

Luminescent Organoboron Quinolate Polymers

*Yang Qin, Cynthia Pagba, Piotr Piotrowiak, and Frieder Jäkle**

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102

Supplementary Material

Materials and General Methods. The compounds 8-hydroxyquinoline (99%), thiophene (99+%), N,N,N',N'-tetramethylethylenediamine (TMEDA; 99%), *n*-BuLi (1.6M in hexanes) and 1-bromohexane (99+%) were purchased from Acros, trimethyltin chloride (98%) was obtained from Strem Chemicals, and 3-bromothiophene (97%) and BBr₃ (99+%) were purchased from Aldrich. 8-Hydroxyquinoline was sublimed and BBr₃ was distilled under high vacuum prior to use. All other chemicals were used as received without further purification. The compounds poly(4-trimethylsilylstyrene)¹, 4-dibromoborylcumene¹, and 2-bromo-3-hexylthiophene² were prepared as previously described. 2-Hexylthiophene was obtained by adaptation of a literature procedure for the synthesis of 2-(bromohexyl)thiophene³. Reactions and manipulations involving reactive boron species were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (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 CaH₂ and degassed via several freeze pump thaw cycles.

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.

The 399.95 MHz ¹H and 100.5 MHz ¹³C NMR spectra were recorded on a Varian VXR-S and the 499.91 MHz ¹H and 125.68 MHz ¹³C NMR spectra were obtained on a Varian INOVA NMR spectrometer equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). ¹¹B NMR and ¹¹⁹Sn NMR data were collected on the VXR-S spectrometer at 128.3 MHz and 149.07 MHz, respectively. All NMR data were obtained at ambient temperature. ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks and ¹¹B and ¹¹⁹Sn NMR spectra were referenced externally to BF₃ · Et₂O (δ = 0) and SnMe₄ (δ = 0) in C₆D₆, respectively. The abbreviations Th and Q are used for thienyl and quinolato, respectively. Two-dimensional proton correlation spectroscopy (COSY^{4,5}), and one bond proton-carbon correlation spectroscopy (HMQC^{6,7}) measurements were recorded on the INOVA spectrometer in the absolute value mode (COSY) or the phase sensitive mode (HMQC) by employing the TPPI improvement^{8,9} of the States-Haberhorn-Ruben Hypercomplex method¹⁰. Selection of desirable coherences and artifact

suppression were accomplished by z-gradients (COSY, echo N-type coherence selection¹¹), or phase cycles of 16 steps (HMQC). The HMQC pulse sequence included the BIRD filter to suppress signals from C12-attached protons¹² and C13-decoupling during proton acquisition, using a 3.6 kHz field strength and the GARP decoupling scheme¹³. Typically, 256 t1 increments of 2K complex data points over 5.5 kHz (proton) and 22.5 kHz (carbon) spectral widths were collected with 1 (COSY) or 16 (HMQC) scans per t1 increment, preceded by 16 or 32 dummy scans, and a relaxation delay of 2 s. Baseline distortion was addressed by properly adjusting the sampling delay and the signal phase¹⁴. Data sets were processed on a Sun Blade 100 workstation (Sun Microsystems Inc., Palo Alto, CA) using the VNMR software package (Varian Inc., Palo Alto, CA). In order to decrease t1 ridges arising from incorrect treatment of the first data point in the discrete Fourier transform (FT) algorithm, the spectrum corresponding to the first t1 value was divided by 2 prior to FT along t1.¹⁵ Shifted (COSY) or unshifted (HMQC) Gaussian window functions were used in both dimensions. Data sets were zero-filled in the t1 dimension yielding 1K x 1K final matrices that have not been symmetrized.

Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Mass spectral data (FAB mode with either 3-nitrobenzylalcohol (NBA) or 2-nitrophenyloctyl ether (NPOE) as the matrix) were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DDR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health.

GPC analyses were performed in THF (1 ml/min) using a Waters Breeze system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; 5 μ m Mix-D, 5 μ m Mix-C, and 10 μ m Mix-B), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories). Multi Angle 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; differential refractive indices dn/dc were determined using a Wyatt Optilab at 690 nm. DSC measurements were performed on a Perkin Elmer Differential Scanning Calorimeter Pyris 1 system with ca. 20 mg of polymer and at a scan rate of 20 °C / min. The reported results correspond to the second heating cycle.

