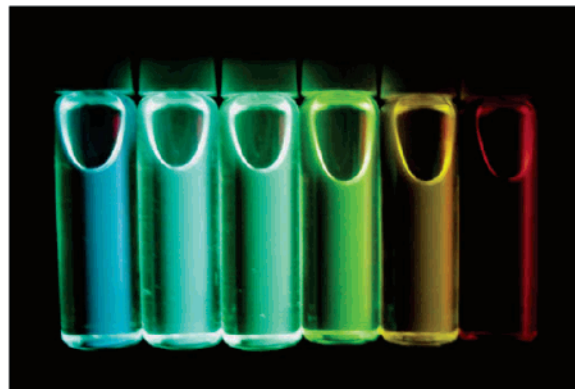
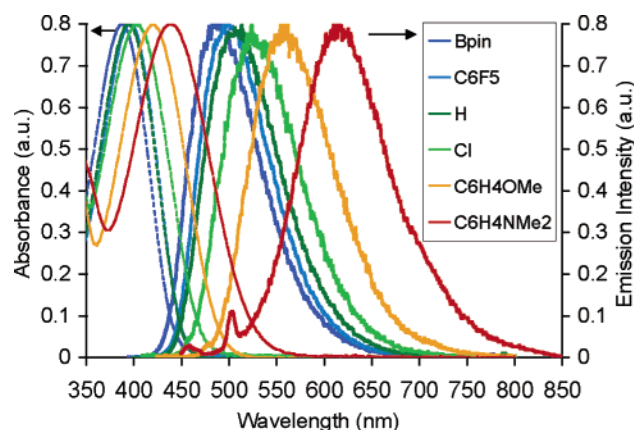


Figure 3. Left: Absorption and emission spectra of the organoboron quinolate polymers **PSBPhQ-X** (refer to Scheme 2 for the polymer structures). The functional group concentration was estimated to ca. 2×10^{-5} M in THF on the basis of the repeat units assuming 100% functionalization; the polymers were excited at the absorption maxima. Right: Photographs of solutions of **PSBPhQ-X** in THF (ca. 2×10^{-3} M) excited with black light at 365 nm (from left to right: X = Bpin, C₆F₅, H, Cl, C₆H₄OMe, C₆H₄NMe₂, respectively).

thiophene substituent with a *tert*-butylphenyl group in the parent polymer **PSBPhQ-H** gives essentially identical optical properties with an absorption maximum at 395 nm and green emission at 507 nm. Thus, the nature of the pendent substituent on boron does not seem to affect the optical properties of these boron quinolate polymers, which is consistent with previous reports that the emission in the organoboron quinolates R₂BQ (R = Et, Ph, Np) is not significantly altered by the R-group but occurs from quinolate-centered states.¹¹

The effect of placing methyl groups at different positions of the quinolato moiety in Ph₂BQ on the emission wavelength has been studied experimentally and by means of theoretical calculations.^{13,14} Moreover, Wang et al. showed in a recent paper that attachment of benzothienyl or naphthyl groups in the 5-position of the quinolate ligand leads to a red-shift in the emission as a result of extended delocalization of the quinolate π -system into the benzothienyl substituent.¹² In a related study, substitution in the 5- and 7-positions of the quinolate ligand of diphenylboron quinolates with extended π systems has been shown to lead to significant red-shifts in the luminescence.¹⁵

Our methodology for the preparation of organoboron quinolate polymers is highly suitable for the tuning of the luminescent properties through modification of the quinolato moiety,^{25,26} because the reactive intermediate **PSBPhBr** is readily accessible and can be treated with a series of different 8-hydroxyquinoline derivatives with varying substitution pattern as shown in Scheme 2. The absorption and emission spectra of this new series of luminescent polymers are displayed in Figure 3, and the photophysical data are summarized in Table 3. The parent polymer **PSBPhQ-H** shows an absorption maximum at 395 nm and green emission at 507 nm, which correlates very well with the previously reported data for Ph₂BQ ($\lambda_{max} = 395$ nm; $\lambda_{em} = 504$ nm) and for (tBuPh)₂BQ ($\lambda_{max} = 395$ nm; $\lambda_{em} = 506$ nm),²² which contains *tert*-butyl groups in the 4-position of the phenyl rings and thus more closely mimics the structure of the polymer. However, the quantum yield for **PSBPhQ-H** of 17% is considerably lower than that reported for Ph₂BQ (30% in CH₂-Cl₂¹¹ and 23% in CHCl₃⁷ at room temperature), while it is almost

