Macromolecules

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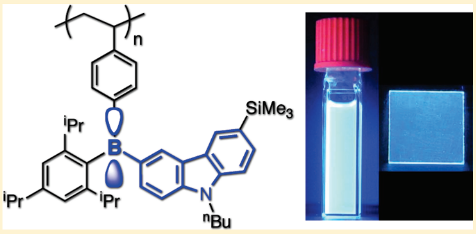
Synthesis and Characterization of Luminescent Polystyrene Derivatives with Sterically Protected Fluorenyl- and Carbazolylborane Moieties

Kshitij Parab, Ami Doshi, Fei Cheng, and Frieder Jäkle*

Department of Chemistry, Rutgers University—Newark, 73 Warren Street, Newark, New Jersey 07102, United States

S *Supporting Information*

ABSTRACT: Polystyrene was functionalized with luminescent fluorenyl- and carbazolylborane pendant moieties. Because of an interaction of the empty p orbital on boron with the extended π-systems of fluorene or carbazole, the resulting polymeric materials exhibit intense blue emission with maxima in the range 390−420 nm. The solution quantum yields were 65% for the fluorene derivative and 68 and 11% for two different carbazole derivatives, respectively. The stability of the borylated polymers was enhanced by attachment of a bulky triisopropylphenyl group to each of the boron centers. Thus, the polymers were found to be stable for a period of over 1 month. Thermal stability up to ca. 250 °C was confirmed by thermogravimetric analysis.



INTRODUCTION

Interaction of the empty boron-centered p-orbital in tricoordinate organoboranes with a conjugated π-system is known to give rise to interesting optical and electronic properties.[1] Various research groups have explored this p−π interaction in organoboranes with respect to its potential for applications, for instance, as emissive materials for OLEDs, in linear and nonlinear optics, and as sensors for nucleophiles.[2] Polymeric materials have also attracted much interest in recent years.[3,4] Following the pioneering work by Chujo and co-workers,[5] a broad range of main-chain type luminescent organoborane polymers have been developed over the past decade.[6] The attachment of organoborane chromophores as pendent or terminal groups to polyolefins and other chain growth polymers has more recently attracted interest since well-defined and more complex polymer architectures can more easily be realized.[4,7] For instance, Fraser and co-workers demonstrated that functionalization of poly(lactic acid) (PLA) with boron diketonate chromophores leads to room temperature phosphorescent materials that are useful for tumor imaging,[8] Chujo and co-workers reported on the functionalization of block copolymers with highly emissive BODIPY functionalities,[9] and our group introduced amphiphilic block copolymers with organoboron quinolato moieties that form micellar solutions in water.[10] In all these cases, the boron center is tetracoordinate and the emissive properties are dominated by the organic chromophore.

In earlier work, we showed that attachment of tricoordinate bithiophene(mesityl)borane chromophores to polystyrene results in fluorescent polymers with substitution-dependent absorption and emission characteristics.[11] Moreover, the presence of the tricoordinate organoborane moieties can be exploited for the fluorescent detection of fluoride and cyanide, the binding of which leads to quenching or a change of the emission color that results in turn-on of fluorescence. We also demonstrated that with ferrocene as one of the pendent organoborane substituents, polymers that show interesting redox behavior can be obtained.[12] In the course of these studies it became apparent that the stability of these boron-containing polymers to oxygen and moisture can be significantly enhanced by replacing 2,4,6-trimethylphenyl (Mes) groups with more sterically demanding 2,4,6-triisopropylphenyl (Tip) groups.[13] Here we report the synthesis and characterization of a new class of triarylborane polymers with improved stability and favorable luminescence characteristics, as a result of boron substitution with fluorene or carbazole derivatives as chromophores and the presence of sterically demanding Tip groups as protective groups.

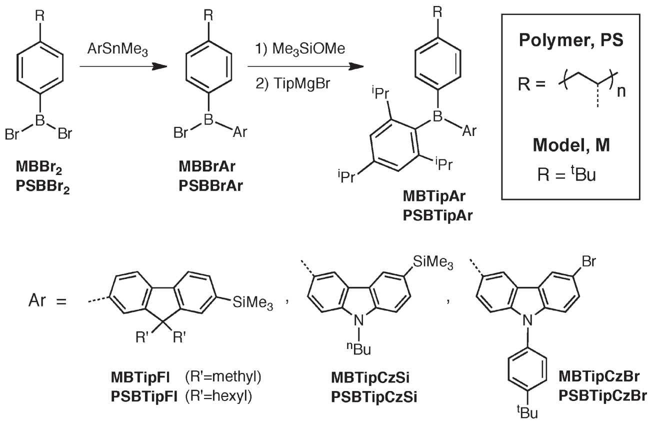
RESULTS AND DISCUSSION

A postpolymerization modification strategy similar to the one introduced earlier for the preparation of ferrocenylborane-substituted polymers[12] was chosen for the functionalization of polystyrene with the desired chromophoric triarylborane moieties. Polystyrene was decorated with BBr_2 groups using a silicon−boron exchange protocol as previously reported.[14] Then, one of the bromines on each of the BBr_2 groups in $PSBBr_2$ was replaced by reaction with a trimethylstannyl-substituted fluorene or carbazole derivative (Scheme 1). The second bromine was then exchanged for a methoxy group by reaction with Me_3SiOMe, and the resulting polymer species PSB(Ar)OMe were treated with TipMgBr, leading to formation of the desired

Received: February 15, 2011
Revised: June 24, 2011
Published: July 15, 2011

dx.doi.org/10.1021/ma200358s | *Macromolecules* 2011, 44, 5961–5967

Scheme 1. Synthesis of Polymers with Pendent Fluorescent Organoborane Moieties (Tip = 2,4,6-Triisopropylphenyl)



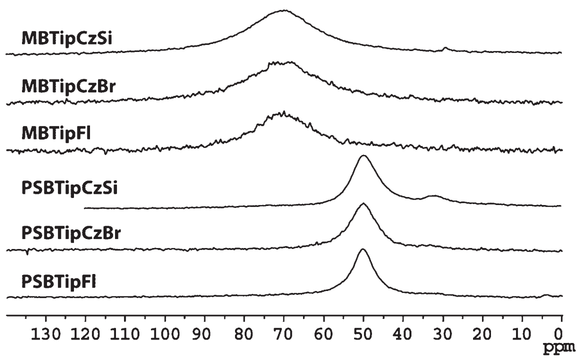


Figure 1. Comparison of ^{11}B NMR spectra of polymers and model compounds.

triarylborane groups in PSBTipAr. Similar methods were used to synthesize molecular model compounds MBTipAr that mimic one of the polymer repeat unit (Scheme 1). The model compounds and polymers were purified by column chromatography, and the polymer solutions were subsequently precipitated first into methanol and then from toluene into ethanol.

