

Supporting Information

Electron-Deficient Triarylborane Block Copolymers: Synthesis by Controlled Free Radical Polymerization and Application in the Detection of Fluoride Ions

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General methods. The 499.9 MHz ^1H 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. The ^1H and ^{13}C NMR spectra were referenced internally to the solvent peaks and the ^{11}B NMR spectra externally to $\text{BF}_3\cdot\text{Et}_2\text{O}$ ($\delta = 0$) in C_6D_6 . Elemental analyses were performed by Quantitative Technologies Inc. (Whitehouse, NJ).

GPC-RI analyses were performed in THF (1.0 mL/min), chloroform (1.0 mL/min) or DMF with 0.2% w/v of $[\text{Bu}_4\text{N}]\text{Br}$ (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 Mix-C and one 10 μm Mix-D), which were kept in a column heater at 35 $^\circ\text{C}$ (THF or chloroform), or a set of two styragel columns (Polymer Laboratories; one 5 μm Mixed-B and one 5 μm Mixed-C) at 65 $^\circ\text{C}$ (DMF), were used for separation. The columns were calibrated with narrow polystyrene standards (Polymer Laboratories, Varian Inc.). Dynamic light scattering (DLS) measurements were performed at 25.0 ± 1 $^\circ\text{C}$ with a Malvern Zetasizer Nano-ZS instrument, equipped with a 4 mW, 633 nm He-Ne laser and an Avalanche photodiode detector at an angle of 173° . Transmission electron microscopy (TEM) was conducted on a FEI Tecnai 12 electron microscope operated at 80 kV. One drop of polymer aggregate solution was cast on a copper grid with a carbon coating.

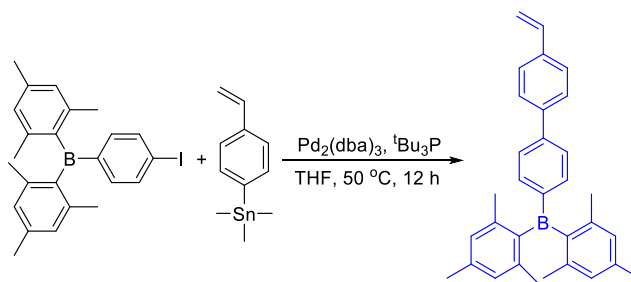
UV-vis absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer with optically dilute solutions ($A < 0.1$). Anthracene was used as the standard and the quantum yield 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 yields were 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. Fluorescence lifetimes were measured using an Horiba Fluorolog-3 spectrofluorometer equipped with a 350 nm nanoLED and a FluoroHub R-928 detector.

Binding constants β were determined using the HyperquadTM program and are given in units of M^{-1} . The boron chromophore concentration ($[B]$) for the block copolymers was estimated using the absorptivity of the homopolymer PBM ($\epsilon = 30000 \text{ cm}^{-1} M^{-1}$ per repeating unit), rather than the NMR or GPC data.

Materials. 1,4-Dioxane and THF were distilled from Na/benzophenone prior to use. Azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. Styrene and 4-vinylpyridine were purified by passing through a neutral alumina column and then distilled under reduced pressure. N-isopropyl acrylamide (NIPAM) was purified by recrystallization in a hexanes/benzene mixture. All other solvents and chemicals were used without further purification. The chain transfer agent benzyl dithiobenzoate (BDTB),¹ dimesityl(4-iodophenyl)borane,² and (4-trimethylstannyl)styrene³ were synthesized according to literature procedures. $[Bu_4N]F \times xH_2O$ (98%) was purchased from Aldrich and used as received.

Synthesis of PNIPAM-CTA. A Schlenk tube was charged with NIPAM (9.04 g, 80.0 mmol), benzyl dithiobenzoate (BDTB) (200 mg, 0.80 mmol), AIBN (26.2 mg, 0.16 mmol), and 20.0 mL of dioxane ($[NIPAM]/[BDTB]/[AIBN] = 100/1/0.2$). After 3 freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and the mixture kept stirring for 24 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. After drying in high vacuum, PNIPAM-CTA was obtained as a pink powder. Yield: 3.06 g (32% conversion). GPC-RI (DMF with 0.2% TBAB): $M_{n, GPC-RI} = 9630 \text{ g/mol}$, $PDI = 1.09$, $m_{GPC} = 82$. ¹H NMR end group analysis: $m_{NMR} = 63$.

