Electronic Supplementary Information

RAFT Polymerization of Luminescent Organoboron 8-Hydroxyquinolate Monomers

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Experimental Methods

Materials and General Methods. mPEG \((M_n = 2000, y = 45; PDI = 1.04)\) was purchased from Aldrich, mPEO \((M_n = 19300, y = 440; PDI = 1.03)\) was purchased from Polymer Source Inc., and BBr\(_3\) (99.9%), 8-hydroxyquinoline (99%), from Acros. Caution! BBr\(_3\) is toxic and corrosive and should be handled appropriately with great care; fluorinated grease was used for ground glass joints in reactions involving boron tribromide. All chemicals were used as received without further purification. The RAFT agent mPEG-BSPA (BSPA=3-benzylsulfanylthiocarbonylsulfanylpropionic acid),\(^1\) 4-trimethylsilyl-1-t-butylbenzene\(^2\) and 4-trimethylstannylstyrene\(^3\) were prepared according to literature procedures. 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); chlorinated solvents were subsequently distilled from CaH\(_2\) and degassed via several freeze-pump-thaw cycles.

The 499.9 MHz \(^1\)H and 125.7 MHz \(^{13}\)C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz \(^{11}\)B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. \(^1\)H and \(^{13}\)C NMR spectra were referenced internally to the solvent peaks and the \(^{11}\)B NMR spectra externally to BF\(_3\)•Et\(_2\)O \((\delta = 0)\) in C\(_6\)D\(_6\). Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

GPC analyses were performed in THF (1 mL/min) or THF/2vol% NEt\(_3\) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual \(\lambda\) absorbance detector, and a 2414 refractive index detector. Two styragel columns (Polymer Laboratories; 5 \(\mu\)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 in-line with the GPC; a Wyatt Optilab refractive index detector operated at 690 nm was used as the concentration detector for in-line GPC-MALLS measurements.

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 QELS software (regularization analysis with DYNALS algorithm, intensity-weighted average hydrodynamic radius).

UV-visible absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse Fluorescence spectrophotometer with optically dilute solutions \((A < 0.1)\). Anthracene was used as the standard and the quantum yield of anthracene \((\Phi = 0.33)\) was adopted from the Handbook of Photochemistry\(^4\). Sample solutions were prepared using a microbalance \((\pm 0.1 \text{ mg})\) and volumetric glassware. The quantum yield was calculated by plotting a graph of integrated fluorescence intensity vs. absorbance of at least 4 solutions with increasing concentration. The
gradient of the graph is proportional to the quantum yield. The formula used to calculate the absolute quantum yield is \( \Phi = \Phi_{\text{standard}} \times \frac{\text{Gradient}_{\text{compound}}}{\text{Gradient}_{\text{standard}}} \)

Fluorescence images were obtained on a Zeiss LSM 510 confocal microscope, utilizing a 63x / 1.4 numerical aperture Plan Apochromat oil objective (Carl Zeiss, Jena, Germany). The excitation wavelength was 458 nm, and a BP 500-550 IR filter was applied for fluorescence detection.