UV-visible measurements were performed in THF using a Varian Cary 500 scan UV-Vis-NIR spectrophotometer with a 1 cm quartz cuvette. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse Fluorescence spectrophotometer with the same solutions as those used in the UV-visible measurements. Anthracene was used as the standard for determination of the quantum yields. The quantum yield of anthracene was adopted from the *'Handbook of Photochemistry, 2nd Edition, Revised and Expanded*. ISBN 0-8247-7911-8' and the concentration of anthracene in THF was $6.86 \cdot 10^{-6}$ M. For the luminescence lifetime measurements thoroughly degassed samples of the polymer and model compound were excited with 5 μ s ~100 mJ pulses at 355 nm (3rd harmonic of a Q-switched Nd:YAG laser, Quantel, Brilliant). The emission was dispersed through a monochromator (Oriel M257) and detected with a Hamamatsu R928 photomultiplier. The transients were recorded using a Tektronix SCD 1000 digital oscilloscope controlled by a Labview subroutine. Fluorescent decays were fitted as single exponentials using the Igor software package by Wavemetrics, Inc.

Synthesis of Precursors and Model Compounds

Synthesis of 2-Hexylthiophene. 2-Hexylthiophene was obtained by adaptation of a literature procedure for the synthesis of 2-(bromohexyl)thiophene.³ Thiophene (20.0 g, 0.238 mol) and TMEDA (30.4 g, 0.262 mol) were dissolved in 250 ml THF, and *n*-BuLi (164 ml, 1.6 M in hexanes, 0.262 mol) was added dropwise at room temperature. The mixture was stirred at room temperature for 2 h. 1-Bromohexane (40 ml, 47.2 g, 0.286 mol) was added dropwise and the mixture was then heated to a gentle reflux and stirred for 8 h. After quenching with ice water and aqueous work-up, the product was distilled at 55 °C under high vacuum. 2-Hexylthiophene was obtained as a colorless liquid (23.0 g, 58 % yield). ¹H NMR (499.893 MHz, CDCl₃): δ = 7.12 (d, *J* = 4.0 Hz, 1H, Th-H3), 6.93 (dd, *J* = 2.5 Hz / 4.0 Hz, 1H, Th-H4), 6.79 (d, *J* = 2.5 Hz, 1H, Th-H5), 2.83 (t, *J* = 7.5 Hz, 2H, Th-CH₂), 1.67 (m, 2H, hexyl-H), 1.35 (m, 6H, hexyl-H), 0.90 (t, *J* = 7.0 Hz, 3H, CH₃).

Synthesis of 5-Hexyl-2-trimethylstannylthiophene. 2-Hexylthiophene (23.0 g, 0.137 mol) was dissolved in 250 ml THF and *n*-BuLi (94 ml, 1.6 M in hexanes, 0.150 mol) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 1 h and then cooled down to -78 °C. A solution of trimethyltin chloride (32.8 g, 0.164 mol) in 100 ml THF was added dropwise. The mixture was allowed to warm slowly to room temperature and stirred for 2 h. After quenching with ice water and aqueous work-up, the product was distilled at 108 °C under high vacuum. 5-Hexyl-2-trimethylstannylthiophene was obtained as a colorless liquid (40.8 g, 90 % yield). ¹H NMR (399.952 MHz, CDCl₃): δ = 7.03 (d, *J* = 3.2 Hz, *J*(^{119/117}Sn,H) = 27 Hz, 1H, Th-H3), 6.91 (d, *J* = 3.2 Hz, 1H, Th-H4), 2.86 (t, *J* = 7.6 Hz, 2H, Th-CH₂), 1.69 (m, 2H, hexyl-H), 1.34 (m, 6H, hexyl-H), 0.90 (t, *J* = 7.0 Hz, 3H, CH₃), 0.35 (s/d, *J*(^{119/117}Sn,H) = 58 Hz/55 Hz, 9H, Sn-Me); ¹³C NMR (125.698 MHz, CDCl₃): δ = 152.1 (Th-C5), 135.2 (s/d, *J*(^{119/117}Sn,C) = 30 Hz, Th-C3), 134.8 (Th-C2), 125.6 (s/d, *J*(^{119/117}Sn,C) = 42 Hz, Th-C4), 32.1, 31.8, 30.2, 29.2, 22.8, 14.3 (hexyl-C), -8.1 (s/d, *J*(^{119/117}Sn,C) = 369 Hz/353 Hz, Sn[CH₃]₃); ¹¹⁹Sn NMR (149.071 MHz, CDCl₃): δ = -27.4.

