Supporting Information

Organoboron Star Polymers via Arm-First RAFT Polymerization: Synthesis, Luminescent Behavior, and Aqueous Self-Assembly

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1. EXPERIMENTAL DETAILS

General methods. 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_2O ($\delta = 0$) in C_6D_6. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

GPC analyses were performed in THF (1.0 mL/min) or DMF with 0.2% w/v Bu_4NBr (0.50 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Three styragel columns (Polymer Laboratories; two 5 μm Mixed-C and one 5 μm Mixed-D), which were kept in a column heater at 35 °C, were used for separation in THF. For separation in DMF/0.2% Bu_4NBr either a set of two polyvinylalcohol columns (Shodex Asahipak 9 μm GF-710 HQ and 5 μm GF-510 HQ) or a set of two styragel columns (Polymer Laboratories; one 10 μm Mixed-B and one 5 μm Mixed-C) was used at 65 °C. 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 T-rEX refractive index detector operated at 658 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 detection using the Wyatt Astra software assuming 100% mass recovery or literature data were used as specified.

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 (0.33 in THF) was adopted from the Handbook of Photochemistry (S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker Inc., New York, 1993.). Sample solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware. The quantum yield was calculated from 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.

Transmission electron microscopy (TEM) characterization was conducted on a FEI Tecnai 12 electron microscope operated at 80 kV. The star polymer solution in chloroform was cast on a copper grid with a carbon coating (no formvar), and stained by RuO_4 vapor for 10 min in a sealed container. To stain the star polymer aggregates, one drop of micelle solution in water was cast on a copper grid. The water was allowed to evaporate, and the sample was stained by exposure to iodine vapor for 30 min.

Dynamic light scattering (DLS) was carried out on a Wyatt Dawn EOS instrument that was modified with a Wyatt QELS attachment. Data were collected either in-line or in batch mode using an avalanche photodiode and an optical fiber. The in-line GPC-QELS data are given as number-average hydrodyanmic diameters. For batch mode measurements, the data was processed using the Wyatt QELS software (regularization analysis, results are given as intensity-average hydrodynamic diameters).

Materials. Tetrahydrofuran (THF) and 1,4-dioxane were distilled from Na/benzophenone prior to use. Dichloromethane (DCM) was dried over CaH_2, followed by vacuum transfer. Azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. Styrene (St) and 4-vinyl pyridine (4VP) were purified by passing the liquid through a neutral alumina column and then distilled under reduced pressure. N-isopropyl acrylamide (NIPAM) was crystallized in hexanes/benzene mixture. The chain transfer agents (Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo, S. H. Thang, *Macromolecules* **2003**, *36*, 2256-2272; M. H. Stenzel, T. P. Davis, A. G. Fane, *J. Mater. Chem.* **2003**, *13*, 2090-2097) and *N*-(4'-bromobutyl)carbazole (C. Barrett, B. Choudhury, A. Natansohn, P. Rochon, *Macromolecules* **1998**, *31*, 4845-4851) used in this work were synthesized according to reported procedures. All the other solvents and chemicals were used without further purification.

Synthesis of Distyrylboron Quinolate (Crosslinker 1). Method 1. To a flame-dried 3-neck flask containing 6.42 g (0.264 mol) of magnesium, were added 300 mL of THF and 1.0 mL of 1,2-dibromoethane. After stirring for 5 min, 33.3 g (0.24 mol) of 4-chlorostyrene were added via an addition funnel. The reaction mixture was stirred at 55 °C for 2 h. The styryl magnesium chloride solution was then added via canula to trimethoxy borane (10.4 g, 0.100 mol) in 30 mL of THF. The reaction mixture was stirred at 45 °C for 1 h, followed by the addition of 14.5 g (0.100 mol) of 8-hydroxy quinoline under nitrogen protection. After stirring for another 6 h at 45 °C, an aqueous solution of $[NH_4][HCO_3]$ was added and the product was extracted into DCM. The crude product was purified by silica gel column chromatography with DCM as the eluent and then crystallized from DCM/hexanes mixture to give a yellow microcrystalline solid (17.1 g, 55%). **Method 2.** In a glove box, 2.35 g (9.37 mmol) of BBr_3 were dissolved in 10 mL of DCM in a Schlenk flask. A solution of 4-trimethylstannyl styrene (5.00 g, 18.73 mmol) in 20 mL of DCM was added dropwise to the BBr_3 solution. The reaction mixture was stirred at room temperature for 4 h, then 1.49 g (9.37 mmol) of 8-methoxy quinoline solution in 10 mL of DCM were added. After another 2 h of stirring, the reaction mixture was worked up with 10% aqueous $[NH_4][HCO_3]$ (3×50 mL). The organic phase was separated and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel with DCM as the eluent, and crystallized in a 1/2 mixture of DCM/ether. The product was obtained in the form of yellow crystals (1.73 g, 51%). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 11.3$ ($w_{1/2} = 430$); ^1H NMR (499.893 MHz, $CDCl_3$): $\delta = 8.58$ (d, $^3J = 5.0$ Hz, 1H, Q-H2), 8.43 (d, $^3J = 8.0$ Hz, Q-H4), 7.68 (pst, $^3J = 8.0$ Hz, 1H, Q-H6), 7.64 (dd, $^3J = 5.0$ Hz and 8.5 Hz, 1H, Q-H3), 7.42 (d, $^3J = 8.0$ Hz, 4H, Ph-H2,6), 7.34 (d, $^3J = 8.0$ Hz, 4H, Ph-H3,5), 7.25 (d, $^3J = 8.5$ Hz, 1H, Q-H5), 7.20 (d, $^3J = 7.5$ Hz, 1H, Q-H7), 6.70 (dd, $^3J = 11.0$ Hz, 18.0 Hz, 2H, vinyl-H), 5.67 (d, $^3J = 18.0$ Hz, 2H, vinyl-H), 5.18 (d, $^3J = 11.0$ Hz, 2H, vinyl-H); ^{13}C (125.698 MHz, $CDCl_3$): $\delta = 158.9$, 147.0, 139.4, 139.0, 137.7, 137.4, 136.5, 133.1, 132.4, 128.6, 125.7, 123.0, 113.1, 112.5, 109.9; UV-Vis (THF, 3.0 x 10^{-5} M): $\lambda_{max} = 395$ nm ($\varepsilon = 3200$); fluorescence (THF, 3.0 x 10^{-5} M): $\lambda_{em,max} = 505$ nm, $\Phi = 0.22$ ($\lambda_{exc} = 395$ nm). High resolution MALDI-MS: Calcd for $C_{25}H_{19}NBO$: 360.1559; obsvd: 360.1574.