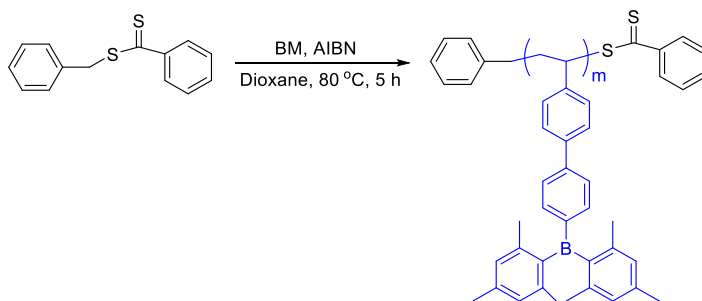
Synthesis of borane monomer BM



In a Schlenk tube, dimesityl(4-iodophenyl)borane (2.00 g, 4.42 mmol) and (4-trimethylstannyl)styrene (1.77 g, 6.63 mmol) were dissolved in 10 mL of THF. A catalyst solution containing $Pd_2(dba)_3$ (162 mg, 0.177 mmol, 4 mol%) and tBu_3P (286 mg, 1.41 mmol) in

5.0 mL of THF was added. The tube was sealed and heated to 50 °C for 12 h. After workup with DCM/water, the crude product was subjected to silica gel column chromatography with hexanes/DCM mixture. The isolated pure fractions were combined and dried in high vacuum, affording a white powder. Yield: 1.37 g (72%). ¹H NMR (499.895 MHz, CDCl₃): δ = 7.65 (d, ³J = 8.3 Hz, 2H), 7.61 (appears as s, 4H), 7.51 (d, ³J = 8.3 Hz, 2H), 6.86 (s, 4H), 6.78 (dd, ³J = 17.6 and 10.9 Hz, 1H), 5.83 (d, ³J = 17.6 Hz, 1H), 5.31 (d, ³J = 10.9 Hz, 1H), 2.34 (s, 6H), 2.07 (s, 12H). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 74 (w_{1/2} = 1500 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 144.7 (broad), 144.0, 141.9 (broad), 141.0, 140.2, 138.8, 137.3, 136.6, 128.4, 127.5, 126.9, 126.5, 114.3, 23.7, 21.4. UV-Vis in THF: λ_{max} = 334 nm. Fluorescence in THF: λ_{em} = 385 nm (λ_{exc} = 334 nm), Φ = 52%. Elemental analysis calculated for C₃₂H₃₃B: C 89.71, H 7.76%; observed: C 89.90, H 7.98%. High res FT-MS (anthracene, pos. mode): 856.5333 (calcd for M₂ (dimer) 856.5351; peak overlapped with M₂ – H peak).

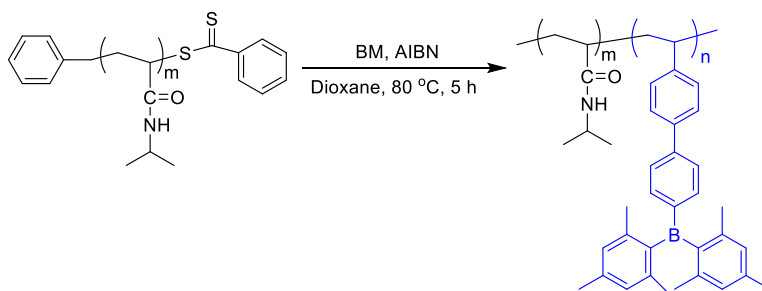
Synthesis of homopolymer PBM



In a Schlenk tube, BM (350 mg, 0.817 mmol), BDTB (4.00 mg, 0.0163 mmol), and AIBN (0.54 mg, 0.0033 mmol) were dissolved in 1.0 mL of 1,4-dioxane ([BM]/[BDTB]/[AIBN] = 50/1/0.2). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in an 80 °C oil bath for 5 h. The crude product was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. The solid was collected by filtration and dried in high vacuum, affording a light pink powder. Yield: 184 mg (51% conversion). ¹H NMR (499.895 MHz, CDCl₃): δ = 7.4, 7.3, 7.1, 6.7, 6.6, 6.4 (aromatic protons), 2.3, 1.9, 1.1~2.7 (broad, overlapped backbone). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 65 (w_{1/2} = 3700 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 145.1 (broad), 144.5, 144.1, 141.9, 140.9, 138.7, 138.1 (broad), 137.2, 128.4, 127.0, 126.3, 40.5 (broad), 23.6, 21.4. GPC-RI (THF): M_n = 9770 g/mol, PDI = 1.25, m_{GPC} = 22.