Synthesis of 4-[8-Hydroxyquinolato-2-(5-hexylthienyl)]borylcumene (M-B5HTQ). 4-Dibromoborylcumene (0.50 g, 1.73 mmol) was dissolved in 20 ml CHCl₃ and a solution of 5-hexyl-2-trimethylstannylthiophene (1.14 g, 3.45 mmol) in 10 ml CHCl₃ was added dropwise. The mixture was stirred at room temperature for 2 h. Conversion to **M-B5HT** was confirmed by NMR spectroscopy and the product was used without further purification. For **M-B5HT**: ¹H NMR (499.893 MHz, CDCl₃): δ = 7.72 (d, *J* = 8.0 Hz, 2H, Ph-H2,6), 7.67 (d, *J* = 3.2 Hz, 2H, Th-H3), 7.34 (d, *J* = 8.0 Hz, 2H, Ph-H3,5), 7.06 (d, *J* = 3.2 Hz, 2H, Th-H4), 3.02 (hept, 1H, *J* = 7.0 Hz, CH[CH₃]₂), 1.36 (d, *J* = 7.0 Hz, 6H, CH[CH₃]₂), 2.97 (t, *J* = 7.6 Hz, 4H, Th-CH₂), 1.79 (m, 4H, hexyl-H), 1.44 (m, 12H, hexyl-H), 0.93 (t, *J* = 7.2 Hz, 6H, hexyl-H); ¹³C NMR (125.698 MHz, CDCl₃): δ = 158.9 (Th-C5), 151.0 (Ph-C4), 143.3 (br., Th-C2), 143.0 (Th-C3), 141.2 (br., Ph-C1), 136.8 (Ph-C2,6), 126.9 (Th-C4), 125.5 (Ph-C3,5), 34.4 (CH[CH₃]₂), 24.1 (CH[CH₃]₂), 31.8, 31.7, 30.8, 29.2, 22.8, 14.3 (hexyl-C). A solution of 8-hydroxyquinoline (0.25 g, 1.73 mmol) in 10 ml CHCl₃ was added dropwise to the reaction mixture. The mixture turned yellow immediately with green luminescence and was kept stirring for 2 h. After removal of all volatile components, the product was recrystallized twice from a mixture of *n*-hexane and chloroform (ca. 2:1 by volume). **M-B5HTQ** was obtained as a yellow solid (0.61 g, 80 % yield). For **M-B5HTQ**: ¹H NMR (499.893 MHz, CDCl₃): δ = 8.62 (d, *J* = 5.0 Hz, 1H, Q-H2), 8.39 (d, *J* = 8.0 Hz, 1H, Q-H4), 7.68 (dd, *J* = 8.5 Hz/8.0 Hz, 1H, Q-H6), 7.61 (dd, *J* = 8.5 Hz/5.0 Hz, 1H, Q-H3), 7.51 (d, *J* = 8.0 Hz, 2H, Ph-H2,6), 7.24 (d, *J* = 8.0 Hz, 1H, Q-H5), 7.17 (d, *J* = 8.0 Hz, 1H, Q-

H7), 7.16 (d, $J = 8.0$ Hz, 2H, Ph-H3,5), 6.91 (d, $J = 3.2$ Hz, 1H, Th-H3), 6.74 (d, $J = 3.2$ Hz, 1H, Th-H4), 2.87 (hept, $J = 7.0$ Hz, 1H, CH[CH₃]₂), 2.77 (t, $J = 8.0$ Hz, 2H, Th-CH₂), 1.63 (m, 2H, hexyl-H), 1.34 (m, 4H, hexyl-H), 1.28 (m, 2H, hexyl-H), 1.23 (d, $J = 7.0$ Hz, 6H, CH[CH₃]₂), 0.87 (t, $J = 7.0$ Hz, 3H, hexyl-H); ¹³C NMR (125.698 MHz, CDCl₃): δ = 158.5 (Q-C8), 147.7, 147.9 (Th-C5 and Ph-C4), 147.2 (br., Th-C2), 143.7 (br., Ph-C1), 139.5 (Q-C2), 138.8 (Q-C4), 137.1 (Q-C9), 132.8 (Q-C6), 131.8 (Ph-C2,6), 130.1 (Th-C3), 128.3 (Q-C10), 125.8 (Ph-C3,5), 124.8 (Th-C4), 122.9 (Q-C3), 112.5 (Q-C5), 109.7 (Q-C7), 34.0 (CH[CH₃]₂), 24.2 (CH[CH₃]₂), 31.9, 31.7, 30.3, 29.0, 22.7, 14.2 (hexyl-C); ¹¹B NMR (128.286 MHz, CDCl₃): δ = 10.4 ($w_{1/2} = 500$ Hz). FAB-MS (NPOE) m/z (%): 441 (53) [M⁺], 322 (75) [M⁺ -ⁱPrPh], 274 (100) [M⁺ -HexTh]. Elemental analysis: calcd. C 76.18, H 7.31, N 3.17; found C 76.33, H 7.49, 3.02. The absence of any cumene in the crude product was confirmed by GC-MS analysis, which showed only one signal for 2-hexylthiophene: $m/z = 168$ (100%).