Synthesis of Polystyrene macro-CTA (PS-CTA). Into a Schlenk tube were loaded styrene (15.6 g, 150 mmol), benzyl dithiobenzoate (BDTB) (122 mg, 0.500 mmol) and AIBN (20.6 mg, 0.125 mmol). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 3.5 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of methanol, followed by drying in high vacuum. The desired PS macro-CTA was obtained as a light pink powder (4.10 g, 26%). GPC-RI (styragel columns, THF): M_n = 8130 g/mol, PDI = 1.16. GPC-MALLS (styragel columns, THF): M_n = 9470 g/mol, PDI = 1.14, dn/dc = 0.178 mL/g.

Synthesis of Poly(*N*-isopropyl acrylamide) macro-CTA (PNIPAM-CTA1). Into a Schlenk tube were loaded NIPAM (3.53 g, 31.2 mmol), 3-benzylsulfanylthiocarbonylsulfanyl propionate (59.6 mg, 0.208 mmol), AIBN (3.42 mg, 20.8 μmol, stock solution in dioxane), and 12 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed in a 60 °C oil bath and kept stirring for 3 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired PNIPAM macro-CTA was obtained as a pink powder (1.15 g, 33%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 8800 g/mol, PDI = 1.18. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 11230 g/mol, PDI = 1.11, dn/dc = 0.074 mL/g.

Synthesis of Poly(*N*-isopropyl acrylamide) macro-CTA (PNIPAM-CTA2). Into a Schlenk tube were loaded NIPAM (4.52 g, 40.0 mmol), benzyl dithiobenzoate (BDTB) (98 mg, 0.40 mmol), AIBN (13.1 mg, 80 μmol), and 4.0 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 20 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired PNIPAM macro-CTA was obtained as a pink powder (1.62 g, 34%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 6800 g/mol, PDI = 1.17. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 7840 g/mol, PDI = 1.08, dn/dc = 0.075 mL/g.

Synthesis of Poly(4-vinylpyridine) macro-CTA (P4VP-CTA). Into a Schlenk tube were loaded 4-vinyl pyridine (15.5 g, 147 mmol), benzyl dithiobenzoate (BDTB) (120 mg, 0.491 mmol), AIBN (16.1 mg, 98.2 μmol), and 1.0 mL of dioxane. After three freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired P4VP macro-CTA was obtained as a pink powder (6.70 g, 42%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 11100 g/mol, PDI = 1.32. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 15200 g/mol, PDI = 1.09**,** dn/dc = 0.143 mL/g.

Synthesis of Poly(*N*-isopropyl acrylamide)-block-polystyrene macro-CTA (PNIPAM-*b*-PS-CTA). Into a Schlenk tube were loaded 50 mg of PNIPAM-CTA2, AIBN (13.1 mg, 80 μmol), 3.0 mL of styrene and 1.0 mL of dioxane. After three freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of methanol, followed by drying in high vacuum. The desired of PNIPAM-*b*-PS macro-CTA was obtained as light pink powder (0.70 g). GPC-RI (styragel columns, THF): M_n = 57900 g/mol, *PDI* = 1.24; GPC-MALLS (styragel columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 75800 g/mol, *PDI* = 1.18, d*n*/d*c* = 0.149 mL/g.

Synthesis of PS Star Polymer. In a Schlenk tube, PS-CTA (547 mg), distyrylboron quinolate (500 mg, 1.38 mmol), and AIBN (0.94 mg, 5.72 μmol; stock solution in dioxane) were dissolved in 6.0 mL of dioxane ([crosslinker]/[PS-CTA]/[AIBN] = 24/1/0.10). After three freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The product mixture was diluted with a small amount of THF and precipitated into a 10-fold volume of methanol. For fractionation, the precipitated polymer was redissolved in 100 mL of THF and MeOH was added dropwise under stirring until precipitation was observed. The mixture was allowed to settle overnight. This procedure was repeated two more times. The isolated material was dried in high vacuum to give the product as a yellow powder (740 mg). GPC-RI (styragel columns, THF): M_n = 73800 g/mol, PDI = 1.21. GPC-MALLS (styragel columns, THF): M_n = 271000 g/mol, *PDI* = 1.38, d*n*/d*c* = 0.169 mL/g.

Synthesis of PNIPAM Star Polymer. In a Schlenk tube, PNIPAM-CTA1 (400 mg), distyrylboron quinolate (289 mg, 0.80 mmol), and AIBN (1.09 mg, 6.67 μmol; stock solution in dioxane) were dissolved in 10.0 mL of dioxane ([crosslinker]/[PNIPAM-CTA1]/[AIBN] = 16/1/0.13). After three freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath under stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The product mixture was diluted with a small amount of CH_2Cl_2 and precipitated into a 10-fold volume of diethyl ether. For fractionation, the precipitated polymer was redissolved in 100 mL of CH_2Cl_2 and diethyl ether was added dropwise under stirring until precipitation was observed. The mixture was allowed to settle overnight. This procedure was repeated two more times. The isolated material was dried in high vacuum to give the product as a yellow powder (240 mg). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 146000 g/mol, *PDI* = 1.32. GPC-MALLS (styragel columns, DMF with 0.2 % (w/v) Bu_4NBr): 334400 g/mol, *PDI* = 1.80, d*n*/d*c* = 0.106 mL/g.