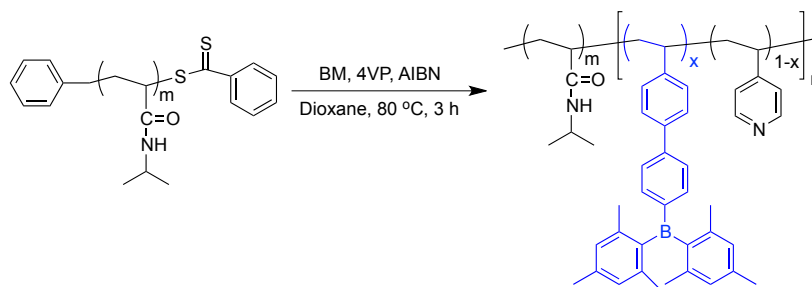
Elemental analysis calculated for $\{C_{32}H_{33}B\}_m$: C 89.14, H 8.08%; observed: C 89.33, H 8.40%.

Synthesis of block copolymer PNIPAM-*b*-PBM



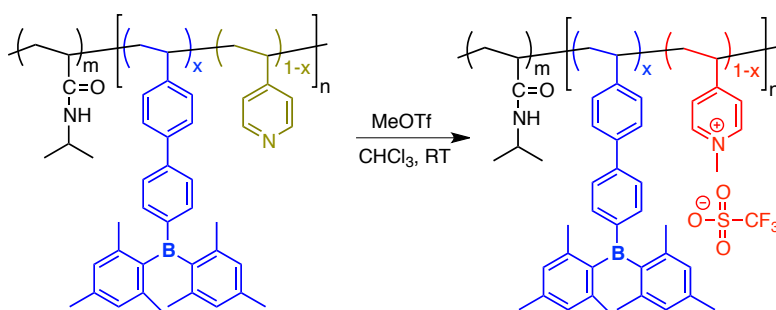
Into a Schlenk tube were loaded PNIPAM-CTA (120 mg, 7380 g/mol based on ^1H NMR end group analysis, 0.0163 mmol), BM (1286 mg, 3.00 mmol), AIBN (1.64 mg, 0.010 mmol), and 4.0 mL of dioxane ($([\text{BM}]/[\text{PNIPAM-CTA}]/[\text{AIBN}]) = 184/1/0.61$). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 5 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was precipitated into a 10-fold volume of diethyl ether and then two more times from THF into a 10-fold volume of hexanes. After drying in high vacuum, the block copolymer was obtained as a light pink powder. Yield: 770 mg (51% conversion). ^1H NMR (499.895 MHz, CDCl_3): $\delta = 7.5, 7.4, 7.2, 6.8, 6.6, 6.4$ (aromatic protons), 4.1, 2.2, 1.9, 1.2, 1.1~2.7 (broad, overlapped backbone). ^{11}B NMR (160.386 MHz, CDCl_3) $\delta = 66$ ($w_{1/2} = 3400$ Hz). ^{13}C NMR (125.698 MHz, CDCl_3): $\delta = 174.4, 145.1$ (broad), 144.5, 144.1, 141.9, 140.9, 138.7, 138.1 (broad), 137.2, 128.4, 127.0, 126.3, 46.4 (broad), 44.3 (broad), 42.6 (broad), 41.5, 40.5 (broad), 23.7, 22.8, 21.4. GPC-RI (chloroform): $M_n = 57470$ g/mol, PDI = 1.20, $m_{\text{GPC}} = 82$, $n_{\text{GPC}} = 111$. $m/n = 0.40$ based on ^1H NMR integration (comparing peaks at 4.1 ppm and 2.2 ppm).