**Experimental Procedures**

**Synthesis of 4-Styryl-4-t-butylphenylboron Quinolate Monomer M1.** To a solution of boron tribromide (2.07 g, 8.62 mmol) in anhydrous toluene (10 mL) was added dropwise under stirring a solution of 1-trimethylsilyl-4-tert-butylbenzene (1.43 g, 6.90 mmol) in toluene (10 mL) at RT. The mixture was stirred at RT overnight, all volatile components were removed under high vacuum and the residue was redissolved in CH\(_2\)Cl\(_2\) (10 mL). Then, a solution of 4-trimethylstannylstyrrene (1.84 g, 6.90 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added slowly under stirring. After 2 h, a solution of 8-methoxyquinoline (1.10 g, 6.91 mmol) CH\(_2\)Cl\(_2\) (10 mL) was added dropwise and the mixture was stirred for an additional hour. The reaction mixture was extracted with 3 x 50 mL of aqueous ammonium bicarbonate (10%) and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude product was recrystallized from CH\(_2\)Cl\(_2\)/ether solvent mixture (v/v=1/2), to give M1 as a yellow microcrystalline solid. Yield: 2.0 g, 74%. \(^1\)H NMR (499.895 MHz, CDCl\(_3\)): \( \delta = 8.60 \) (d, \( ^3J = 5.0 \) Hz, 1H, Q-H2), 8.40 (d, \( ^3J = 8.5 \) Hz, 1H, Q-H4), 7.66 (pst, \( ^3J = 8.0 \) Hz, 1H, Q-H6), 7.62 (dd, \( ^3J = 5.0 \) Hz and 8.5 Hz, 1H, Q-H3), 7.46 (d, \( ^3J = 7.5 \) Hz, 2H, Ph-H2,6), 7.37 (d, \( ^3J = 8.0 \) Hz, 2H, Sty-H2,6), 7.33 (d, \( ^3J = 8.0 \) Hz, 2H, Ph-H3,5), 7.33 (d, \( ^3J = 8.5 \) Hz, 2H, Sty-H3,5), 7.24 (d, \( ^3J = 8.0 \) Hz, 1H, Q-H5), 7.18 (d, \( ^3J = 7.5 \) Hz, 1H, Q-H7), 6.70 (dd, \( ^3J = 11.0, 17.5 \) Hz, 1H, Vi), 5.70 (d, \( ^3J = 17.5 \) Hz, 1H, Vi), 5.16 (d, \( ^3J = 11.0 \) Hz, 1H, Vi), 1.30 (s, 9H, \( \text{CMCe}_3 \)); \(^{13}\)C NMR (125.698 MHz, CDCl\(_3\)): \( \delta = 159.1 \) (Q-C8), 149.8 (Ph-C4), 143.8 (br., Ph-C1), 139.5 (Q-C2/4), 138.8 (Q-C2/4), 137.9 (Q-C9), 137.5 (vinyl-C), 136.4 (styril-C4), 133.1 (Q-C6), 132.4 (styril-C2,6), 132.0 (Ph-C2,6), 128.7 (Q-C10), 125.7 (styril-C3,5), 124.7 (Ph-C3,5), 122.9 (Q-C3), 113.0 (vinyl-C), 112.3 (Q-C5), 109.9 (Q-C7), 34.6 (CMCe3), 31.6 (CMCe3), styril-C1 not observed; \(^{11}\)B NMR (160.386 MHz, CDCl\(_3\)): \( \delta = 11.4 \) (w\(_{\text{tBu}}\)= 400 Hz). Elemental analysis for C\(_{27}\)H\(_{36}\)BNO: calc C 82.87, H 6.70, N 3.58; found C 82.60, H 6.75, N 3.49%.