Synthesis of 3-Hexyl-2-trimethylstannylthiophene. To a Grignard solution prepared from 2-bromo-3-hexylthiophene (21.6 g, 87.4 mmol) and Mg turnings (4.25 g, 175 mmol) in 300 ml THF was added dropwise a solution of trimethyltin chloride (21.0 g, 105 mmol) in THF. The mixture was then heated to reflux overnight and subsequently quenched with ice water. Following standard workup, distillation (10⁻³ torr, 85–86 °C) gave 19.8 g (68%) of 3-Hexyl-2-trimethylstannylthiophene as a colorless liquid. ¹H NMR (499.893 MHz, CDCl₃): δ = 7.59 (d, $J = 5.0$ Hz, $J(^{119/117}\text{Sn},\text{H}) = 13$ Hz, 1H, Th-H5), 7.17 (d, $J = 5.0$ Hz, 1H, Th-H4), 2.71 (t, $J = 8.0$ Hz, 2H, Th-CH₂), 1.67 (m, 2H, hexyl-H), 1.39 (m, 6H, hexyl-H), 0.98 (t, $J = 7.0$ Hz, 3H, CH₃), 0.46 (s/d, $J(^{119/117}\text{Sn},\text{H}) = 57$ Hz/55 Hz, 9H, Sn[CH₃]₃); ¹³C NMR (125.698 MHz, CDCl₃): δ = 151.0 (Th-C3), 131.5 (Th-C2), 130.7 (s/d, $J(^{119/117}\text{Sn},\text{C}) = 23$ Hz, Th-C4), 129.5 (s/d, $J(^{119/117}\text{Sn},\text{C}) = 42$ Hz, Th-C5), 32.8, 32.4, 32.0, 29.6, 22.8, 14.3 (hexyl), -7.8 (s/d, $J(^{119/117}\text{Sn},\text{C}) = 368$ Hz/351 Hz, Sn[CH₃]₃).

Synthesis of 4-(8-Hydroxyquinolato-2-(3-hexylthienyl))borylcumene (M-B3HT). 4-Dibromoborylcumene (0.50 g, 1.73 mmol) was dissolved in 20 ml CH₂Cl₂ and a solution of 3-hexyl-2-trimethylstannylthiophene (1.26 g, 3.80 mmol) in 10 ml CH₂Cl₂ was added dropwise. The mixture was stirred at room temperature for 48 h. Conversion to **M-B3HT** was confirmed by NMR spectroscopy and the product was used without further purification. For **M-B3HT**: ¹H NMR (499.893 MHz, CDCl₃): δ = 7.73 (d, $J = 5.0$ Hz, 2H, Th-H5), 7.59 (d, $J = 7.5$ Hz, 2H, Ph-H2,6), 7.26 (d, $J = 7.5$ Hz, 2H, Ph-H3,5), 7.16 (d, $J = 5.0$ Hz, 2H, Th-H4), 2.98 (hept, $J = 7.0$ Hz, 1H, CH[CH₃]₂), 1.31 (d, $J = 7.0$ Hz, 6H, CH[CH₃]₂), 2.41 (t, $J = 7.5$ Hz, 4H, Th-CH₂), 1.44 (m, 4H, hexyl-H), 1.17 (m, 4H, hexyl-H), 1.06 (m, 8H, hexyl-H), 0.78 (t, $J = 7.0$ Hz, 6H, hexyl-H). A solution of 8-hydroxyquinoline (0.28 g, 1.9 mmol) in 10 ml CH₂Cl₂ was added dropwise. The mixture was kept stirring for 24 h. After removal of all volatile components, the product was recrystallized twice from a mixture of *n*-hexane and THF (ca. 3:1 by volume). The organoboron quinolate **M-B3HTQ** was obtained as a yellow solid (0.35 g, 46% yield). ¹H NMR (399.844 MHz, CDCl₃): δ = 8.70 (d, $J = 5.2$ Hz, 1H, Q-H2), 8.41 (d, $J = 8.4$ Hz, 1H, Q-H4), 7.65 (m, 2H, Q-H3 and Q-H6), 7.47 (d, $J = 8.0$ Hz, 2H, Ph-H2,6), 7.25 (m, 2H, Th-H5 and Q-H5), 7.15 (m, 3H, Ph-H3,5 and Q-H7), 6.99 (d, $J = 4.8$ Hz, 1H, Th-H4), 2.86 (hept, $J = 7.0$ Hz, 1H, CH[CH₃]₂), 2.40 (m, 2H, Th-CH₂), 1.53 (m, 2H, hexyl-H), 1.33 (m, 2H, hexyl-H), 1.22 (d, $J = 7.0$ Hz, 6H, CH[CH₃]₂), 1.00 (m, 4H, hexyl-H), 0.82 (t, 3H, CH₃). ¹³C NMR (100.541 MHz, CDCl₃): δ = 158.7 (Q-C8), 147.7, (Ph-C4), 146.3 (Th-C3), 146.1 (br., Th-C2), 140.5 (br., Ph-C1), 140.1 (Q-C2), 139.1 (Q-C4), 137.7 (Q-C9), 133.1 (Q-C6), 131.7 (Ph-C2,6), 130.9 (Th-C5), 128.6 (Q-C10), 125.8 (Ph-C3,5), 125.5 (Th-C4), 122.9 (Q-C3), 112.5 (Q-C5), 110.1 (Q-C7), 34.1 (CH[CH₃]₂), 24.2 (CH[CH₃]₂), 31.9, 31.8, 30.7, 29.6, 22.8, 14.3 (hexyl-C). ¹¹B NMR (128.286