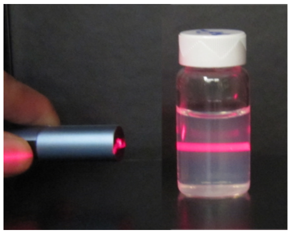
Synthesis of P4VP Star Polymer. In a Schlenk tube, P4VP-CTA (300 mg), distyrylboron quinolate (233 mg, 0.645 mmol), and AIBN (0.589 mg, 3.58 μmol; stock solution in dioxane) were dissolved in 3.0 mL of dioxane and 1.0 mL of DMF ([crosslinker]/[PNIPAM-CTA1]/[AIBN] = 33/1/0.18). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath under stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The product mixture was diluted with a small amount of MeOH and precipitated into a 10-fold volume of diethyl ether. For fractionation, the precipitated polymer was redissolved in 50 mL of MeOH and diethyl ether was added dropwise under stirring until precipitation was observed. The mixture was allowed to settle overnight. This procedure was repeated two more times. The isolated polymer was dried in high vacuum to give the product as 180 mg of yellow powder. GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v)

Bu_4NBr): M_n = 294000 g/mol, *PDI* = 1.46. GPC-MALLS (styragel columns, DMF with 1 % (v/v) pyridine): M_n = 320000 g/mol, *PDI* = 1.98, d*n*/d*c* = 0.143 mL/g.

Synthesis of PNIPAM-*b*-PS Star Polymer. In a Schlenk tube, PNIPAM-*b*-PS-CTA (175 mg), distyrylboron quinolate (33 mg, 0.183 mmol), and AIBN (0.167 mg, 1.02 μmol; stock solution in dioxane) were dissolved in 1.0 mL of dioxane ([crosslinker]/[PNIPAM-*b*-PS-CTA]/[AIBN] = 79/1/0.44). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The product mixture was diluted with a small amount of THF and precipitated into a 10-fold volume of diethyl ether. For fractionation, the precipitated polymer was redissolved in 30 mL of THF and diethyl ether was added dropwise under stirring until precipitation was observed. The mixture was allowed to settle overnight. This procedure was repeated two more times. The isolated polymer was dried in high vacuum to give the product as a yellow powder (135 mg). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) TBAB): M_n = 729000 g/mol, PDI = 1.19. GPC-MALLS (styragel columns, DMF with 0.2 % (w/v) Bu_4NBr): M_n = 5046000 g/mol, *PDI* = 1.40, d*n*/d*c* = 0.127 mL/g.

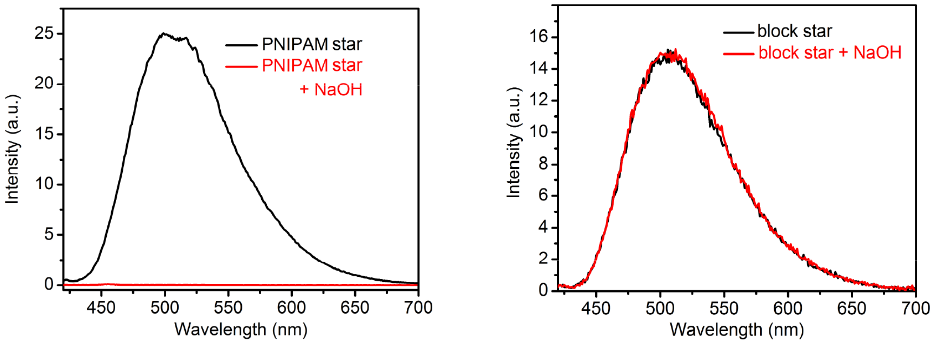
Self-assembly of PNIPAM-*b*-PS star polymer. The PNIPAM-*b*-PS star polymer (1.2 mg) was dissolved in 6.0 mL of THF. The star polymer solution was loaded into dialysis tubing (cut-off molecular weight = 6000~8000) and dialyzed against ~1L of deionized water for 3 days. The THF solvent was completely removed by changing water 5 times.

Figure S1. Photograph illustrating light scattering of PNIPAM-*b*-PS star polymer aggregates in water.



Stability Studies of PNIPAM and PNIPAM-*b*-PS Star Polymers in Strongly Basic Water. The PNIPAM star polymer was dissolved in water (c = 0.2 mg/mL) and NaOH was added (c_{NaOH} = 0.1 M). Similarly, NaOH was added to a solution of PNIPAM-*b*-PS star polymer in water (c_{NaOH} = 0.1 M). For both samples, fluorescence spectra were taken before and 12 h after NaOH addition.

Figure S2. Fluorescence spectra of (left) PNIPAM star polymer before and after addition of NaOH solution; (right) PNIPAM-*b*-PS star polymer before and after addition of NaOH solution.



Solubility Test of P4VP-Cz Star Polymer in Water. The P4VP-Cz star polymer was dissolved in water at 0.1 mg/mL. A chosen inorganic salt (NaI, $NaBF_4$, Bu_4NBr or K_2CO_3) was dissolved in the star polymer solution (c_{salt} = 0.1 M). A flocky precipitate was observed within minutes after addition.

Carbazole Modification of P4VP Star Polymer (Synthesis of P4VP-Cz Star). In a vial, P4VP star polymer (40 mg) was dissolved in 4.0 mL of DMF, followed by addition of 230 mg of *N*-(4'-bromobutyl)carbazole. Nitrogen was bubbled through the tube for 5 min and the tube was sealed. After stirring at 45 °C for 2 days, the polymer solution was precipitated in ether three times, and then dried under high vacuum to give the product as a light yellow solid (56 mg).

Figure S3a. ^{1}H NMR spectra of P4VP (red) and P4VP-Cz (black) star polymers in DMSO-d6.