Synthesis of PNIPAM-*b*-P(BM-*ran*-4VP)



Into a Schlenk tube were loaded PNIPAM-CTA (360 mg, 7380 g/mol based on ^1H NMR end group analysis, 0.0488 mmol), 4-vinyl pyridine (1.70 g, 16.2 mmol), BM (771 mg, 1.80 mmol), AIBN (2.96 mg, 0.018 mmol), and 3.0 mL of THF ([4VP]/[BM]/[PNIPAM-CTA]/[AIBN] = 332/37/1/0.37). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °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 3 times from THF into a 10-fold volume of diethyl ether. After drying in high vacuum, the block copolymer was obtained as a light pink powder. Yield: 1.33 g (39% conversion). ^1H NMR (499.895 MHz, CDCl_3): δ = 8.3 (Py), 6.4 (Py), 6.2~7.8 (overlapped, aromatic protons), 4.0 (PNIPAM) 3.3 (water), 2.2, 1.9, 1.1~2.7 (broad overlapped, backbone). ^{11}B NMR (160.386 MHz, CDCl_3) δ = 70 ppm ($w_{1/2}$ = 3300 Hz). ^{13}C NMR (125.698 MHz, CDCl_3): δ = 174.4, 152.2 (Py, broad), 150.1 (Py), 144.9, 143.4, 141.9, 140.9, 139.2, 138.7, 137.2 (broad), 128.4, 127.3 (broad), 126.3, 122.6 (Py), 44.9 (broad), 44.1 (broad), 43.5 (broad), 42.4 (broad), 41.4, 40.3 (broad), 38.1~31.1 (broad), 23.7, 22.8, 21.4. GPC-RI (DMF/pyridine = 99/1): M_n = 25500 g/mol, PDI = 1.33. ^1H NMR determination of ratio of 4VP to BM: $x_{\text{BM}} = 0.14$; $m/n = 0.36$ (using peaks at 8.3, 4.0 and 2.2 ppm as reference).

Synthesis of PNIPAM-*b*-P(BM-*ran*-4VPMeOTf)



To a solution of PNIPAM-*b*-P(BM-*ran*-4VP) (40 mg, 0.029 mmol boron chromophore, 0.18 mmol pyridine moieties) in 3.0 mL of CHCl₃ was added methyl triflate (300 mg, 1.83 mmol; large excess) dropwise under stirring. A yellow suspension appeared within seconds. After stirring for 1.0 h at room temperature, the suspension was precipitated into a 10-fold volume of diethyl ether. After filtration, the product was dried in high vacuum to give a light yellow powder. Yield: 45 mg. ¹H NMR (499.895 MHz, DMSO-*d*₆): δ = 8.7 (Py), 7.6, 7.5 (Py/Ph) 7.4-7.1 (Ph), 6.9 (Mesityl C-H), 6.8-6.6 (Ph), 4.2 (Py-Me), 3.8 (PNIPAM C-H) 2.3, 2.0 (Mesityl Me), 2.0~1.2 (backbone protons), 1.0 (PNIPAM Me). ¹¹B NMR (160.386 MHz, DMSO-*d*₆) δ = 62 ppm (very broad). The degree of quaternization was estimated to >95% based on ¹H NMR integration of the N-Me peak relative to other NMR signals.

Self-assembly of PNIPAM-*b*-PBM in DMF. In a typical procedure for the preparation of block copolymer micelles in DMF/THF = 99/1 (w/w), 100 mg of block copolymer were dissolved in 4.00 g of THF. Then, 396 g of DMF were slowly added under stirring.

The as-prepared micelle solution was used for transmittance measurements at 400 nm, where the block copolymer shows no absorption. A TBAF stock solution in THF (*c* = 0.050 mol/L) was used for fluoride titration. Transmittance was recorded upon each fluoride addition (from 0-0.20 equiv., step = 0.02 equiv.; from 0.2-1.0 equiv., step = 0.20 equiv.). Photographs were taken under natural light and UV irradiation (handheld UV lamp, 365 nm) before and after fluoride addition.

For DLS analyses, the micelle solution was examined before and after addition of 0.050 M TBAF solution in THF (1 equiv relative to amount of boron chromophores).