MHz, CDCl₃): Δ = 10.2 ($w_{1/2}$ = 400 Hz). FAB-MS (NPOE) m/z (%): 441 (30) [M⁺], 322 (82) [M⁺ - iPrPh], 274 (100) [M⁺ - HexTh]. Elemental analysis: calcd. C 76.18, H 7.31, N 3.17; found C 76.18, H 7.21, N 3.06.

Synthesis of Polymers

Synthesis of poly[4-(8-hydroxyquinolato-2-thienyl)borylstyrene] (PS-BTQ). A solution of **PS-BBr** prepared from BBr₃ (3.11 g; 12.4 mmol) and **PS-Si** (2.0 g; ca. 11.3 mmol repeating units; M_w = 26,000; PDI = 1.13) in 20 ml CH₂Cl₂ was treated with a solution of 2-(trimethylstannyl)thiophene (6.10 g; 28.3 mmol) in CH₂Cl₂ (10 ml) and the mixture was stirred for 12 h. The reaction solution was concentrated under high vacuum to ca. 5 ml and the polymer was recovered by repeated precipitation into hexanes. The resulting white solid was washed with hexanes and dried under high vacuum for 24 h at 50 °C to give 2.5 g (80%) **PS-BT**. For **PS-BT**: ¹H NMR (499.893 MHz, CDCl₃): Δ = 8.0-7.4 (br., 6H, Ph-H2,6 and Th-H3,5), 7.08 (br., 2H, Th-H4), 6.9-6.7 (br., 2H, Ph-H3,5), 2.6-1.4 (br. m, 3H, CH₂CH); ¹³C NMR (125.681 MHz, CDCl₃): Δ = 149.2, 148.4 (br., Ph-C4), 145.1 (Th-C2), 142.3 (Th-C5), 140.9 (br., Ph-C1), 137.4 (br., Ph-C2,6), 137.0 (Th-C3), 129.0 (Th-C4), 127.1 (br., Ph-C3,5), 47-42 (br., CH₂CH), 41 (br., CH₂CH); ¹¹B NMR (160.370 MHz, CDCl₃): Δ = 50 ($w_{1/2}$ = 2,500 Hz). Elemental analysis: calcd. C 68.58, H 4.68; found C 68.17, H 4.50. **PS-BT** (0.50 g, 1.78 mmol) was dissolved in 20 ml CH₂Cl₂ and a solution of 8-hydroxyquinoline (0.27 g, 1.87 mmol) in 10 ml CH₂Cl₂ was added dropwise. The mixture was stirred for 24 h and then concentrated to a small volume (~2 ml). The polymer **PS-BTQ** was recovered as a yellow solid by precipitation into hexanes (yield: 78%). ¹H NMR (499.893 MHz, CDCl₃): Δ = 8.5-6.0 (aromatic protons), 2.2-0.7 (br., polymer backbone); ¹¹B NMR (128.286 MHz, CDCl₃): Δ = 7 ($w_{1/2}$ = 750 Hz); ¹³C NMR data could not be obtained due to the poor solubility of the polymer. DSC measurement: T_g = 221 °C (onset).