Table 3. Photophysical Data of the Organoboron Quinolate Polymers

compound ^a	THF				thin film ^d	
	λ_{max} (nm) ^b	ϵ (L mol ⁻¹ cm ⁻¹) ^b	λ_{em} (nm) ^c	Φ (%)	λ_{max} (nm)	λ_{em} (nm) ^c
PSBPhQ-Bpin	389	4930	486	14	391	490
PSBPhQ-C₆F₅	395	4880	497	28	400	502
PSBPhQ-H	395	3210	507	17	399	510
PSBPhQ-Cl	404	3203	525	6	415	531
PSBPhQ-C₆H₄OMe	419	3970	560	2	426	564
PSBPhQ-C₆H₄NMe₂	439	3980	615	0.1	446	622

^a Refer to Scheme 2 for polymer structures. ^b The functional group concentration was estimated to ca. 2×10^{-5} M in THF on the basis of the repeat units assuming 100% functionalization. ^c Excited at the absorption maxima. ^d Thin films were spin-coated on glass slides from toluene solution.

identical to that of (tBuPh)₂BQ (17%). At this point, the reasons for these differences are not obvious. Substitution at the 5-position with electron-withdrawing and electron-donating groups, respectively, strongly impacts the absorption and emission spectra of the polymers. The emission bands span a range from the blue (486 nm; X = Bpin)²⁷ to the red (615 nm; X = C₆H₄NMe₂), thus covering almost the entire visible spectrum. Intriguingly, we found that when the 5-substituent on the quinolato ligand is changed from electron-withdrawing to electron-donating functionalities, the absorption bands experience a distinct red shift. This observation is in agreement with the results described for related aluminum quinolate derivatives.²⁵ However, a comparison of various AlQ₃ derivatives reported in the literature with the organoboron polymers indicates that the emission from the boron quinolate chromophores is generally blue-shifted by up to 20 nm. For instance, the parent polymer **PSBPhQ-H** emits at 507 nm relative to 526 nm for AlQ₃²⁵ in CH₂Cl₂ solution. This trend is very interesting, in that blue emitting materials, which continue to be in strong demand for device applications, should be more easily accessible using organoboron quinolates. Indeed, the pentafluorophenyl substituted derivative **PSBPhQ-C₆F₅** emits at 497 nm (AlQ₃ derivative: 516 nm) and attachment of a pinacoloborane

HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Two Styragel columns (Polymer Laboratories; 5 μ m Mix-C), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories). Multiangle laser light scattering (MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument either in a batch mode or in-line with the GPC as specified; a Wyatt Optilab refractive index detector operated at 690 nm was used as the concentration detector for in-line GPC-MALLS measurements; differential refractive indices dn/dc were calculated from in-line GPC-MALLS mode with the Wyatt Astra software assuming 100% mass recovery. Dynamic light scattering (DLS) studies were performed using the Wyatt Dawn EOS modified with a Wyatt QELS attachment. Data were collected at an angle of 108° using an avalanche photodiode and an optical fiber and processed with the Wyatt QELSBatch software (cumulant analysis). DSC measurements were performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 system with ca. 10 mg of the polymer and at a scan rate of 20 °C/min. The results reported are from the second heating cycle. The DSC instrument was calibrated with indium ($T_{\text{transition}} = 156.60$ °C) and zinc ($T_{\text{transition}} = 419.47$ °C) for temperature and indium for enthalpy change. TGA measurements were performed on a Perkin-Elmer Pyris 1 Thermogravimetric analyzer at a scan rate of 20 °C/min and up to 800 °C. The TGA instrument was calibrated with alumel (Curie point: 154.2 °C) and perkalloy (Curie point: 596 °C). Thin films of the polymers were prepared on glass slides with ca. 5–10 mg/mL of polymer in toluene (data in Table 3) or chlorobenzene (TOC picture) using a Specialty Coatings Systems (SCS) G3P-8 Spin-Coater (0–2000 rpm over 25 s, 2000–5000 rpm over 25 s, and 5000–0 rpm over 25 s). Solution UV–vis measurements were performed in THF using a Varian Cary 500 scan UV–vis–NIR spectrophotometer with a 1 cm quartz cuvette. Absorbances (ϵ) for the polymers are reported per repeating unit assuming 100% chromophore functionalization. The fluorescence data were measured on a Varian Cary Eclipse fluorescence spectrophotometer with the same solutions as those used in the UV–vis measurements. Anthracene was used as the standard for determination of the quantum yields. The quantum yield of anthracene ($\Phi = 0.30$ in THF) was adopted from the *Handbook of Photochemistry*,³³ and the concentration of anthracene in THF was 5×10^{-6} M. Photophysical data for thin films of the polymer on glass slides were obtained on the same instruments. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ; combustion aid was added in all cases.

Caution! BBr₃ is toxic and highly corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide.

Synthesis of PSBPhBr. PSSiMe₃ (1.0 g, 5.67 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (1.70 g, 6.80 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to –20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (2.53 g, 8.51 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture was slowly warmed up to room temperature and stirred for another 4 h. The solution was then concentrated to ~2 mL and precipitated into a large excess of hexanes. **PSBPhBr** was recovered as a white solid by freeze-drying from benzene (1.6 g, 86%). ¹H NMR (499.893 MHz, CDCl₃): δ = 7.74 (Ph–H_{2,6}; 'Ph–H_{2,6}), 7.35 ('Ph–H_{3,5}), 6.67, 6.55, 6.41 (Ph–H_{3,5}), 2.2–1.2 (polymer backbone), 1.28 (CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): δ = 156.5 ('Ph–C₄), 150.2 (Ph–C₄), 137.7 (Ph–C_{2,6}; 'Ph–C_{2,6}), 137.0 ('Ph–C₁), 127.4 (Ph–C_{3,5}), 125.0 ('Ph–C_{3,5}), 46–41 (polymer backbone), 35.3 (CMe₃), 31.3 (CMe₃). Ph–C₁ not observed. ¹¹B NMR (160.380 MHz, CDCl₃): δ = 58 ($w_{1/2} = 3520$ Hz).

Synthesis of PSBPhQ-H. PSSiMe₃ (0.33 g, 1.89 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.57 g, 2.27 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to –20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (0.86 g, 2.91 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture

was slowly warmed up to room temperature and stirred for another 4 h. 8-Hydroxyquinoline (1.10 g, 7.56 mmol) and triethylamine (1.53 g, 15.1 mmol) in 10 mL of CH₂Cl₂ were then added slowly, and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. **PSBPhQ-H** was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (0.49 g, 66% yield). ¹H NMR (499.893 MHz, CDCl₃): δ = 8.6–5.6 (very br, all aromatic H's), 2.4–0.8 (polymer backbone and CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): δ = 158.9 (Q–C₈), 149.4 ('Ph–C₄), 144.3 (Ph–C_{1,4}; 'Ph–C₁), 139.5 (Q–C_{2/4}), 138.5 (Q–C_{2/4}), 137.4 (Q–C₉), 132.1 (Ph–C_{2,6}; 'Ph–C_{2,6}; Q–C₆), 128.3 (Q–C₁₀), 127.1 (Ph–C_{3,5}), 124.6 (Ph–C_{3,5}), 123.1 (Q–C₃), 112.2 (Q–C₅), 109.2 (Q–C₇), 46–38 (polymer backbone), 34.6 (CMe₃), 31.7 (CMe₃). ¹¹B NMR (160.380 MHz, CDCl₃): δ = 7 ($w_{1/2} = 570$ Hz). GPC-MALLS (THF, 1 mL/min): $M_n = 119\,000$, $M_w = 135\,700$, PDI = 1.14, $dn/dc = 0.194$ mL/g, $R_H = 6$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 240$ °C; TGA (20 °C/min, onset): $T_{\text{dec}} = 385$ °C, 90% total weight loss. UV–vis (2.1×10^{-5} M in THF): $\lambda_{\text{max}} = 395$ nm, $\epsilon = 3210$ cm^{–1} M^{–1}. Fluorescence: $\lambda_{\text{exc}} = 395$ nm, $\lambda_{\text{em}} = 507$ nm, $\Phi = 17\%$. Anal. Calcd for C₂₇H₂₆BNO: C, 82.87; H, 6.70; N, 3.58. Found: C, 81.77; H, 6.22; N, 3.06.