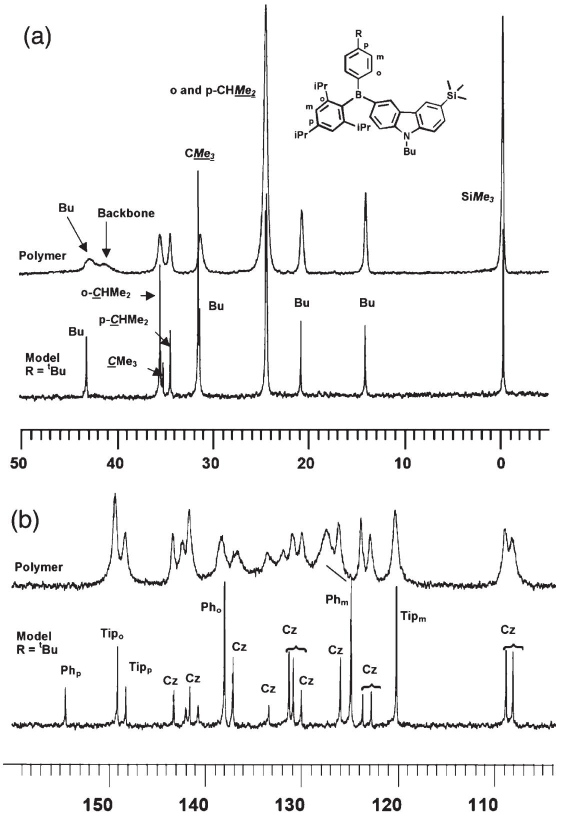


Figure 2. ^{13}C NMR overlay of PSBTipCzSi and MBTipCzSi. Key: (a) aliphatic region; (b) aromatic region.

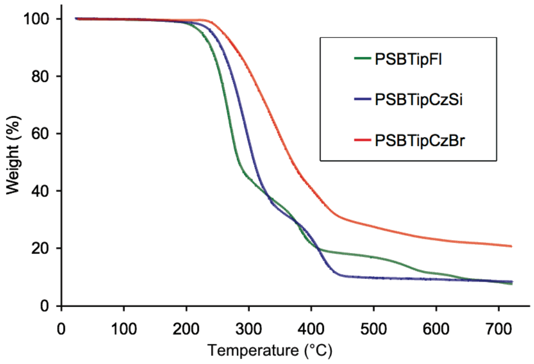


Figure 3. Thermogravimetric analysis (TGA) plots of polymers PSBTipAr.

Both the polymers as well as model compounds were characterized by multinuclear NMR spectroscopy. The ^{11}B NMR shifts for the model compounds were in the expected range for triarylboron containing compounds with a very broad peak at ~70 ppm (Figure 1). A significant upfield shift to ~50 ppm and narrowing of the signals was evident for the polymers, which may be due to relaxation phenomena and shielding effects of neighboring groups in the polymer chain, as suggested by our previous studies on related triarylborane polymers.[11,12] The presence of small shoulder peaks in the ^{11}B NMR spectra of the polymers around 30−40 ppm was observed in some cases, possibly due to the presence of a small amount of boronic acid ($ArB(OH)_2$) or borinic acid (Ar_2BOH) functionalities as a result of incomplete substitution with the functional aryl groups (Figure 1). The peaks in the ^{1}H NMR spectra of the polymers were broad and not very informative, but integration of the protons in the aromatic and aliphatic regions was close to the calculated number of protons for each repeat unit of the polymer. Also, the ^{13}C NMR spectra of the polymers matched well with those of the model compounds, thus supporting a structure in which the fluorene or carbazole aryl groups as well as the 2,4,6-triisopropylphenyl moieties are attached to boron (Figure 2).

The molecular weights from GPC-RI analysis in THF relative to PS standards were higher than that of the silylated precursor (M_n = 21100, M_w = 23800, PDI = M_w/M_n = 1.13), but in the range expected considering the presence of much larger side groups (PSBTipFl, M_w = 42800, M_n = 36900, PDI = 1.16; PSBTipCzSi, M_n = 38300, M_w = 44000, PDI = 1.15; PSBTipCzBr, M_n = 32500, M_w = 37200, PDI = 1.14). The polydispersity increased only slightly; however, a small high molecular weight shoulder ($\%_{Area}$ = 5−20) was observed in all cases, which corresponds to about twice the molecular weight of the main peak ($\%_{Area}$ = 80−95), indicating that homocoupling at the end

Table 1. Comparison of Photophysical Data of Polymers and Model Compounds in Solution and as Thin Films

polymer	PSBTipFl	PSBTipCzSi	PSBTipCzBr
λ_{abs} [nm][a]	332 (sh), 345	285, 305, 345	271, 306, 342
λ_{em} [nm][b]	422	397	392
Φ_F[c]	0.65[e]	0.68	0.11[e]
λ_{abs} film [nm][d]	332, 346	345	312, 340
λ_{em} film [nm][b,d]	396	392	387
model	**MBTipFl**	**MBTipCzSi**	**MBTipCzBr**
λ_{abs} [nm][a]	330 (sh), 341	286, 304, 344	269, 305, 341
λ_{em} [nm][b]	390	410	391
Φ_F[c]	0.80	0.72	0.12[e]

[a] Data were acquired in CH_2Cl_2 solution unless noted otherwise. [b] Excited at the longest wavelength absorption maxima. [c] Anthracene used as a standard. [d] Thin film cast from toluene. [e] Measured in THF.

groups may have occurred to a small extent. An alternative explanation is that substitution of the boron centers during the attachment of the bulky Tip group was incomplete. As mentioned above, the presence of small shoulder peaks in the ^{11}B NMR spectra could be due to boronic acid ($ArB(OH)_2$) or borinic acid (Ar_2BOH) functionalities, which might lead to the formation of chemical cross-links giving rise to a small fraction of higher molecular weight polymers.