Synthesis of Poly[4-(8-hydroxyquinolato-2-(5-hexylthienyl))borylstyrene] (PS-B5HTQ). A solution of **PS-BBr** prepared from BBr₃ (3.27 g, 13.04 mmol) and **PS-Si** (2.00 g, ca. 11.34 mmol repeat units; M_w = 26,000; PDI = 1.13) in 30 ml CH₂Cl₂ was treated with 5-hexyl-2-trimethylstannylthiophene (11.26 g, 34.02 mmol) and stirred for 24 h. All volatile material was removed under high vacuum and the product was dried at 60 °C for 3 h. Conversion to **PS-B5HT** was confirmed by NMR spectroscopy; for **PS-B5HT**: ¹H NMR (499.893 MHz, CDCl₃): Δ = 8.0-6.6 (aromatic protons), 3.0, 1.9, 1.6, 1.1 (hexyl-H), polymer backbone protons were not resolved; ¹³C NMR (125.698 MHz, CDCl₃): Δ = 158.1 (Th-C5), 147 (br., Ph-C4), 143.0 (Th-C3), 142.0 (br., Ph-C1), 136.6 (Ph-C2,6), 126.6 (Th-C4 and Ph-C3,5), 47-42 (br., polymer backbone), 31.7, 31.6, 30.6, 29.1, 22.7, 14.2 (hexyl-C), Th-C2 was not resolved. The crude product was redissolved in 30 ml CH₂Cl₂ and used without further purification. A solution of 8-hydroxyquinoline (3.96 g, 27.22 mmol) in 20 ml CH₂Cl₂ was then added dropwise. The mixture turned immediately yellow with green luminescence and was kept stirring for 24 h. The reaction solution was concentrated under high vacuum to ca. 5 ml and then precipitated into hexanes (ca. 500 ml). The product was reprecipitated twice from THF into methanol and subsequently from THF into hexanes. Polymer **PS-B5HTQ** was obtained as a yellow powder and dried at 60 °C under high vacuum for 24 h (yield: 4.0 g, 83%). For **PS-B5HTQ**: ¹H NMR (499.893 MHz, CDCl₃): Δ = 8.6-6.0 (br., all aromatic protons), 2.73, 1.59, 1.24, 0.83 (br., backbone and hexyl-H); ¹³C NMR (125.698 MHz, CDCl₃): Δ = 158.3 (Q-C8), 147.6 (Th-C5 and Ph-C4), 146-142 (very br., Th-C2 and Ph-C1), 139.6 (Q-C2), 139.2 (Q-C4), 136.9 (Q-C9), 132.0 (Q-C6), 131.7

(Ph-C2,6), 130.2 (Th-C3), 128.2 (Q-C10), 127.2 (br., Ph-C3,5), 125.0 (Th-C4), 123.2 (Q-C3), 112.6 (Q-C5), 109.5 (Q-C7), 45-38 (br., $[\text{CH}_2\text{CH}]_n$), 32.0, 31.8, 30.4, 29.2, 22.8, 14.3 (hexyl-C); ^{11}B NMR (128.286 MHz, CDCl_3): $\Delta = 5$ ($w_{1/2} = 600$ Hz). Static light scattering (Zimm plot; $dn/dc = 0.205$ ml/g): $M_w = 62,000$; $A_2 = -6.707 \times 10^{-4}$ mol \cdot ml/g 2 . In-line GPC-LS: $M_w = 71,000$, $PDI = 1.04$. Elemental analysis: calcd. C 76.23, H 6.63, N 3.29; found C 75.99, H 6.66, N 3.07. DSC measurement: $T_g = 146$ °C (onset).

Synthesis of Poly[4-(8-hydroxyquinolato-2-(3-hexylthienyl))borylstyrene] (PS-B3HTQ). A solution of **PS-BBr** prepared from BBr_3 (0.85 g; 3.40 mmol) and **PS-Si** (0.50 g, ca. 2.84 mmol repeat units; $M_w = 26,000$; $PDI = 1.13$) in 30 ml CH_2Cl_2 was treated with 3-hexyl-2-trimethylstannylthiophene (3.66 g, 11.05 mmol) and stirred for 3 d. All volatile material was removed under high vacuum and the product was dried at 60 °C for 3 h. Conversion to **PS-B3HT** was confirmed by NMR spectroscopy; for **PS-B3HT**: ^1H NMR (499.893 MHz, CDCl_3): $\Delta = 7.8$ -6.2 (br., aromatic protons), 2.35, 1.40, 1.10, 0.94, 0.71 (br., hexyl-H), polymer backbone protons were not resolved; ^{13}C NMR (125.698 MHz, CDCl_3): $\Delta = 153.7$ (br., Th-C3), 149 (br., Ph-C4), 141.8 (Th-C2), 141 (br., Ph-C1), 140.9 (Th-C5), 137.9 (br., Ph-C2,6), 133.9 (Th-C4), 130.8 (Th-C4), 127.0 (br., Ph-C3,5), 45-40 (very br., polymer backbone), 32.4, 31.7, 29.4, 22.8, 14.3 (hexyl-C). The crude product was redissolved in 30 ml CH_2Cl_2 and used without further purification. A solution of 8-hydroxyquinoline (0.83 g, 5.68 mmol) in 10 ml CH_2Cl_2 was then added dropwise. The mixture was kept stirring for 2 d. The reaction solution was concentrated under high vacuum to ca. 5 ml and then precipitated into hexanes (ca. 500 ml). The crude material was reprecipitated twice from THF into methanol and subsequently from THF into hexanes. Polymer **PS-B3HTQ** was obtained as a yellow powder and dried at 60 °C under high vacuum for 24 h (yield: 0.80 g, 67%). ^1H NMR (499.893 MHz, CDCl_3): $\Delta = 8.6$ -5.0 (br., aromatic protons), 2.31, 1.07, 0.74 (br., backbone and hexyl-H); ^{13}C NMR (125.698 MHz, CDCl_3): $\Delta = 158.5$ (Q-C8) 146.1 (Th-C3), 146-142 (very br. Ph-C4, Th-C2, Ph-C1), 140.0 (Q-C2), 139.0 (Q-C4), 137.2 (Q-C9), 132.6 (Q-C6), 131-130 (Th-C5 and Ph-C2,6), 128.2 (Q-C10), 127.5-126.5 (Ph-C3,5 and Th-C4), 123.1 (Q-C3), 112.5 (Q-C5), 109.5 (Q-C7), 45-39 (very br., polymer backbone), 31.9, 31.0, 30.6, 29.5, 22.8, 14.4 (hexyl-C); ^{11}B NMR (128.286 MHz, CDCl_3): $\Delta = 5$ ($w_{1/2} = 500$ Hz). Static light scattering (Zimm plot; $dn/dc = 0.201$ ml/g): $M_w = 64,000$; $A_2 = -9.499 \times 10^{-4}$ mol \cdot ml/g 2 . In-line GPC-LS: $M_w = 66,000$, $PDI = 1.06$. Elemental analysis: calcd. C 76.23, H 6.63, N 3.29; found C 76.17, H 6.65, N 3.25. DSC measurement: $T_g = 146$ °C (onset).