Synthesis of PSBPhQ-Cl. PSSiMe₃ (0.33 g, 1.89 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.57 g, 2.27 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to –20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (0.86 g, 2.91 mmol) in 15 mL of CH₂Cl₂ was slowly added and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 5-Chloro-8-hydroxyquinoline (1.36 g, 7.56 mmol) and triethylamine (1.53 g, 15.1 mmol) in 10 mL of CH₂Cl₂ were then added slowly and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. **PSBPhQ-Cl** was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (0.52 g, 65% yield). ¹H NMR (499.893 MHz, CDCl₃): δ = 8.7–5.6 (very br, all aromatic H's), 2.4–0.6 (polymer backbone and CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): δ = 158.0 (Q–C₈), 149.8 ('Ph–C₄), 143.3 (Ph–C_{1,4}; 'Ph–C₁), 140.4 (Q–C_{2/4}), 137.8 (Q–C₉), 136.2 (Q–C_{2/4}), 132.0 (Ph–C_{2,6}; 'Ph–C_{2,6}; Q–C₆), 127.0 (Ph–C_{3,5}), 126.4 (Q–C₁₀), 124.7 ('Ph–C_{3,5}; Q–C₃), 115.1 (Q–C₅), 109.6 (Q–C₇), 46–38 (polymer backbone), 34.6 (CMe₃), 31.7 (CMe₃). ¹¹B NMR (160.380 MHz, CDCl₃): δ = 8 ($w_{1/2} = 560$ Hz). GPC-MALLS (THF, 1 mL/min): $M_n = 127\,600$, $M_w = 144\,100$, PDI = 1.13, $dn/dc = 0.190$ mL/g, $R_H = 7$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 238$ °C; TGA (20 °C/min, onset): $T_{\text{dec}} = 305$ °C, 85% total weight loss. UV–vis (2.2×10^{-5} M in THF): $\lambda_{\text{max}} = 404$ nm, $\epsilon = 2310$ cm^{–1} M^{–1}. Fluorescence: $\lambda_{\text{exc}} = 404$ nm, $\lambda_{\text{em}} = 525$ nm, $\Phi = 6\%$. Anal. Calcd for C₂₇H₂₅BClNO: C, 76.17; H, 5.92; N, 3.29. Found: C, 75.97; H, 5.73; N, 2.96.