Thermogravimetric analysis (TGA) data indicated that the polymers are thermally stable up to ~250 °C, above which multistep decomposition was observed. The residual weights at 750 °C were 7−9% for PSBTipFl and PSBTipCzSi, while the polymer PSBTipCzBr showed a residual weight of 23% (Figure 3). The thermal stability and the residual ceramic yields of the polymers are comparable to those of the previously reported (bithiophene)mesitylborane-substituted polymers,[11] thus indicating that the presence of the bulkier Tip group has little to no effect on the thermal stability of the newly synthesized fluorene and carbazole containing polymer.

However, the new polymers and the corresponding model compounds show much improved stability to oxygen and moisture in both solution as well as the solid state. For example, in C_6D_6 or $CDCl_3$, the model compound MBTipCzSi and polymer PSBTipCzSi are stable for a period of ca. 1 month and in the solid state they are stable toward both oxygen and moisture for over 3 months. A similar trend is observed for the other model compounds and polymers, thus indicating that the presence of a more sterically demanding Tip group and a chromophore like the fluorene or carbazole moiety significantly enhances the stability in comparison to polymers[11] that contain bithiophenes as the chromophore and mesityl groups for steric protection.

The longest wavelength absorption maxima of the polymers in CH_2Cl_2 solution are found in a narrow range from ca. 340 to 345 nm (Table 1, Figure 4). The spectrum of PSBTipFl shows a single absorption maximum at 345 nm with a high-energy shoulder at 332 nm, whereas for PSBTipCzSi we find multiple bands at 285, 305, 345 nm and for PSBTipCzBr at 271, 306, 342 nm. The polymer spectra generally resemble those of the respective model compounds. For example, PSBTipFl and MBTipFl display absorption maxima at 345 and 341 nm, respectively. Thin film absorption data also show very similar features to those of the polymer solutions in CH_2Cl_2 (Figure S1, Supporting Information).

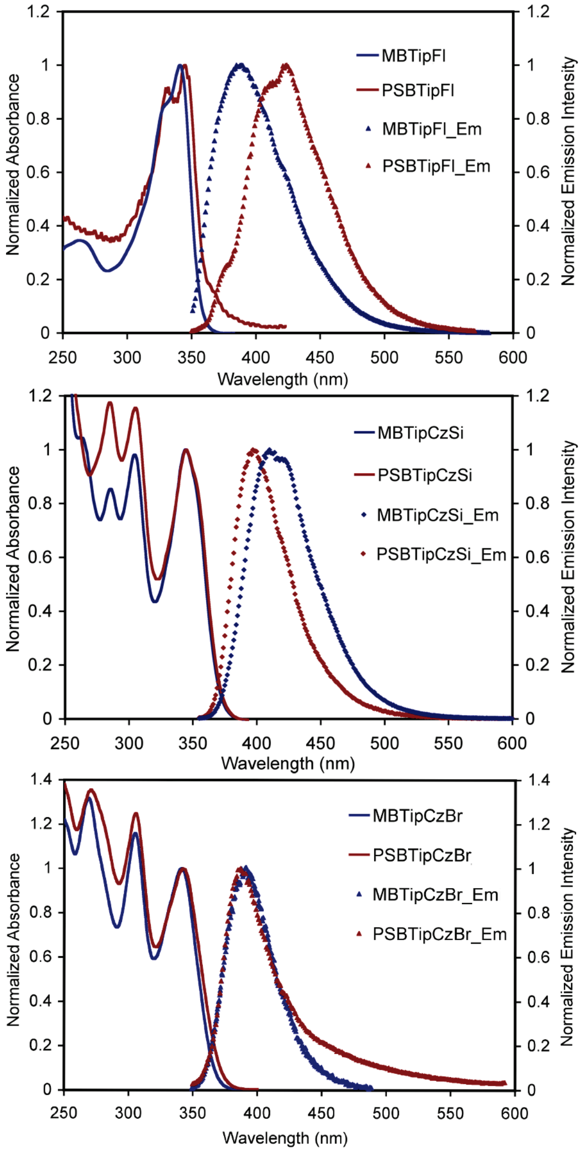


Figure 4. Comparison of the normalized absorption and emission spectra of (top) MBTipFl and PSBTipFl, (middle) MBTipCzSi and PSBTipCzSi, and (bottom) MBTipCzBr and PSBTipCzBr in CH_2Cl_2 Solution.

Upon excitation at the longest wavelength absorption maxima, the polymers and their respective model compounds emit bright blue light in solution as well as in the thin film state (Figure 4, Figure S1, Supporting Information). The emission of thin films of PSBTipCzBr is similar to that of polymer solutions in CH_2Cl_2, and both are almost unchanged in comparison to that of the molecular model compound MBTipCzBr. This suggests that the chromophore units act independently and excimer formation is not favorable. In contrast, the emission spectra of the other polymers and model compounds show some interesting trends. While the emission maximum for the polymer PSBTipFl in CH_2Cl_2 is red-shifted by ca. 30 nm relative to that of the model compound MBTipFl, upon casting a thin film the emission shifts back to higher energy giving rise to a profile similar to that of the molecular species MBTipFl. These observations are attributed to the generation of excimer states for PSBTipFl that result from attachment of planar π-conjugated side groups to the atactic

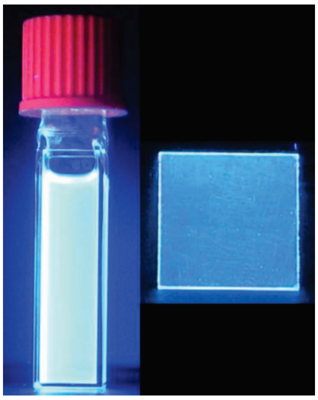


Figure 5. Photographs illustrating the blue emission of a CH_2Cl_2 solution and of a thin film of PSBTipCzSi on a glass slide (excited with a hand-held UV lamp at λ_{max} = 365 nm).

polymer backbone. Formation of multiple excimer states has, for example, been reported for poly(*N*-vinylcarbazole) and poly(vinylnaphthalene).[15] Packing effects in thin films of PSBTipFl may lead to orientations of the side groups that prevent effective formation of these excimer states, resulting in the observed blue-shift of the emission. For the trimethylsilyl-functionalized carbazole compounds, PSBTipCzSi and MBTipCzSi, a different behavior was observed in that the polymer emission (λ_{em} = 397 nm) is blue-shifted by ~13 nm in comparison to that of the model compound (λ_{em} = 410 nm) and the emission of a polymer thin film (λ_{em} = 392 nm) is further blue-shifted by ~5 nm. The blue-shift of the emission of the polymer PSBTipCzSi relative to its model system could also be a result of the particular orientation of neighboring carbazole groups in the polymer chain. Another possibility is that steric effects of the polymer chains prevent optimal overlap of the boron-centered empty p-orbital with the organic π-system, leading to a less conjugated system.