References:

- (1) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672
- (2) Michalitsch, R.; Elkassmi, A.; Yassar, A.; Garnier, F. *J. Heterocyclic Chem.* **2001**, *38*, 649.
- (3) (a) Barbarella, G.; Bongini, A.; Massimo, Z. *Macromolecules* **1994**, *27*, 3039;
(b) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051.
- (4) Aue, W. P., Bartholdi, E., and Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
- (5) Bax, A., and Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.

- (6) Muller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481.
- (7) Bax, A., and Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.
- (8) Redfield, A. G., and Kunz, S. D. *J. Magn. Reson.* **1975**, *19*, 250.
- (9) Marion, D., and Wuthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967.
- (10) States, D. J., Haberkorn, R. A., and Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286.
- (11) von Kienlin, M., Moonen, C. T. W., van der Toorn, A., and van Zijl, P. C. M. *J. Magn. Reson.* **1991**, *93*, 432.
- (12) Garbow, J. R., Weitekamp, D. P., and Pines, A. *Chem. Phys. Lett.* **1982**, *93*, 504.
- (13) Shaka, A. J., Barker, P. B., and Freeman, R. *J. Magn. Reson.* **1985**, *64*, 547.
- (14) Hoult, D. I. *J. Magn. Reson.* **1983**, *51*, 110
- (15) Otting, G., Widmer, H., Wagner, G., and Wuthrich, K. *J. Magn. Reson.* **1986**, *66*, 187.

Figure S1. Absorption and emission spectra of **PS-B3HTQ** and **M-B3HTQ** in THF

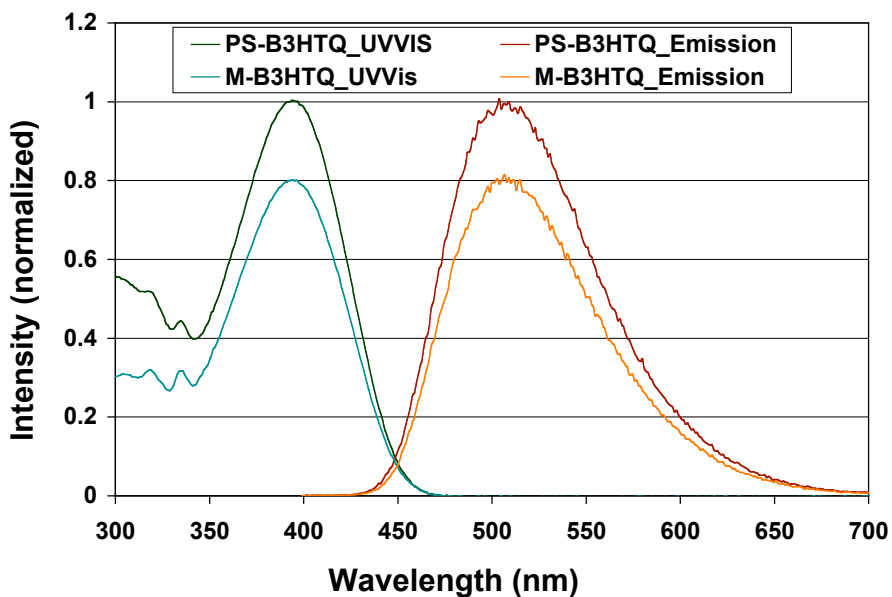


Figure S2. Aromatic region of the gCOSY NMR spectrum of **M-B5HTQ** in CDCl_3 .