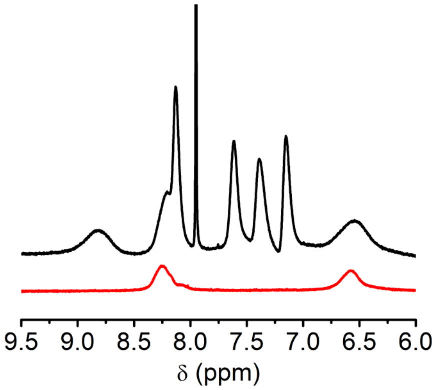
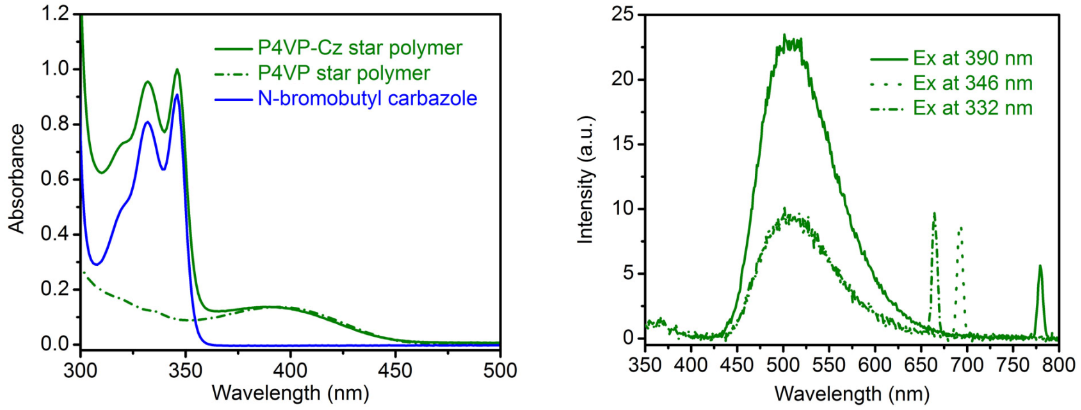
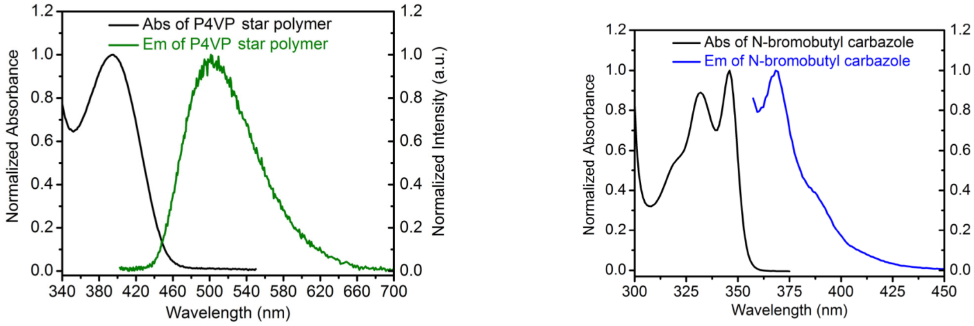


Figure S3b. a) UV-vis and fluorescence spectra of P4VP-Cz star polymers in DMF at different excitation wavelengths and comparison to spectra obtained for the b) P4VP star polymer and c) *N*-(4'-bromobutyl)carbazole.

a) UV-vis and fluorescence spectra of P4VP-Cz star polymers





b) P4VP star polymer (λ_{exc} = 395 nm)

c) N-(4'-bromobutyl)carbazole (λ_{exc} = 346 nm)

2. ADDITIONAL EXPERIMENTAL DATA

Figure S4. ^{1}H, ^{11}B (A) and ^{13}C NMR (B) spectra of crosslinker **1** ($CDCl_3$)