The fluorene and silylcarbazole polymers and model compounds emit light with very high quantum yields of ca. 65–80% (Table 1, see also Figure 5). These values are comparable to those of the bithiopheneborane derivatives reported previously (~75% for the models and ~66% for the polymers[11]). The significantly lower quantum yield of PSBTipFl in comparison to MBTipFl might be due to randomly distributed traps in the polymer chains. PSBTipCzBr and the model MBTipCzBr show comparatively much lower quantum yields of ca. 11–12%. The lower quantum yields are attributed to the presence of the bromine atoms, which induce quenching of fluorescence due to heavy atom effects.

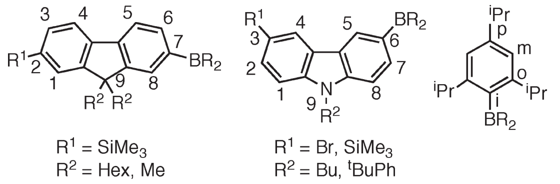
CONCLUSIONS

In summary, we have prepared new organoborane polymers that feature fluorene or carbazole moieties as the chromophores, while steric protection of the boron centers is provided by bulky Tip groups. The presence of the Tip groups imparts good stability, to a much greater extent than what was observed previously for related mesityl-substituted polymers. The polymers are well soluble in common organic solvents such as CH_2Cl_2, THF, and toluene. Both, polymers as well as model compounds emit in the blue region of the spectrum and show high quantum yields, except for the compounds that have a bromo substituent attached to the chromophore. Our results suggest that these compounds could be of interest for OLED applications as well as in the recognition of anions on the basis of changes in the fluorescence characteristics upon anion binding.

EXPERIMENTAL SECTION

Materials and Methods. *n*-BuLi (1.6 M in hexanes) and BBr_3 (99.9%) were purchased from Acros, Me_3SiOMe (98%) from Aldrich, and Me_3SnCl (98%) from Strem Chemicals. BBr_3 was further purified by vacuum distillation. Caution! *BBr_3 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. The compounds 2,4,6-triisopropylphenylmagnesium bromide,[16] 2,7-dibromo-9,9-dihexylfluorene,[17] 2-bromo-7-trimethylsilyl-9,9-dimethylfluorene,[18] 2-trimethylstannyl-7-trimethylsilyl-9,9-dimethylfluorene, 2-trimethylstannyl-7-trimethylsilyl-9,9-dihexylfluorene, 3-bromo-6-trimethylsilyl-9-*n*-butylcarbazole,[19] and 3,6-dibromo-9-(4-*tert*-butylphenyl)carbazole[20] were synthesized according to literature procedures. Poly(4-trimethylsilylstyrene) (**PSSi**) of M_n = 21 100; M_w = 23 800; PDI = 1.13 (GPC-RI) was prepared as previously reported.[14] All reactions were carried out under inert atmosphere using Schlenk techniques or a glovebox (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH_2 and degassed via several freeze–pump–thaw cycles.

Instrumentation. All 499.9 MHz ^{1}H, 125.7 MHz ^{13}C, 160.4 MHz ^{11}B NMR, 99.3 MHz ^{29}Si, and 186.4 MHz ^{119}Sn NMR spectra were recorded on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{11}B NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ ($\delta = 0$), ^{119}Sn NMR spectra were referenced to $SnMe_4$ in C_6D_6 ($\delta = 0$) and ^{29}Si NMR spectra were referenced to $SiMe_4$ in C_6D_6 (δ = 0). ^{11}B NMR spectra were acquired with boron-free quartz NMR tubes. All NMR spectra were recorded at ambient temperature unless noted otherwise. The abbreviations Ph (phenyl), Hex (*n*-hexyl), Cz (carbazolyl), Me (methyl), Bu (*n*-butyl), ^{t}BuPh (4-*tert*-butylphenyl), and Tip (2,4,6-triisopropylphenyl) are used for the peak assignments and the labeling scheme shown here was applied.



Solution UV–visible measurements were performed in CH_2Cl_2 using a Varian Cary 500 scan UV–vis-NIR spectrophotometer with a 1 cm quartz cuvette. The fluorescence data were measured on a Varian Cary Eclipse fluorescence spectrophotometer using optically dilute solutions ($A < 0.1$). Anthracene was used as the standard for determination of quantum yields (ϕ = 0.30)[21] using a relative method that is generally assumed to be accurate to ±10%. An SCS|G3P-8 Spin Coat System from Specialty Coating Systems Inc. was used to spin-cast thin films from toluene on 1 cm ×1 cm glass slides from Fisher Scientific at 3000 rpm.

Gel permeation chromatography (GPC) analyses (THF, 1 mL/min) were performed using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2998 photodiode array detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; two 5 μm Mix-C columns in series), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with narrow PS standards (Polymer Laboratories). Thermogravimetric analyses (TGA) were performed under N_2 atmosphere using a Perkin-Elmer Pyris 1 system with ca. 5 mg of polymer at a heating rate of 10 °C/min from 50 to 750 °C.

GC-MS spectra were acquired on a Hewlett-Packard HP 6890 Series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. A temperature profile with a heating rate of 20 °C/min from 50 to 300 °C was used. High resolution mass spectral data for the complexes were obtained on an Apex-ultra 70 Hybrid FT-MS (Bruker Daltonics) using electrospray ionization. Elemental analyses were obtained from Quantitative Technologies Inc. Whitehouse, NJ.