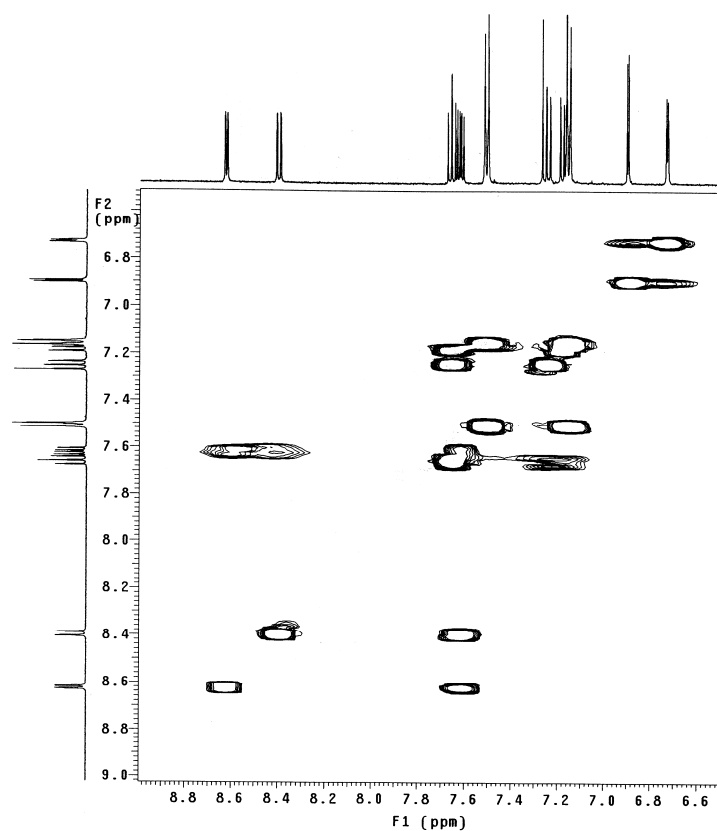


Figure S3. Region of aromatic C-H resonances of the HMQC NMR spectrum of **M-B5HTQ** in CDCl_3 .

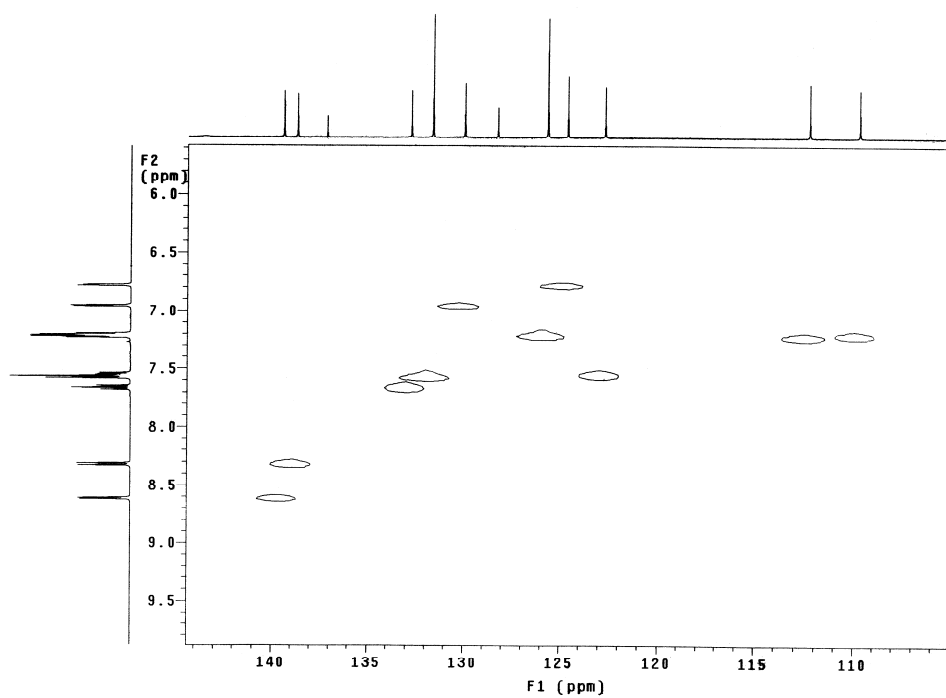


Figure S4. Luminescence Lifetime Measurements for **PS-B5HTQ** and **M-B5HTQ** in THF.