Synthesis of PSBPhQ-C₆H₄OMe. PSSiMe₃ (0.50 g, 2.84 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.78 g, 3.12 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to –20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (1.05 g, 3.55 mmol) in 15 mL of CH₂Cl₂ was slowly added and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 5-(4-Methoxyphenyl)-8-hydroxyquinoline (0.86 g, 3.41 mmol) and triethylamine (0.86 g, 8.52 mmol) in 10 mL of CH₂Cl₂ were then added slowly and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. **PSBPhQ-C₆H₄OMe** was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (1.15 g, 82% yield). ¹H NMR (499.893 MHz, CDCl₃): δ = 9.2–5.8 (very br, all aromatic H's), 3.8 (OMe), 2.4–0.6 (polymer backbone and CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): δ = 159.1 (Q–C₈), 158.2 ('Ph–C₁), 149.3 ('Ph–C₄), 144.2 (Ph–C_{1,4}; 'Ph–C₁), 139.5 (Q–C_{2/4}), 137.6 (Q–C_{2/4,9}), 132.0 (Ph–C_{2,6}; 'Ph–C_{2,6}; Q–C₆), 130.8 ('Ph–C_{3,4,5}), 126.8 (Ph–C_{3,5}; Q–C₁₀), 125.6 (Q–C₅), 124.7 ('Ph–C_{3,5}), 123.0 (Q–C₃), 114.4 ('Ph–C_{2,6}), 109.1 (Q–C₇), 55.5 (OMe), 46–38 (polymer backbone), 34.5 (CMe₃), 31.7

(*CMe*₃). ¹¹B NMR (160.380 MHz, CDCl₃): $\delta = 7$ ($w_{1/2} = 410$ Hz). GPC-MALLS (THF, 1 mL/min): $M_n = 150\,700$, $M_w = 169\,800$, PDI = 1.13, $dn/dc = 0.208$ mL/g, $R_H = 7$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 220$ °C; TGA (20 °C/min, onset): $T_{dec} = 465$ °C, 72% total weight loss. UV-vis (2.0 $\times 10^{-5}$ M in THF): $\lambda_{max} = 419$ nm, $\epsilon = 3790$ cm⁻¹ M⁻¹. Fluorescence: $\lambda_{exc} = 419$ nm, $\lambda_{em} = 560$ nm, $\Phi = 2\%$. Anal Calcd for C₃₄H₃₂BNO₂: C, 82.09; H, 6.48; N, 2.82. Found: C, 81.57; H, 6.29; N, 2.46.

Synthesis of PSBPhQ-C₆H₄NMe₂. PSSiMe₃ (0.50 g, 2.84 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.78 g, 3.12 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to -20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (1.10 g, 3.69 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 5-(4-Dimethylaminophenyl)-8-methoxyquinoline (0.95 g, 3.41 mmol) in 10 mL of CH₂Cl₂ was then added slowly and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. PSBPhQ-C₆H₄NMe₂ was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (1.15 g, 79% yield). ¹H NMR (499.893 MHz, CDCl₃): $\delta = 8.8$ –5.6 (very br, all aromatic H's), 3.0 (NMe₂), 2.4–0.4 (polymer backbone and *CMe*₃). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 157.8$ (Q-C8), 149.9 (Ph-C4), 149.1 (Ph-C1), 144.4 (Ph-C1,4; Ph-C1), 139.5 (Q-C2,4), 137.7 (Q-C2,4,9), 132.1 (Ph-C2,6; Ph-C2,6; Q-C6), 130.5 (Ph-C3,5), 126.6 (Ph-C3,5; Ph-C4; Q-C5,10), 124.5 (Ph-C3,5), 123.0 (Q-C3), 112.9 (Ph-C2,6), 109.1 (Q-C7), 40.8 (NMe₂), 46–38 (polymer backbone), 34.5 (*CMe*₃), 31.7 (*CMe*₃). ¹¹B NMR (160.380 MHz, CDCl₃): $\delta = 7$ ($w_{1/2} = 350$ Hz). GPC-MALLS (1 mL/min, 0.2% Bu₄NBr in THF): $M_n = 161\,200$, $M_w = 178\,900$, PDI = 1.11, $dn/dc = 0.229$ mL/g, $R_H = 7$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 230$ °C; TGA (20 °C/min, onset): $T_{dec} = 375$ °C, 76% total weight loss. UV-vis (2.1 $\times 10^{-5}$ M in THF): $\lambda_{max} = 439$ nm, $\epsilon = 3980$ cm⁻¹ M⁻¹. Fluorescence: $\lambda_{exc} = 439$ nm, $\lambda_{em} = 615$ nm, $\Phi = 0.1\%$. Anal. Calcd for C₃₅H₃₅BNO₂: C, 82.53; H, 6.91; N, 5.49. Found: C, 81.28; H, 6.66; N, 5.11.