Synthesis of 3-Trimethylstannyl-6-trimethylsilyl-9-*n*-butylcarbazole. A solution of nBuLi (1.6 M in hexanes, 10.2 mL, 16.3 mmol) was added dropwise over a period of 90 min to a solution of 3-bromo-6-trimethylsilyl-9-*n*-butylcarbazole (6.10 g, 16.3 mmol) in diethyl ether (350 mL) at −78 °C. The mixture was stirred for 25 min and then allowed to slowly warm up to 0 °C. After cooling the reaction mixture back down to −78 °C, a solution of Me_3SnCl (3.40 g, 17.1 mmol) in ether (20 mL) was added dropwise. The mixture was stirred at −78 °C for 3 h and then for an additional 12 h at ambient temperature. Aqueous NH_4Cl solution was added, and the organic layer was extracted with ether. A yellowish-brown oily material was obtained upon evaporation of the solvents. Crystallization from hot methanol gave the pure product as a white crystalline solid (5.69 g, 76%). ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 8.29 (s, 1H, Cz-4), 8.26 (s, 1H, Cz-5), 7.61 (d, ^{3}J = 8.0 Hz, 1H, Cz-7), 7.54 (d, ^{3}J = 8.5 Hz, 1H, Cz-2), 7.43 (d, ^{3}J = 8.0 Hz, 1H, Cz-8), 7.29 (d, ^{3}J = 8.0 Hz, 1H, Cz-1), 4.28 (t, 2H, ^{3}J = 7.0 Hz, Bu), 1.84 (m, 2H, Bu), 1.39 (m, 2H, Bu), 0.95 (t, 3H, ^{3}J = 7.0 Hz, Bu), 0.30 (s/d, $^{2}J(^{117/119}\mathrm{Sn,H})$ = 52.5/54.5 Hz, 9H, $SnMe_3$). ^{13}C NMR (125.69 MHz, $CDCl_3$): 141.1, 141.0, 132.7 (s/d, $^{3}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 44 Hz), 130.7, 130.2, 129.1, 127.9 (s/d, $^{2}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 41 Hz), 125.7, 123.3, 122.7, 108.9 (s/d, $^{2}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 52 Hz), 108.5, 43.0, 31.4, 20.8, 14.1, −0.3, −9.0 (s/d, $^{1}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 333/347 Hz, $SnMe_3$); ^{119}Sn NMR (186.413 MHz, $CDCl_3$): δ = −23.3; GC−MS (t = 23.5 min): m/z (%): 459 [M^+] (20), 444 [$M^+ - CH_3$] (100).

Synthesis of 3-Trimethylstannyl-6-bromo-9-(4-*tert*-butylphenyl)carbazole. A solution of nBuLi (1.6 M in hexanes, 12.6 mL, 20.2 mmol) was added dropwise over a period of 90 min to a solution of 3,6-dibromo-9-(4-*tert*-butylphenyl)carbazole (9.40 g, 20.5 mmol) in THF (350 mL) at −78 °C. The mixture was stirred for 25 min and then allowed to slowly warm up to 0 °C. After cooling the reaction mixture back down to −78 °C, a solution of Me_3SnCl (4.00 g, 20.1 mmol) in THF (30 mL) was added dropwise. The mixture was stirred at −78 °C for 3 h and then for an additional 12 h at ambient temperature. Aqueous NH_4Cl solution was added, and the organic layer was extracted with $CHCl_3$. A white solid was obtained upon evaporation of the solvents. The product was further purified by crystallization from warm hexanes (8.2 g, 75%). ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 8.29 (d, ^{4}J = 2.0 Hz, 1H, Cz-4), 8.22 (s, 1H, Cz-5), 7.62 (d, ^{3}J = 8.5 Hz, 2H, Ph_o), 7.53 (dd, $^{3/4}J$ = 7.5/1.0 Hz, 1H, Cz), 7.47 (dd, $^{3/4}J$ = 8.5/2.0 Hz, 1H, Cz), 7.44 (d, ^{3}J = 8.5 Hz, 2H, Ph_m), 7.42 (d, ^{3}J = 8.0 Hz, 1H, Cz), 7.29 (d, ^{3}J = 8.5 Hz, 1H, Cz), 1.44 (s, 9H, C*Me*$_3$), 0.38 (s/d, $^{2}J(^{117/119}\mathrm{Sn,H})$ = 52.5/54.5 Hz, 9H, Sn*Me*$_3$). ^{13}C NMR (125.69 MHz, $CDCl_3$): 151.0, 141.9, 139.7, 134.7, 133.7 (s/d, $^{3}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 43 Hz), 132.1, 128.7, 128.0, 127.1, 126.7, 125.0, 123.2, 122.7, 112.8, 111.6, 110.3 (s/d, $^{2}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 50 Hz), 35.1, 31.6, −9.0 (s/d, $^{1}J(^{117/119}\mathrm{Sn},{}^{13}\mathrm{C})$ = 333/348 Hz, $SnMe_3$); ^{119}Sn NMR (186.413 MHz, $CDCl_3$): δ = −22.6. GC−MS (t = 35.0 min): m/z (%): 541 [M^+] (19), 526 [$M^+ - CH_3$] (100).

Synthesis of PSBTipFl. A solution of BBr_3 (0.36 g, 1.44 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **PSSi** (0.21 g, ca. 1.19 mmol of Me_3Si groups) in CH_2Cl_2 (10 mL) and stirred for 20 h. A solution of 2-trimethylstannyl-7-trimethylsilyl-9,9-dihexylfluorene (0.99 g, 1.72 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the reaction mixture turned light green. The mixture was allowed to stir for 20 h at room temperature, Me_3SiOMe (0.55 mL, 3.99 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The greenish solid residue was taken up into THF (10 mL), a solution of TipMgBr (0.35 M in THF, 7.2 mL, 2.5 mmol) was added, and the mixture was allowed to react for 1 h at room temperature and then kept at reflux for 5 days. The polymer solution was passed through a short alumina column using toluene as the eluent to remove the magnesium salts. The solution was then concentrated to ca. 1.5 mL and precipitated into methanol (50 mL), followed by precipitation from toluene into ethanol (50 mL). The product was dried, taken up into benzene, and obtained as white powdery material upon freeze-drying from benzene (0.15 g, 17%). For PSBTipFl, data are as follows. ^{11}B NMR (160.41 MHz, $CDCl_3$): δ = 51 ($w_{1/2}$ = 1000 Hz). ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 8.00−7.45 (br, 8H, Ph_o, Ph_m, Fl), 7.30−6.00 (very br, 4H, Ph_m, Tip_m), 2.80 (very br, 1H, *p*-C*H*Me$_2$), 2.37 (very br, 2H, *o*-C*H*Me$_2$), 1.90−0.50 (br m, 47H, *o*-CH*Me*$_2$, *p*-CH*Me*$_2$, polymer backbone, Hex), 0.29 (br, 9H, Si*Me*$_3$); ^{13}C NMR (125.69 MHz, $CDCl_3$): δ = 151.8 (Fl), 149.0 (Tip_o), 148.2 (Tip_p), 141.6 (Fl), 138.0 (Fl), 137.0 (br, Ph_o), 131.5 (Fl), 127.6 (br, Fl, Ph_m), 119.9 (Fl, Tip_m), 40.3 (polymer backbone), 35.3 (*o*-*C*HMe$_2$), 34.3 (*p*-*C*HMe$_2$), 31.5 (Hex), 29.7 (Hex), 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$), 22.6 (Hex), 14.1 (Hex), −0.7 (*Me*$_3$Si), not observed Ph_i/Tip_i/Fl_i. GPC−RI (THF vs PS standards): M_n = 36 900, M_w = 42 800, *PDI* = 1.16, high molecular weight shoulder: M_n = 91800, M_w = 99800, PDI = 1.08 ($\%_{\mathrm{Area}}$ = 78:22). TGA (10 °C/min; N_2): 51% weight loss between 215 and 280 °C; 20% weight loss between 315 and 400 °C; 10% weight loss between 437 and 570 °C; 7% residual mass at 800 °C. Anal. Calcd: C, 84.72; H, 9.90. Found: C, 80.12; H, 9.22.