For TEM analyses, a similar micelle solution was prepared in DMF/THF = 19/1; a drop of the solution of placed on a TEM grid, the solvent was allowed to evaporate and the sample analyzed without further manipulation.

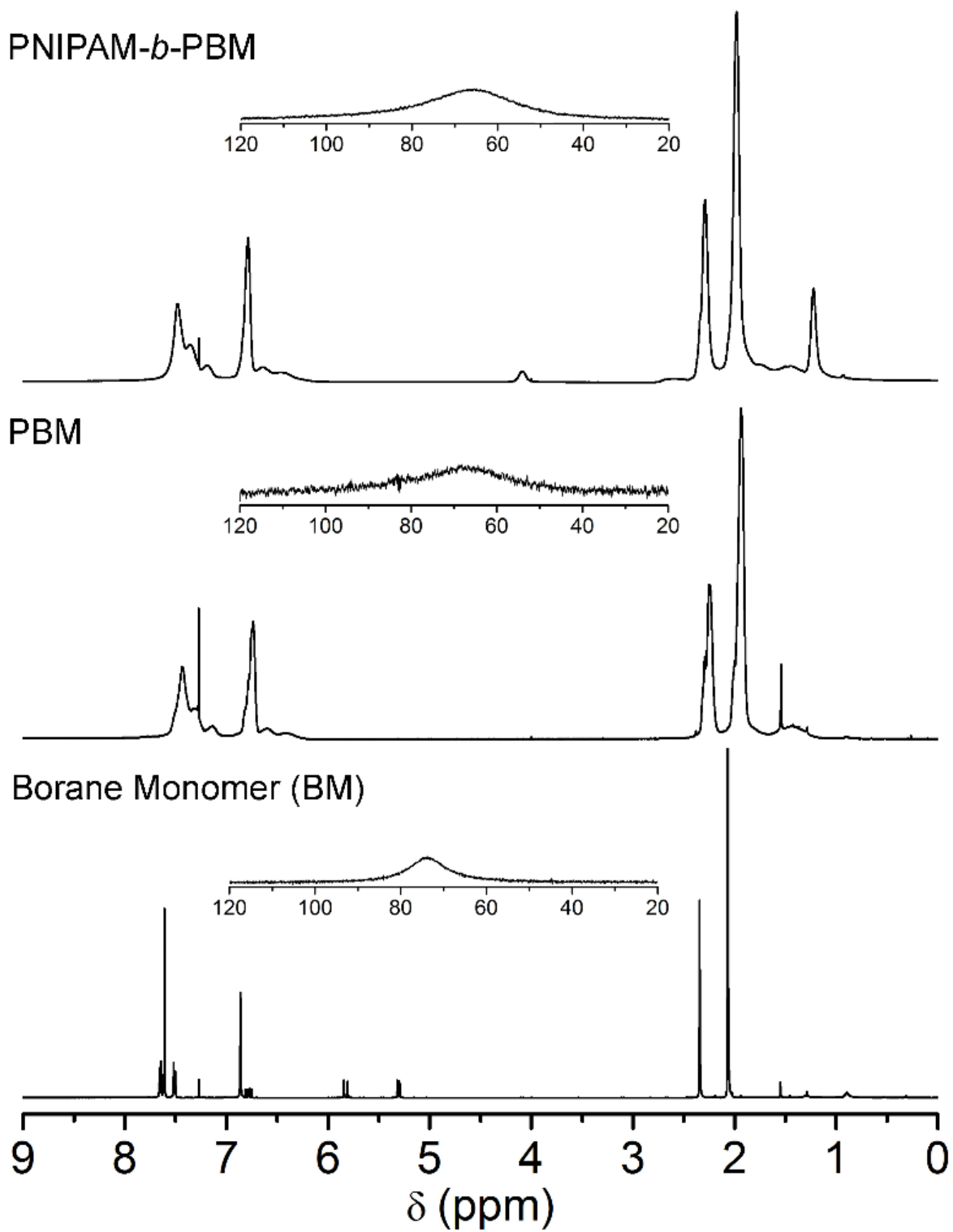


Figure S1. Comparison of ^1H and ^{11}B (inserts) NMR spectra of BM, PBM, and PNIPAM-*b*-PBM in CDCl_3 .