Synthesis of PSBPhQ-C₆F₅. PSSiMe₃ (0.30 g, 1.70 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.45 g, 1.79 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to -20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (0.58 g, 1.96 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 5-Pentafluorophenyl-8-methoxyquinoline (0.61 g, 1.87 mmol) in 10 mL of CH₂Cl₂ was then added slowly, and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. PSBPhQ-C₆F₅ was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (0.81 g, 85% yield). ¹H NMR (499.893 MHz, CDCl₃): $\delta = 8.8$ –5.8 (very br, all aromatic H's), 2.4–0.6 (polymer backbone and *CMe*₃). ¹⁹F NMR (470.365 MHz, CDCl₃): $\delta = -140.8$ (F2,6), -155.5 (F4), -162.5 (F3,5). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 160.4$ (Q-C8), 149.8 (Ph-C4), 146–142 (Ph-C1,4; Ph-C1; Ph-C2,4,6), 140.1 (Q-C2,4), 139–137 (Ph-C3,5), 137.2 (Q-C9), 136.1 (Q-C2,4,6), 131.9 (Ph-C2,6; Ph-C2,6), 127.0 (Ph-C3,5; Q-C10), 124.7 (Ph-C3,5; Q-C3), 112.4 (Ph-C1), 109.0 (Q-C7), 108.5 (Q-C5), 46–38 (polymer backbone), 34.5 (*CMe*₃), 31.5 (*CMe*₃). ¹¹B NMR (160.380 MHz, CDCl₃): $\delta = 7$ ($w_{1/2} = 560$ Hz). GPC-MALLS (THF, 1 mL/min): $M_n = 161\,000$, $M_w = 189\,200$, PDI = 1.18, $dn/dc = 0.163$ mL/g, $R_H = 7$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 245$ °C; TGA (20 °C/min, onset): $T_{dec} = 350$ °C, 85% total weight loss. UV-vis (1.8 $\times 10^{-5}$ M in THF): $\lambda_{max} = 395$ nm, $\epsilon = 4880$ cm⁻¹ M⁻¹. Fluorescence: $\lambda_{exc} = 395$ nm, $\lambda_{em} = 497$ nm, $\Phi = 28\%$. Anal. Calcd for C₃₃H₂₅BF₅NO: C, 71.11; H, 4.52; N, 2.51. Found: C, 72.05; H, 4.74; N, 2.27.

Synthesis of PSBPhQ-Bpin. PSSiMe₃ (0.30 g, 1.70 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (0.45 g, 1.79 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The

mixture was stirred under nitrogen for 12 h and then cooled down to -20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (0.58 g, 1.96 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 5-Pinacolato-8-methoxyquinoline (0.58 g, 2.04 mmol) in 10 mL of CH₂Cl₂ was then added slowly, and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. PS-BPhPinQ was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (0.60 g, 68% yield). ¹H NMR (499.893 MHz, CDCl₃): $\delta = 9.2$ –5.8 (very br, all aromatic H's), 2.4–0.6 (polymer backbone, *CMe*₃ and *Me*₂CC*Me*₂). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 162.1$ (Q-C8), 149.0 (Ph-C4), 146–141 (Ph-C1,4; Ph-C1; Q-C6), 140.2 (Q-C2,4), 137.6 (Q-C9), 132.1 (Ph-C2,6; Ph-C2,6; Q-C10), 127.3 (Ph-C3,5), 124.5 (Ph-C3,5; Q-C3), 111.6 (Q-C5), 109.2 (Q-C7), 83.6 (*Me*₂CC*Me*₂), 46–38 (polymer backbone), 34.5 (*CMe*₃), 31.5 (*CMe*₃), 25.2 (*Me*₂CC*Me*₂). ¹¹B NMR (160.380 MHz, CDCl₃): $\delta = 24$ ($w_{1/2} = 850$ Hz), 7 ($w_{1/2} = 520$ Hz). GPC-MALLS (THF, 1 mL/min): $M_n = 150\,600$, $M_w = 172\,700$, PDI = 1.15, $dn/dc = 0.177$ mL/g, $R_H = 7$ nm. DSC (20 °C/min, onset, second heating curve): $T_g = 245$ °C; TGA (20 °C/min, onset): $T_{dec} = 350$ °C, 85% total weight loss. UV-vis (2.2 $\times 10^{-5}$ M in THF): $\lambda_{max} = 389$ nm, $\epsilon = 4930$ cm⁻¹ M⁻¹. Fluorescence: $\lambda_{exc} = 389$ nm, $\lambda_{em} = 486$ nm, $\Phi = 14\%$. Anal. Calcd for C₃₃H₃₇B₂NO₃: C, 76.62; H, 7.21; N, 2.71. Found: C, 76.07; H, 6.92; N, 2.44.