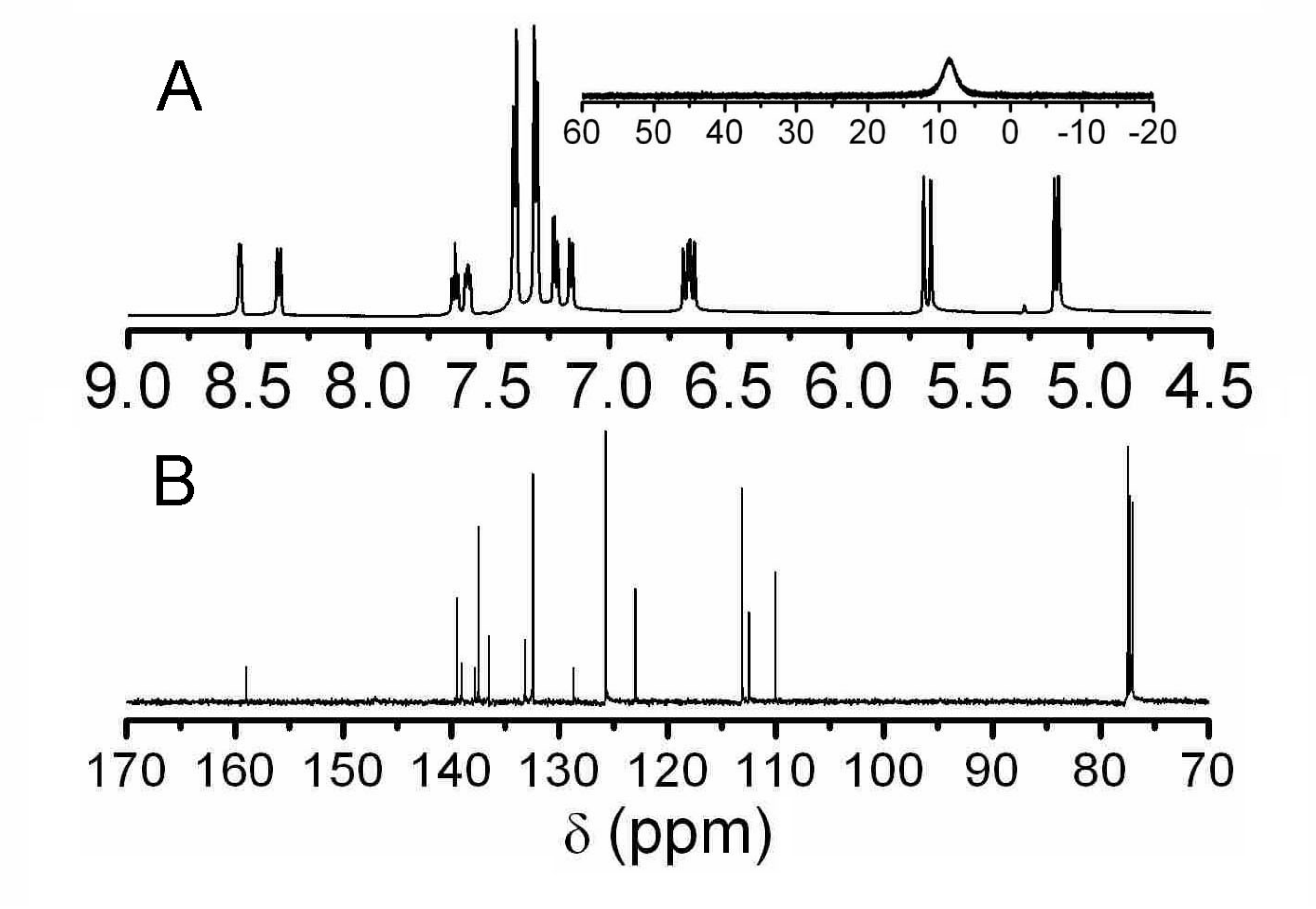


Figure S5. ^{1}H NMR spectra of all star polymers in $CDCl_3$. Note that the signals for the 8-hydroxyquinolate core are strongly broadened as a result of incorporation into a crosslinked matrix and only clearly observed in case of the PNIPAM and PS stars. Incorporation of the crosslinker was in all cases further confirmed by ^{11}B NMR and UV-visible analysis (see Table 1 in the main manuscript for the core fraction determined by UV-visible analysis). Weak signals at ca. 5-6 ppm in the spectra for the PS and PNIPAM stars are attributed to residual vinyl groups (as a result of reaction of only one of the vinyl groups of the crosslinker).

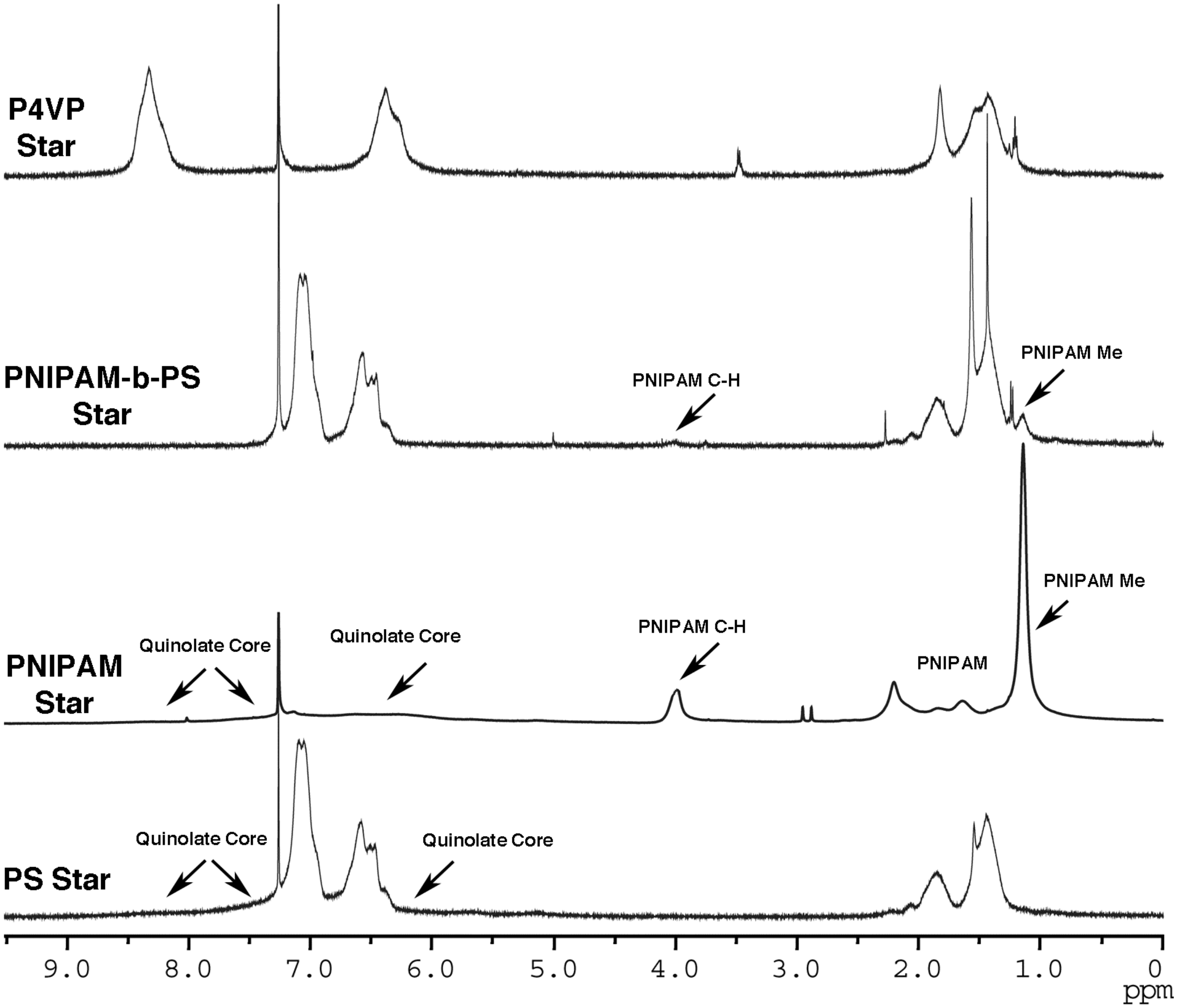


Figure S6. GPC overlays of PNIPAM (top), P4VP (middle), and PNIPAM-*b*-PS (bottom) star polymers and their corresponding arm precursors.