Synthesis of PSBTipCzSi. A solution of BBr_3 (0.41 g, 1.64 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **PSSi** (0.25 g, ca. 1.42 mmol of Me_3Si groups) in CH_2Cl_2 (10 mL) and stirred for 20 h. A solution of 3-trimethylstannyl-6-trimethylsilyl-9-*n*-butylcarbazole (0.93 g, 2.03 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the reaction mixture turned light green. The mixture was allowed to stir for 20 h at room temperature, Me_3SiOMe (0.70 mL, 5.08 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The greenish solid residue was taken up into THF (10 mL), a solution of TipMgBr (0.50 M in THF, 9.0 mL, 4.5 mmol) was added, and the mixture was allowed to react for 1 h at room temperature and then kept at reflux for 5 days. The polymer solution was passed through a short alumina column using toluene as the eluent to remove the magnesium salts. The solution was then concentrated to ca. 1.5 mL and precipitated into methanol (50 mL), followed by precipitation from toluene into ethanol (50 mL). The product was dried, taken up into benzene, and obtained as white powdery material upon freeze-drying from benzene (0.37 g, 43%). For PSBTipCzSi, data are as follows. ^{11}B NMR (160.386 MHz, $CDCl_3$): δ = 49 ($w_{1/2}$ = 1200 Hz). ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 8.40 (br, 1H, Cz-5), 8.11 (br, 1H, Cz-4), 7.77 (br, 1H, Cz-7), 7.52 (br, 2H, Ph_o), 7.30−6.00 (very br, 7H, Ph_m, Tip_m, Cz-1,2,8), 4.3−3.4 (very br, 2H, Bu), 2.80 (very br, 1H, *p*-C*H*Me$_2$), 2.40 (very br, 2H, *o*-C*H*Me$_2$), 1.90−0.50 (br m, 18H, *o*-CH*Me*$_2$, *p*-CH*Me*$_2$, Bu), 0.26 (br, 9H, Si*Me*$_3$); ^{13}C NMR (125.69 MHz, $CDCl_3$): δ = 149.0 (Tip_o), 147.9 (Tip_p), 143.0 (Cz), 142.0 (Ph_i/Tip_i), 141.3 (Cz), 137.9 (br, Ph_o), 136.4 (Cz), 133.3 (Cz_i), 131.6 (Cz), 129.7 (Cz), 129.6 (Cz), 127.1 (Ph_m), 125.9 (Cz), 123.6 (Cz), 122.6 (Cz), 120.0 (Tip_m), 108.6 (Cz), 107.9 (Cz), 42.7 (Bu), 42−40 (polymer backbone), 35.4 (*o*-CHMe$_2$), 34.3 (*p*-CHMe$_2$), 31.2 (Bu), 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$), 20.6 (Bu), 13.9 (Bu), −0.4 (*Me*$_3$Si); GPC−RI (THF vs PS standards): M_n = 38300, M_w = 44000, PDI = 1.15, high molecular weight shoulder: M_n = 79500, M_w = 81600, PDI = 1.03 ($\%_{\mathrm{Area}}$ = 95:5). TGA (10 °C/min; N_2): 56% weight loss between 256 and 320 °C; 14% weight loss between 396 and 427 °C; 8% residual mass at 750 °C. Anal. Calcd: C, 82.46; H, 8.90; N, 2.29. Found: C, 80.43; H, 8.61; N, 2.32.

Synthesis of PSBTipCzBr. A solution of BBr$_3$ (0.31 g, 1.24 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise to a solution of **PSSi** (0.18 g, ca. 1.02 mmol of Me$_3$Si groups) in CH$_2$Cl$_2$ (10 mL) and stirred for 20 h. A solution of 3-trimethylstannyl-6-bromo-9-(4-*tert*-butylphenyl)carbazole (0.79 g, 1.46 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise, and the reaction mixture turned light green. The mixture was allowed to stir for 20 h at room temperature, Me$_3$SiOMe (0.45 mL, 3.26 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The greenish solid residue was taken up into THF (10 mL), a solution of TipMgBr (0.50 M in THF, 6.5 mL, 3.25 mmol) was added, and the mixture was allowed to react for 1 h at room temperature and then kept at reflux for 5 days. The polymer solution was passed through a short alumina column using toluene as the eluent to remove the magnesium salts. The solution was then concentrated to ca. 1.5 mL and precipitated into methanol (50 mL), followed by precipitation from toluene into acetone (50 mL). After drying the product was obtained as an off-white powdery material (0.31 g, 44%). For PSBTipCzBr, data are as follows. ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 50 ($w_{1/2}$ = 1200 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 8.60−8.25 (br, 2H, Cz), 8.20−7.90 (br, 3H, Cz, Ph$_\text{o}$), 7.78−6.25 (br, 9H, Cz, Cz−Ph$_\text{o,m}$, Ph$_\text{m}$, Tip$_\text{m}$), 2.76 (very br, 1H, *p*-C*H*Me$_2$), 2.31 (very br, 2H, *o*-C*H*Me$_2$), 1.90−0.30 (br m, 30H, *o*-CH*Me*$_2$, *p*-CH*Me*$_2$, polymer backbone, C*Me*$_3$). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 150.7 (Ph$_\text{p}$, Cz−Ph$_\text{p}$), 148.8 (Tip$_\text{o}$, Tip$_\text{p}$, Cz−Ph$_\text{o}$), 143.7 (Cz), 141.4 (Cz), 139.9 (Cz), 137.8 (Cz), 134.4 (Cz), 126.7 (Cz, Ph$_\text{m}$, Cz−Ph$_\text{m}$), 123.2 (Cz), 122.1 (Cz), 120.0 (Tip$_\text{m}$), 113.2 (Cz), 111.6 (Cz), 109.3 (Cz), 42−40 (polymer backbone), 35.0 (*C*Me$_3$), 34.9 (*o*-*C*HMe$_2$), 34.3 (*p*-*C*HMe$_2$), 31.6 (C*Me*$_3$), 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$). GPC−RI (THF vs PS standards): M_n = 32 500, M_w = 37 200, PDI = 1.14, high molecular weight shoulder: M_n = 79700, M_w = 81400, PDI = 1.02 (%$_\text{Area}$ = 96:4); TGA (10 °C/min; N$_2$): 68% weight loss between 233 and 540 °C; 9% weight loss between 540 and 580 °C; 21% residual mass at 750 °C. Anal. Calcd: C, 77.81; H, 7.11; N, 2.02. Found: C, 76.08; H, 6.82; N, 2.13.