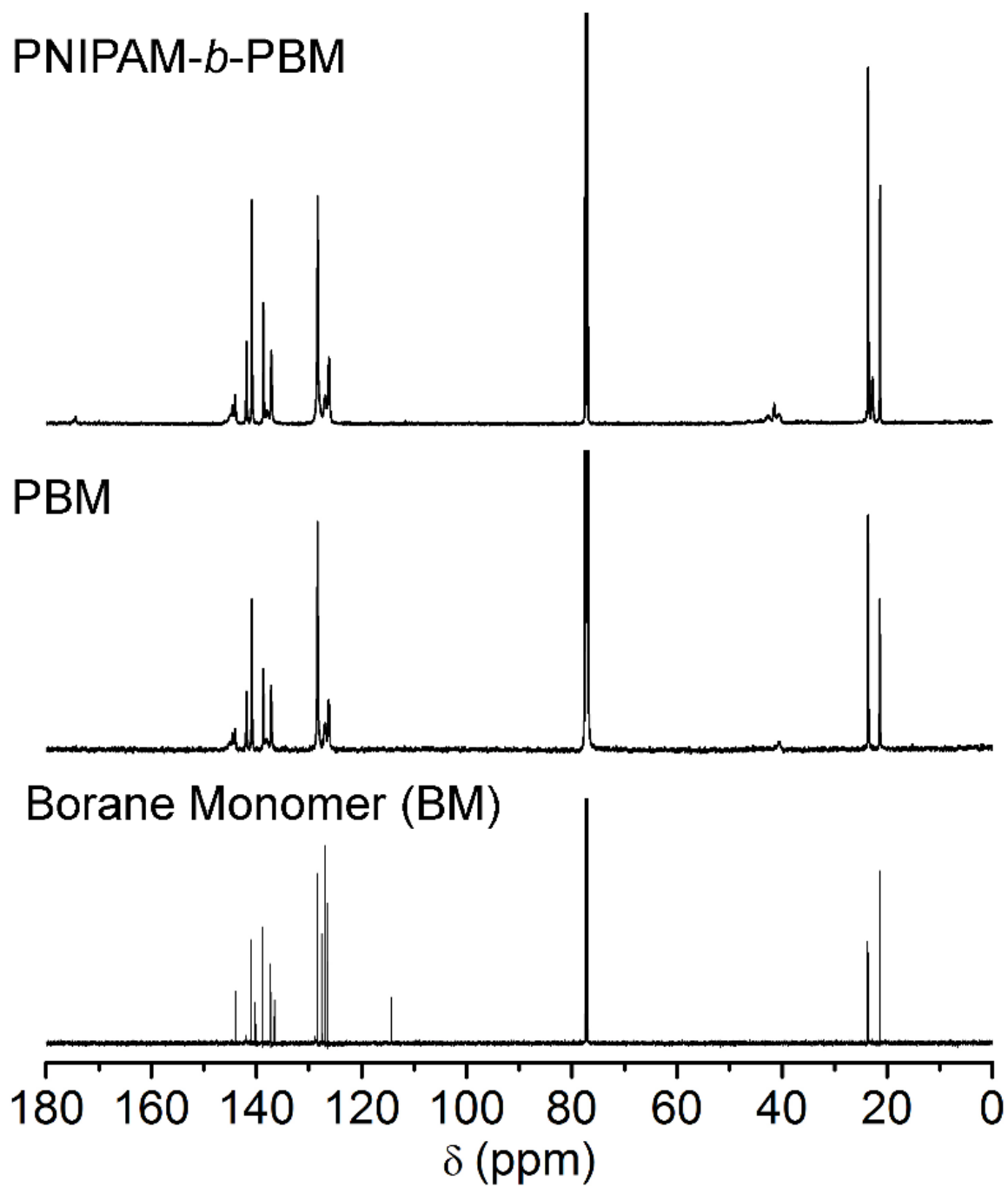


Figure S2. Comparison of ^{13}C NMR spectra of BM, PBM, and PNIPAM-*b*-PBM in CDCl_3 .