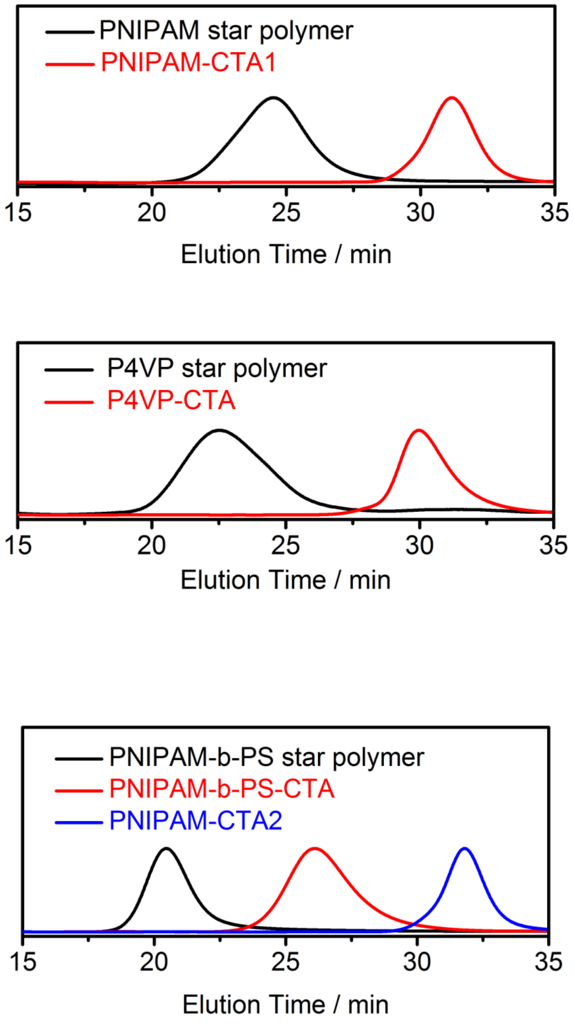


Figure S7. Low magnification TEM image of low dispersity PNIPAM-*b*-PS star polymers with crosslinked organoboron quinolate cores. The sample was deposited from $CHCl_3$ solution and stained with RuO_4 vapour.

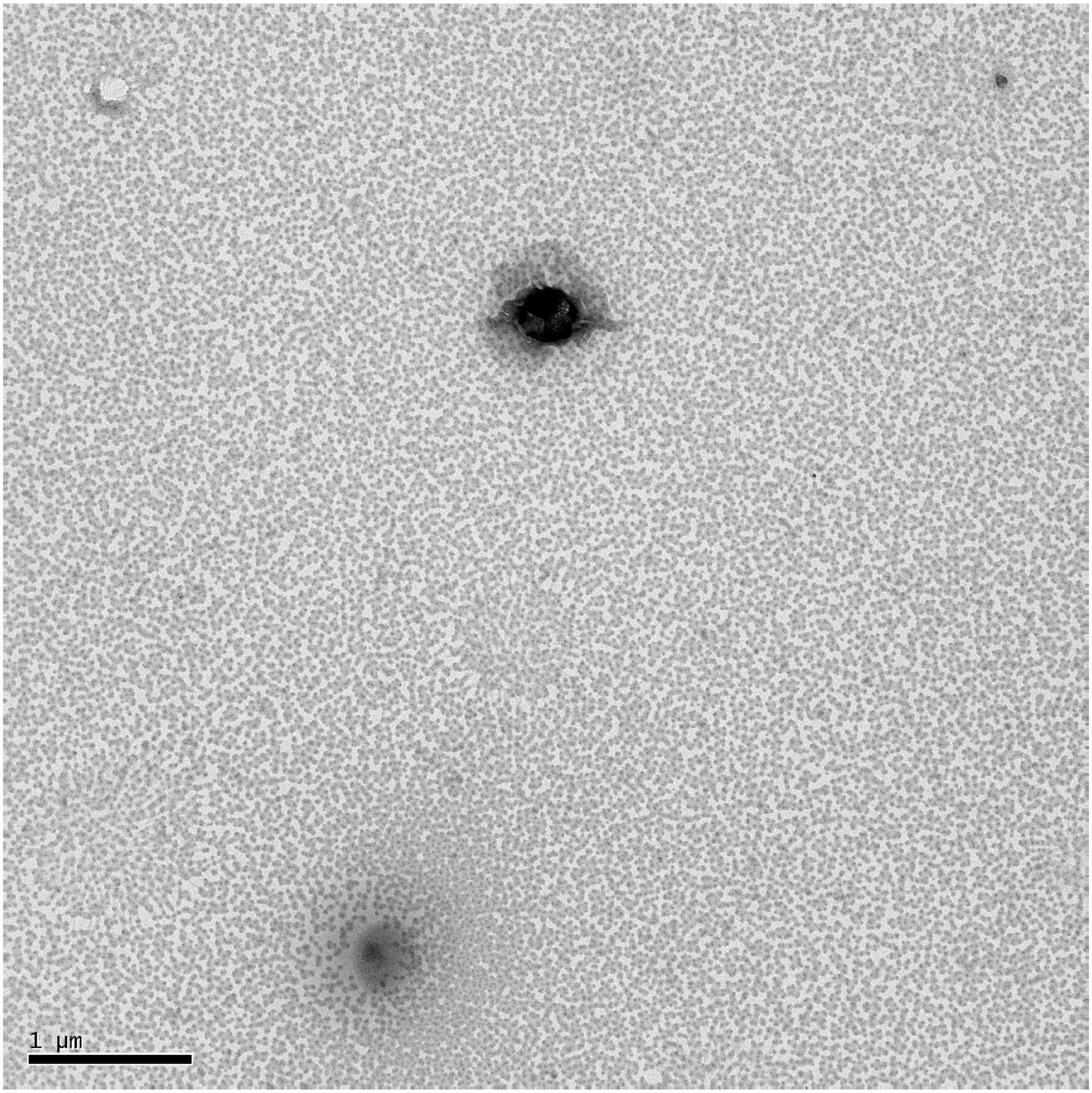
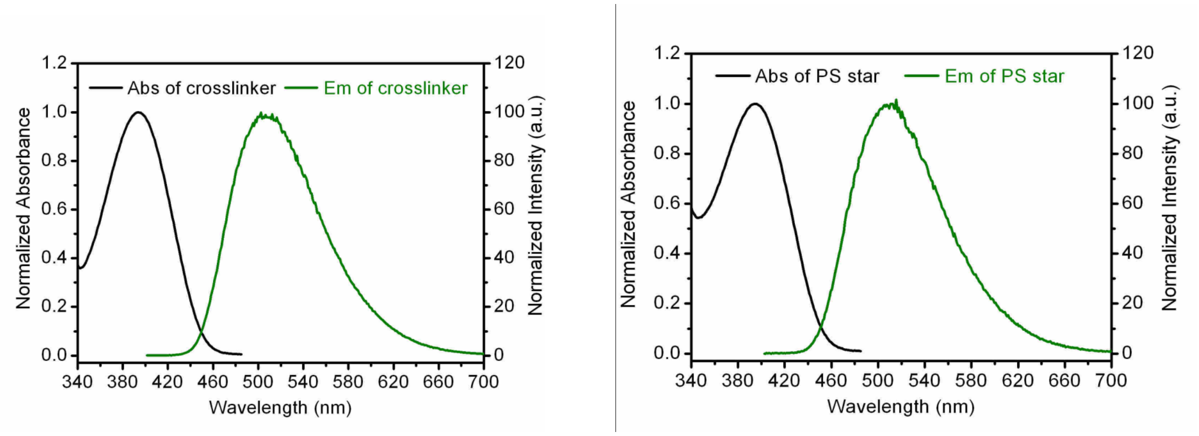