Synthesis of MBTipFl. A solution of 2-trimethylstannyl-7-trimethylsilyl-9,9-dimethylfluorene (0.50 g, 2.09 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to ca. −10 °C and added dropwise to a precooled solution (−10 °C) of 4-$^\text{t}$BuC$_6$H$_4$BBr$_2$ (0.35 g, 1.15 mmol) in CH$_2$Cl$_2$ (5 mL). The clear colorless reaction mixture was allowed to warm to room temperature and then stirred for 1 h. Me$_3$SiOMe (0.35 mL, 2.54 mmol) was added neat and the resulting reaction mixture was stirred for 1 h. All volatile components were removed under high vacuum. The residue was taken up into THF (10 mL) and a solution of TipMgBr (0.50 M in THF, 2.8 mL, 1.4 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then heated to 80 °C for 4 days. The solvent was removed under high vacuum to leave behind a colorless solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave a white oily material. Extraction with acetonitrile and drying of the residue under high vacuum gave the product as a powdery white solid (0.38 g, 54%). For MBTipFl, data are as follows. ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 71 ($w_{1/2}$ = 2100 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 7.84 (s, 1H, Fl), 7.78 (m, 5H, Ph$_\text{o}$, Fl), 7.60 (s, 1H, Fl), 7.54 (d, ^3J = 8.0 Hz, 1H, Fl), 7.49 (d, ^3J = 8.0 Hz, 2H, Ph$_\text{m}$), 7.00 (s, 2H, Tip$_\text{m}$), 2.96 (m, 1H, *p*-C*H*Me$_2$), 2.44 (m, 2H, *o*-C*H*Me$_2$), 1.49 (s, 6H, Fl-*Me*$_2$), 1.38 (s, 9H, CMe$_3$), 1.34 (d, ^3J = 6.5 Hz, 6H, *p*-CH*Me*$_2$), 0.97 (m, 12H, *o*-CH*Me*$_2$) 0.33 (s, 9H, Si*Me*$_3$). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 155.1 (Ph$_\text{p}$), 154.0 (Fl), 153.0 (Fl), 149.0 (Tip$_\text{o}$), 148.4 (Tip$_\text{p}$), 142.7 (Fl), 142.2 (Ph$_\text{i}$), 141.2 (Fl), 140.6 (Tip$_\text{i}$), 139.8 (Fl), 138.1 (Ph$_\text{o}$), 137.7 (Fl), 132.3 (Fl), 132.2 (Fl), 127.6 (Fl), 124.8 (Ph$_\text{m}$), 120.1 (Tip$_\text{m}$), 119.4 (Fl), 47.0 (Fl-Me$_2$), 35.6 (*o*-*C*HMe$_2$), 35.2 (*C*Me$_3$), 34.4 (*p*-*C*HMe$_2$), 31.5 (C*Me*$_3$), 27.2, 24.4, 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$), −0.6 (Si*Me*$_3$).

Synthesis of MBTipCzSi. A solution of 3-trimethylstannyl-6-trimethylsilyl-9-*n*-butylcarbazole (0.24 g, 0.52 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to ca. −10 °C and added dropwise to a precooled solution (−10 °C) of 4-$^\text{t}$BuC$_6$H$_4$BBr$_2$ (0.15 g, 0.49 mmol) in CH$_2$Cl$_2$ (5 mL). The greenish solution was allowed to warm to room temperature and then stirred for 1 h. Me$_3$SiOMe (0.12 mL, 0.87 mmol) was added neat and the resulting faint green reaction mixture was stirred for 1 h. All volatile components were removed under high vacuum. The residue was taken up into THF (10 mL) and a solution of TipMgBr (0.50 M in THF, 1.1 mL, 0.55 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then heated to 80 °C for 4 days. The solvent was removed under high vacuum to leave behind a green solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave the product as a white powdery material (0.24 g, 76%). For MBTipCzSi, data are as follows: ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 69 ($w_{1/2}$ = 2000 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 8.69 (s, 1H, Cz-5), 8.28 (s, 1H, Cz-4), 7.84 (d, ^3J = 8.5 Hz, 1H, Cz-7), 7.79 (d, ^3J = 8.0 Hz, 2H, Ph$_\text{o}$), 7.63 (d, ^3J = 8.0 Hz, 1H, Cz-8), 7.51 (d, ^3J = 8.0 Hz, 2H, Ph$_\text{m}$), 7.44 (d, ^3J = 8.0 Hz, 1H, Cz-2), 7.40 (d, ^3J = 8.0 Hz, 1H, Cz-1), 7.03 (s, 2H, Tip$_\text{m}$), 4.32 (t, ^3J = 7.0 Hz, 2H, Bu), 2.98 (m, 1H, *p*-C*H*Me$_2$), 2.54 (m, 2H, *o*-C*H*Me$_2$), 1.89 (m, 2H, Bu), 1.44 (m, 2H, Bu), 1.40 (s, 9H, CMe$_3$), 1.35 (d, ^3J = 7.0 Hz, 6H, *p*-CH*Me*$_2$), 0.97 (m, 12H, *o*-CH*Me*$_2$), 0.87 (m, 3H, Bu), 0.36 (s, 9H, Si*Me*$_3$). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 154.4 (Ph$_\text{p}$), 149.0 (Tip$_\text{o}$), 148.2 (Tip$_\text{p}$), 143.2 (Cz), 142.0 (Ph$_\text{i}$/Tip$_\text{i}$), 141.5 (Cz), 140.7 (Tip$_\text{i}$/Ph$_\text{i}$), 137.9 (Ph$_\text{o}$), 137.1 (Cz), 133.4 (Cz$_\text{i}$), 131.3 (Cz), 130.8 (Cz), 130.0 (Cz), 125.9 (Cz), 124.8 (Ph$_\text{m}$), 123.6 (Cz), 122.7 (Cz), 120.1 (Tip$_\text{m}$), 108.8 (Cz), 108.0 (Cz), 43.2 (Bu), 35.5 (*o*-*C*HMe$_2$), 35.2 (*C*Me$_3$), 34.4 (*p*-*C*HMe$_2$), 31.5 (C*Me*$_3$), 31.4 (Bu), 24.5, 24.4, 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$), 20.8 (Bu), 14.1 (Bu), −0.3 (*Me*$_3$Si). Anal. Calcd: C, 82.34; H, 9.42; N, 2.18. Found: C, 81.69; H, 9.09; N, 2.14. High-res ESI−MS (positive mode): m/z = 664.4507 (calcd for [M + Na]$^+$ ^{12}C$_{44}$^{1}H$_{60}$^{11}B^{14}N^{28}Si^{23}Na 664.4488).