Synthesis of PSBPhQ-H-co-PSSiMe₃. PSSiMe₃ (0.50 g, 2.84 mmol SiMe₃) was dissolved in 20 mL of CH₂Cl₂, and a solution of BBr₃ (71 mg, 0.28 mmol) in 10 mL of CH₂Cl₂ was added dropwise. The mixture was stirred under nitrogen for 12 h and then cooled down to -20 °C. A solution of 1-trimethylstannyl-4-tert-butylbenzene (89 mg, 0.29 mmol) in 15 mL of CH₂Cl₂ was slowly added, and the mixture was slowly warmed up to room temperature and stirred for another 4 h. 8-Hydroxyquinoline (0.165 g, 1.14 mmol) and triethylamine (0.29 g, 2.84 mmol) in 10 mL of CH₂Cl₂ were then added slowly, and the mixture was stirred for 12 h prior to removal of volatile materials under vacuum. PSBPhQ-H-co-PSSiMe₃ was recovered by repeated precipitation from THF into methanol and dried at 60 °C under high vacuum overnight (0.40 g, 80% yield). ¹H NMR (499.893 MHz, CDCl₃): $\delta = 8.5$ –5.6 (all aromatic H's), 2.4–1.0 (polymer backbone and *CMe*₃), 0.25 (SiMe₃). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 159.2$ (Q-C8), 149.4 (Ph-C4), 146.3 (SiPh-C4), 144.1 (Ph-C1,4; Ph-C1), 139.3 (Q-C2,4), 138.5 (Q-C2,4), 137.5 (Q-C9), 137.2 (SiPh-C1), 134.8 (Q-C6), 133.3 (Ph-C2, 6; SiPh-C2,6), 131.9 (Ph-C2,6), 128.5 (Q-C10), 127.4 (Ph-C3,5; SiPh-C3,5), 124.6 (Ph-C3,5), 122.8 (Q-C3), 112.0 (Q-C5), 109.8 (Q-C7), 47–40 (polymer backbone), 34.5 (*CMe*₃), 31.7 (*CMe*₃). ¹¹B NMR (160.380 MHz, CDCl₃): $\delta = 9$ ($w_{1/2} = 1350$ Hz). GPC-MALLS (1 mL/min, THF): $M_n = 59\,660$, $M_w = 68\,860$, PDI = 1.15, $dn/dc = 0.148$ mL/g, $R_H = 4$ nm. UV-vis (2.9 $\times 10^{-5}$ M in THF, assuming 10% functionality): $\lambda_{max} = 398$ nm, $\epsilon = 2420$ cm⁻¹ M⁻¹. Fluorescence: $\lambda_{exc} = 398$ nm, $\lambda_{em} = 508$ nm, $\Phi = 18\%$. Anal. Calcd for C₁₂₆H₁₇₀Si₉BNO: C, 76.50; H, 8.66; N, 0.71. Found: C, 76.36; H, 8.59; N, 0.30.

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