Table S1. Photophysical data of distyrylboron quinolate crosslinker and star polymers in THF

Sample	λ_{abs} (nm)	λ_{em} (nm) [b]	Quantum efficiency [c]
Crosslinker **1**	395	505	0.22
PS star	395	505	0.064
PNIPAM star	394	506	0.11
PNIPAM-b-PS star	395	505	0.18
P4VP star	395	505	0.12
P4VP-Cz star	332[d], 346[d], 390	505	0.089

[a] Measurements in THF, except for the P4VP and P4VP-Cz stars which were investigated in $CHCl_3$. T[b] The excitation wavelength is 395 nm for the crosslinker and all the star polymers. [c] Anthracene (quantum yield = 0.33 in THF) was used as standard. [d] Carbazole-centered absorption bands.

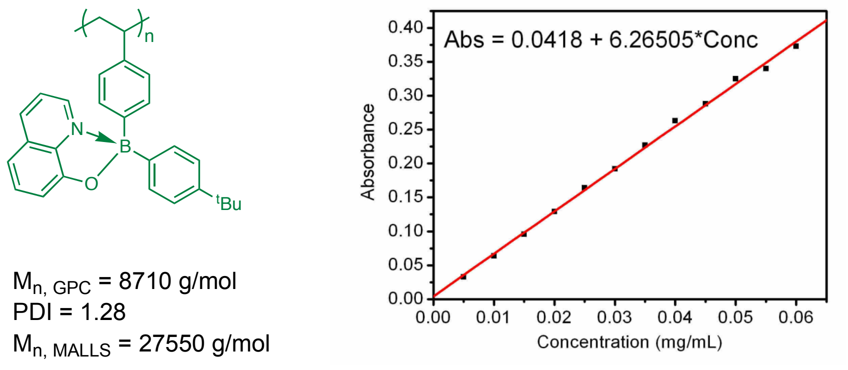
Figure S8. UV-visible and fluorescence (λ_{exc} = 395 nm) spectra of distyrylboron quinolate (left) and PS star polymer (right) in THF.



3. Determination of the mass fraction of the core (*frac*$_{\mathrm{core}}$) of star polymers from the UV-vis absorption at 395 nm using a linear boron quinolate polymer as standard

The *frac*$_{\mathrm{core}}$ of the star polymers containing a crosslinked boron quinolate core is calculated based on comparison of the absorption at λ_{abs} = 395 nm with that of a linear boron quinolate polymer ($M_{\mathrm{n,\,GPC}}$ = 8710 g/mol, PDI = 1.28, $M_{\mathrm{n,\,MALLS}}$ = 27550 g/mol) as standard.

Figure S9. (A) Structure of the linear boron quinolate polymer standard. (B) Calibration curve for the absorbance of the linear boron quinolate polymer at λ_{abs} = 395 nm used for the estimation of the mass fraction of the core (*frac*$_{\mathrm{core}}$) of star polymers.



Assuming that the boron quinolate chromophores in the linear polymer and the crosslinked core of the star polymers have a similar absorptivity ε at λ_{abs} = 395 nm, and given that the arms of the star polymers show no absorbance at this wavelength, the *frac*$_{\mathrm{core}}$ of star polymers is given by:

$$frac_{core} = \frac{Abs_{\mathrm{star}} \times Conc_{\mathrm{stan}}}{Conc_{\mathrm{star}} \times Abs_{\mathrm{stan}}} = \frac{Abs_{\mathrm{star}}}{Conc_{\mathrm{star}} \times 6.265},$$

where Abs_{star}, Abs_{stan}, $Conc_{\mathrm{star}}$ and $Conc_{\mathrm{stan}}$ are the absorbance of the star polymer and standard, and the concentration of the star polymer and standard, respectively. The calculated *frac*$_{\mathrm{core}}$ of the star polymers are listed in Table 1 of the main manuscript.

4. Determination of the average number of arms (f_{arm}) of star polymers

From the *frac*$_{\mathrm{core}}$ of the star polymers and the absolute molecular weights of the star polymers and arm precursors, we can calculate the average number of arms (f_{arm}) of the star polymers using the formula,

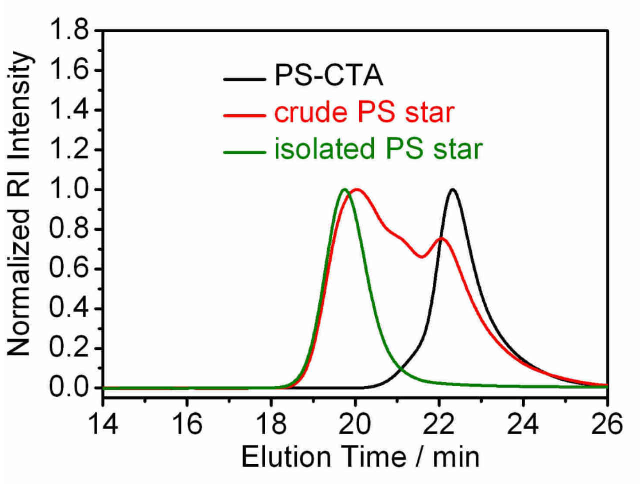
$$f_{arm} = \frac{M_{n,star} \times (1 - frac_{core})}{M_{n,arm}}$$

where $M_{n,star}$ and $M_{n,arm}$ are the absolute molecular weights of the star polymers and arm precursors, respectively.