**Synthesis of M2.** To a solution of boron tribromide (1.62 g, 6.47 mmol), in 10 mL of anhydrous toluene was added dropwise of a solution of 1-trimethylsilyl-4-tert-butylbenzene (0.89 g, 4.31 mmol) in 10 mL anhydrous toluene at RT under stirring. The mixture was stirred overnight, followed by removing the excess boron tribromide and toluene under high vacuum. The residue was redissolved in 10 mL of dry CH\(_2\)Cl\(_2\). Then, a solution of 4-trimethylstannylstyrrene (1.15 g, 4.31 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise under stirring. After 2 h, a solution of 5-(4’-dimethylamino phenyl)-8-methoxyquinoline (1.20 g, 4.31 mmol) in CH\(_2\)Cl\(_2\) (25 mL) was added dropwise and the mixture was stirred for another 2 h. The reaction mixture was worked up with 3x50 mL of aqueous ammonium bicarbonate (10%), and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude monomer was purified by column chromatography on silica gel with CH\(_2\)Cl\(_2\) as the eluent.
Recrystallization from CH₂Cl₂/hexanes=1/2 (v/v) mixture gave M₂ as an orange microcrystalline solid. Yield: 1.80 g, 82%. ¹H NMR (499.895 MHz, CDCl₃): δ = 8.60 (d, ³J = 4.0 Hz, 1H, Q-H2), 8.59 (overlapped, 1H, Q-H4), 7.62 (d, ³J = 8.0 Hz, 1H, Q-H6), 7.57 (dd, ³J = 5.0 Hz and 8.0 Hz, 1H, Q-H3), 7.51 (d, ³J = 8.0 Hz, 2H, styryl-H2,6), 7.44 (d, ³J = 8.0 Hz, 2H, Ph-H2,6), 7.4-7.3 (m, 6H, Ph-H3,5, Ph-H3,6, styryl-H3,5), 7.22 (d, ³J = 8.0 Hz, 2H, Q-H7), 6.89 (d, ³J = 8.5 Hz, 2H, Ph-H2,6), 6.72 (dd, ³J = 11.0, 17.5 Hz, 1H, Vi), 5.72 (d, ³J = 17.5 Hz, 1H, Vi), 5.18 (d, ³J = 11.0 Hz, 1H, Vi), 3.05 (s, 6H, NMe₂), 1.32 (s, 9H, CMe₃); ¹³C NMR (125.698 MHz, CDCl₃): δ = 157.7 (Q-C8), 150.1 (Ph-C1), 149.7 (Ph-C4), 139.3 (Q-C2/4), 138.3 (Q-C2/4), 138.0 (Q-C9) 137.6 (vinyl-C), 136.3 (styryl-C4), 132.6 (Q-C6), 132.5 (styryl-C2,6), 132.0 (Ph-C2,6), 130.5 (Ph-C3,5), 127.2 (Q-C10), 126.8 (Q-C5), 126.2 (Q-C4), 125.7 (styryl-C3,5), 124.7 (Ph-C3,5), 122.6 (Q-C3), 113.0 (vinyl-C), 112.9 (Ph-C2,6), 109.9 (Q-C7), 40.8 (NMe₂), 34.6 (CMe₃), 31.6 (CMe₃), n.o. (Ph-C1, styryl-C1); ¹¹B NMR (160.386 MHz, CDCl₃) δ = 11.4 (w₁/₂ = 400 Hz). Elemental analysis for C₃₅H₃₅BN₂O × 0.5(C₆H₁₄): calcd C 82.45, H 7.65, N 5.06; found C 82.01, H 7.81, N 4.97%. The amount of cocrystallized hexanes was independently confirmed by ¹H NMR integration.

**Example for the Synthesis of P1.** A Schlenk tube was filled with methyl 3-benzyloxysulfonylthiocarbonylsulfanylpropionate (CTA1) (11.0 mg, 0.0384 mmol), M₁ (500 mg, 1.28 mmol), AIBN (2.1 mg, 0.0128 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. To determine the conversion of monomer at different times, one drop of solution was taken out with a syringe at 30 min, 75 min, 150 min, 270 min and 360 min for ¹H NMR analysis (the integral ratio of the vinyl signal at 5.16 ppm and the methyl group of anisole at 3.86 ppm was used to determine the monomer conversion). The polymerization was quenched at liquid nitrogen temperature after 360 min. The polymer was purified by two precipitations into a 10-fold volume of methanol and then dried under high vacuum. GPC-RI (THF, 1 mL/min): Mₙ = 5840, Mₙ = 7090, PDI = 1.21. The NMR data of P₁ were in good agreement with those reported for the polymer prepared by post-modification procedures,⁵ and no indication of different tacticity was found based on comparison of the ¹³C NMR spectra.

**Example for the Synthesis of P2.** A Schlenk tube was filled with methyl 3-benzyloxysulfonylthiocarbonylsulfanylpropionate (CTA1) (6.73 mg, 0.0235 mmol), M₂ (600 mg, 1.18 mmol), AIBN (1.29 mg, 0.00784 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 9 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by 2 precipitations into a 10-fold volume of hexanes/methanol=2/1 (v/v) and then dried under high vacuum. The conversion of monomer based on the weight of the final product (350 mg) was determined to be 58%. GPC-RI (THF, 1 mL/min): Mₙ = 5220, Mₙ = 6550, PDI = 1.25. The NMR data of P₂ were in good agreement with those reported for the polymer prepared by post-modification procedures,⁵ and no indication of different tacticity was found based on comparison of the ¹³C NMR spectra.

A similar procedure was used for a kinetic study, the results of which are given in Table 1 in the manuscript and illustrated in Figure S1 of the electronic supplementary information (ESI).