Synthesis of MBTipCzBr. A solution of 3-trimethylstannyl-6-bromo-9-(4-*tert*-butylphenyl)carbazole (0.64 g, 1.18 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to ca. −10 °C and added dropwise to a precooled solution (−10 °C) of 4-$^\text{t}$BuC$_6$H$_4$BBr$_2$ (0.31 g, 1.02 mmol) in CH$_2$Cl$_2$ (5 mL). This greenish solution was allowed to warm to room temperature and then stirred for 1 h. Me$_3$SiOMe (0.35 mL, 2.54 mmol) was added neat, and the resulting faint green reaction mixture was stirred for another 1 h. All volatile components were removed under high vacuum. The residue was taken up into THF (10 mL), and a solution of TipMgBr (0.50 M in THF, 3.3 mL, 1.65 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then heated to 80 °C for 4 days. The solvent was removed under high vacuum to leave behind a green solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave the pure product as a white powdery material (0.37 g, 50%). For MBTipCzBr, data are as follows. ^{11}B NMR (160.386 MHz, CDCl$_3$): δ = 70 ($w_{1/2}$ = 2000 Hz). ^{1}H NMR (499.893 MHz, CDCl$_3$): δ = 8.61 (s, 1H, Cz-5), 8.25 (s, 1H, Cz-4), 7.85 (d, ^3J = 8.0 Hz, 1H, Cz-7), 7.77 (d, ^3J = 8.0 Hz, 2H, Ph$_\text{o}$), 7.62 (d, ^3J = 8.5 Hz, 2H, Cz−Ph$_\text{o}$), 7.49 (m, 5H, Ph$_\text{m}$, Cz−Ph$_\text{m}$, Cz-8), 7.41 (d, ^3J = 8.5 Hz, 1H, Cz-2), 7.31 (d, ^3J = 8.5 Hz, 1H, Cz-1), 7.03 (s, 2H, Tip$_\text{m}$), 2.97 (m, 1H, *p*-C*H*Me$_2$), 2.51 (m, 2H, *o*-C*H*Me$_2$), 1.43 (s, 9H, Cz−PhC*Me*$_3$), 1.39 (s, 9H, C*Me*$_3$), 1.35 (d, ^3J = 7.0 Hz, 6H, *p*-CH*Me*$_2$), 0.98 (m, 12H, *o*-CH*Me*$_2$). ^{13}C NMR (125.69 MHz, CDCl$_3$): δ = 154.6 (Ph$_\text{p}$), 151.3 (Cz−Ph$_\text{p}$), 149.0 (Tip$_\text{o}$), 148.4 (Tip$_\text{p}$), 143.9 (Cz), 141.5 (Cz), 140.3 (Cz), 137.8 (Ph$_\text{o}$), 137.6 (Cz), 134.4 (Cz), 131.6 (Cz), 128.8 (Cz), 127.1 (Cz−Ph), 126.7 (Cz−Ph), 125.9 (Cz), 124.8 (Ph$_\text{m}$), 123.4 (Cz), 122.1 (Cz), 120.2 (Tip$_\text{m}$), 113.4 (Cz), 111.8 (Cz), 109.5 (Cz), 35.6 (*o*-*C*HMe$_2$), 35.2, 35.1 (*C*Me$_3$/Cz−Ph*C*Me$_3$), 34.4 (*p*-*C*HMe$_2$), 31.6, 31.5 (C*Me*$_3$/Cz−PhC*Me*$_3$), 24.5, 24.4, 24.3 (*o*-CH*Me*$_2$, *p*-CH*Me*$_2$), Ph$_\text{i}$ and Tip$_\text{i}$ not observed. High-res ESI-MS (positive mode): m/z = 764.3539 (calcd for [M + Na]$^+$ ^{12}C$_{47}$^{1}H$_{55}$^{11}B^{79}Br^{14}N^{23}Na 746.3511). Anal. Calcd: C, 77.90; H, 7.65; N, 1.93. Found: C, 77.57; H, 7.65; N, 1.85.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. UV−vis and emission spectra for thin films of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail fjaekle@rutgers.edu.

■ ACKNOWLEDGMENT

Acknowlegment is made to the National Science Foundation (CHE-0809642 and MRI 0116066) for support of this research. F.J. thanks the Alexander von Humboldt Foundation for a Friedrich Wilhelm Bessel Research Award. We thank Dr. Roman Brukh for acquisition of ESI−MS data and Pangkuan Chen for acquisition of ^{11}B NMR data of MBTipCzSi.

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