5. Synthesis of PS star polymer with divinyl benzene (DVB) as crosslinker

In a Schlenk tube, PS-CTA (547 mg), DVB (180 mg), and AIBN (0.94 mg) were dissolved in 3.0 mL of dioxane ([DVB]/[PS-CTA]/[AIBN] = 20/1/0.083). After three freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath under stirring for 24 h. After quenching in liquid nitrogen, the polymer was precipitated into a 10-fold volume of methanol. The precipitated polymer was fractionated in THF/methanol twice. The isolated polymer was dried under high vacuum. GPC-RI: M_n = 44240 g/mol, *PDI* = 1.13.

Figure S10. GPC overlay of the PS-CTA, the crude and the isolated PS star polymers with a PDVB core. The samples were characterized by GPC with THF as the solvent at 1.0 mL/min with PS calibration.



It should be pointed out that, under the same conditions as for the PS star polymer synthesis with the organoboron quinolate crosslinker, with DVB mainly linear species were obtained. To favor the star formation with DVB as the crosslinker, we used a somewhat higher concentration (less solvent) and longer reaction time. Under these conditions, no star-star coupling reaction was observed and narrow PS star polymer was isolated. It should also be noted that the experimental conditions for the star formation with the DVB crosslinker were not optimized, and the incorporation of the PS precursor into the final star is moderate based on the GPC analysis of the crude product. We expect that by further increasing the concentration or reaction time, higher PS precursor incorporation can be easily realized. By comparing the PS star polymer synthesis with organoboron quinolate and DVB crosslinkers, we can see that the reactivity difference of the crosslinkers influences the structural parameters of the final star polymers. Under optimized conditions, well-defined star polymers can be synthesized with different functional crosslinkers.

X-ray Diffraction Analysis of 1 (CCDC 843756)

Crystals of crosslinker **1** suitable for single crystal X-ray diffraction analysis were grown by the slow evaporation of a solution in $CDCl_3$ at room temperature. X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer at 100(2) K using CuKα (1.54178 Å) radiation. SADABS absorption corrections was applied, the structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.

Figure S11. Molecular Structure of (**1**) (ORTEP, 50% probability). Hydrogen Atoms are Omitted for Clarity. Selected Bond Lengths (Å) and Angles (deg): B1-C1 = 1.609(2), B1-C9 = 1.605(2), B1-N1 = 1.637(2), B1-O1 = 1.523(2), O(1)-B(1)-C(9) = 110.52(10), O(1)-B(1)-C(1) = 111.06(10), C(1)-B(1)-C(9) = 116.28(10), O(1)-B(1)-N(1) = 98.95(9), C(9)-B(1)-N(1) = 110.56(9), C(1)-B(1)-N(1) = 108.06(9).

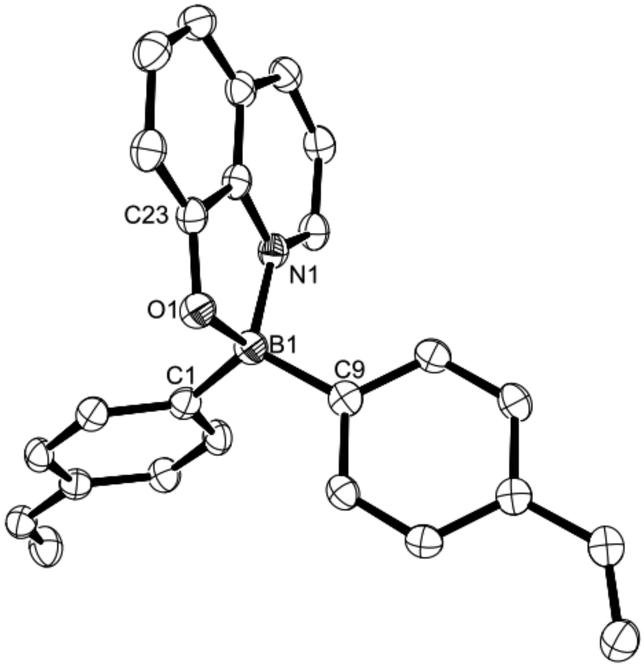


Table S2. Crystal Data and Structure Refinement Details of (Styryl)$_2$BQ (**1**)

	(Styryl)$_2$BQ (1)
empirical formula	$C_{25}H_{20}BNO$
formula weight	361.23
T, K	100(2)
wavelength, Å	1.54178
crystal system	Monoclinic
space group	P2(1)/c
a, Å	14.0629(3)
b, Å	14.0772(3)
c, Å	9.7274(2)
α, deg	90
β, deg	98.3180(10)
γ, deg	90
V, Å^3	1900.56(7)
Z	4
ρ_{calcd}, g cm^{-3}	1.262
μ, mm^{-1}	0.585 (CuK$_\alpha$)
F(000)	760
crystal size, mm	0.34 x 0.21 x 0.21
limiting indices	–16<=h<=16
	–16<=k<=15
	–11<=l<=11
θ range, deg	3.18 – 67.07
reflns collected	14033
independent reflns	3299
absorption correction	Semi-empirical from equivalents
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	3299 / 0 / 253
goodness-of-fit on F^2	1.027
final *R* indices	R1 = 0.0367
$[I > 2\sigma(I)]$[a]	wR2 = 0.0989
R indices (all data)[a]	R1 = 0.0401
	wR2 = 0.1022
peak/hole (e Å^{-3})	0.237 / –0.194

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.