**Kinetic analysis of the chain extension of CTA2 with M₁.** A flame-dried Schlenk tube was filled with CTA2 (45 mg, 0.020 mmol), M₁ (780 mg, 2.00 mmol), AIBN (2.6 mg, 0.016 mmol in 3 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C and samples were withdrawn at predetermined times. Data from a kinetic analysis are provided in Figure S2.
Synthesis of P1-b-PEO(440). A flame-dried Schlenk tube was filled with CTA3 (360 mg, 0.0184 mmol), AIBN (1.0 mg, 0.0061 mmol), M1 (720 mg, 1.84 mmol in 4 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10-fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.60 g. The conversion of monomer based on the weight of the final product was determined to be ca. 33%. Elemental analysis for C7H7(C57H58BN)3O(C2H4O)440OCH3: calcld C 66.51, H 8.07, N 1.51; found C 66.68, H 7.64, N 1.55%.

Synthesis of P2-b-PEO(440). A flame-dried Schlenk tube was filled with CTA3 (391 mg, 0.020 mmol), AIBN (1.1 mg, 0.0067 mmol), M2 (510.5 mg, 1.00 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10-fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.57 g. The conversion of monomer based on the weight of the final product was determined to be ca. 35%. Elemental analysis for C7H7(C35H35BN)2O14O(C2H4O)440OCH3: calcld C 61.91, H 8.51, N 1.46; found C 61.61, H 8.60, N 1.45%.

Aqueous Self-assembly of Block Copolymers. The block copolymer under investigation (2.5 mg) was dissolved in THF as a common solvent (5.0 mL), and deionized water was added dropwise under magnetic stirring. The final concentration of the polymer was 0.01 mg/mL. Then, the solution was dialyzed against deionized water for 3 days to remove THF (the water was replaced >5 times over this period).

References
Fig. S1. (A) Kinetic plot for the polymerization of M2 (344 mg) in anisole (1 mL) at 80 °C; [M1]:[CTA1]:[AIBN]=33:1:0.33; (B) plot of $M_n$ (from GPC vs. PS standards) vs. monomer conversion as determined by $^1$H NMR integration (vinyl signal of M2 vs anisole methyl group); (C) GPC curves for the polymerization of M2.
Fig. S2. (A) Kinetic plot for the chain extension of CTA2 with M1 (780 mg) in anisole (3 mL) at 80 °C; molar ratio of [M1]:[CTA2]:[AIBN]=100:1:0.8; (B) plot of $M_n$ (from GPC vs. PS standards) vs. monomer conversion as determined by $^1$H NMR integration (vinyl signal of M1 vs anisole methyl group); (C) GPC curves for the chain extension of PEO with M1.
**Fig. S3.** $^1$H NMR spectra of P1, P2, P1-b-PEO(440) and P2-b-PEO(440) in CDCl$_3$.

**Fig. S4.** $^{11}$B and $^{13}$C NMR spectra of the block copolymer P1-b-PEO(440) and comparison to the $^{13}$C NMR of M1 monomer.
**Fig. S5.** UV-Vis and fluorescence spectra in THF (for M1, P1, P1-b-PEO(440)  $\lambda_{\text{exc}} = 395$ nm; for M2, P2, P2-b-PEO(440) $\lambda_{\text{exc}} = 506$ nm)

![Normalized absorbance and intensity spectra](image)

**Table S1.** Photophysical data of monomers and polymers in THF solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>M1</th>
<th>P1</th>
<th>P1-b-PEO(440)</th>
<th>M2</th>
<th>P2</th>
<th>P2-b-PEO(440)</th>
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<tr>
<td>$\lambda_{\text{abs}}$ (nm)</td>
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<td>395</td>
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<td>440</td>
<td>440 (440 in H$_2$O)</td>
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<tr>
<td>$\lambda_{\text{em}}$ (nm)</td>
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<td>506</td>
<td>506 (503 in H$_2$O)</td>
<td>640</td>
<td>619</td>
<td>619 (621 in H$_2$O)</td>
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<td>$\Phi_{\text{Fl}}$ (%)</td>
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<td>20</td>
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**Fig. S6.** Fluorescence microscopy image (10µm×10µm) of an aqueous solution of P1-b-PEO(440) drop-cast onto a plastic substrate; $\lambda_{\text{exc}} = 450$ nm, detected at $\lambda = 500$-550 nm. Spot size is diffraction-limited and shows correct particle location but not dimensions.
Fig. S7. DLS correlation functions for solutions of P1-b-PEO(440) and P2-b-PEO(440) in water.