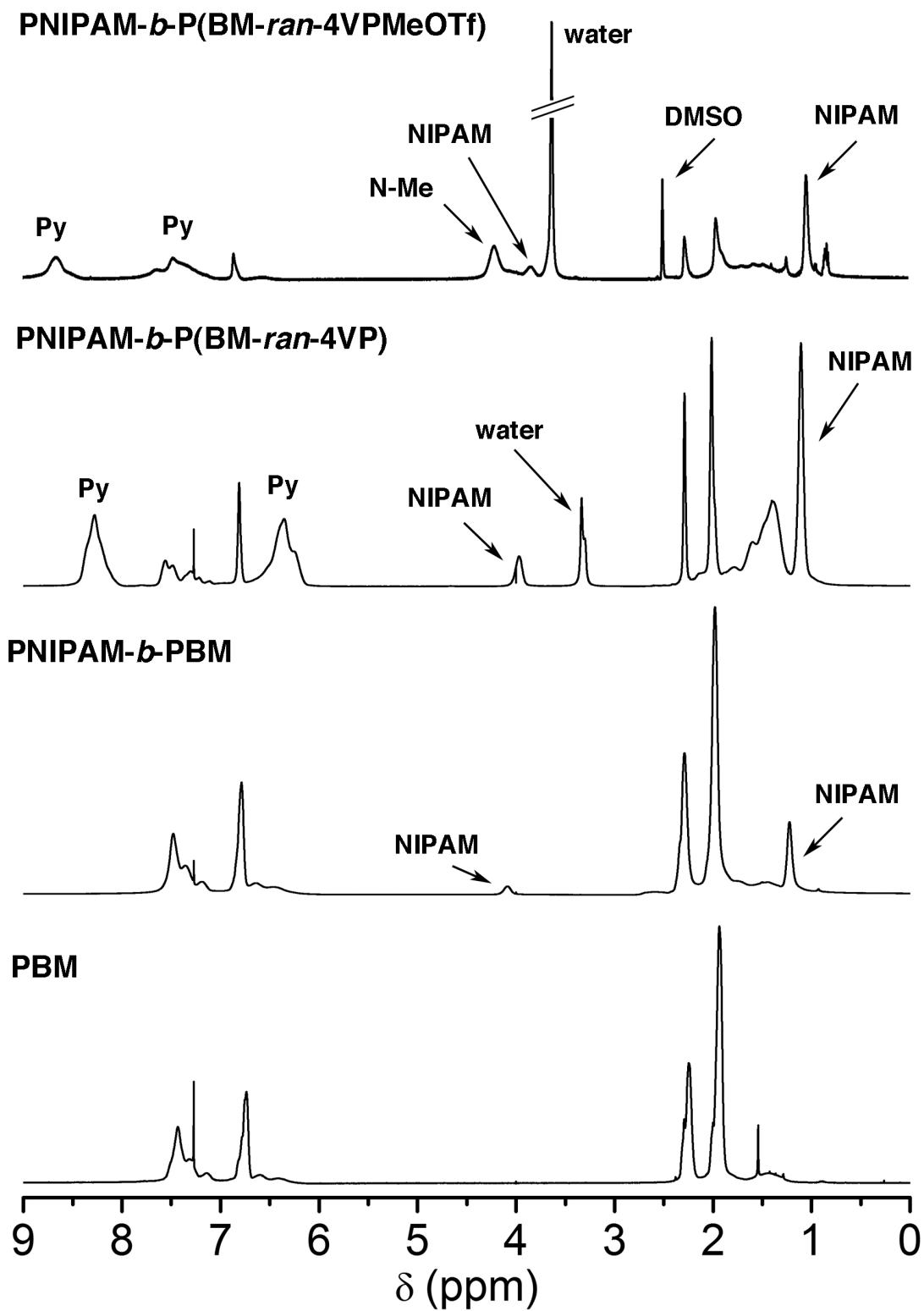


Figure S3. Comparison of ^1H NMR spectra of PBM, $\text{PNIPAM-}b\text{-PBM}$, $\text{PNIPAM-}b\text{-P(BM-}i\text{ran-4VP)}$ in CDCl_3 and $\text{PNIPAM-}b\text{-P(BM-}i\text{ran-4VPMeOTf)}$ in $\text{DMSO-}d_6$.

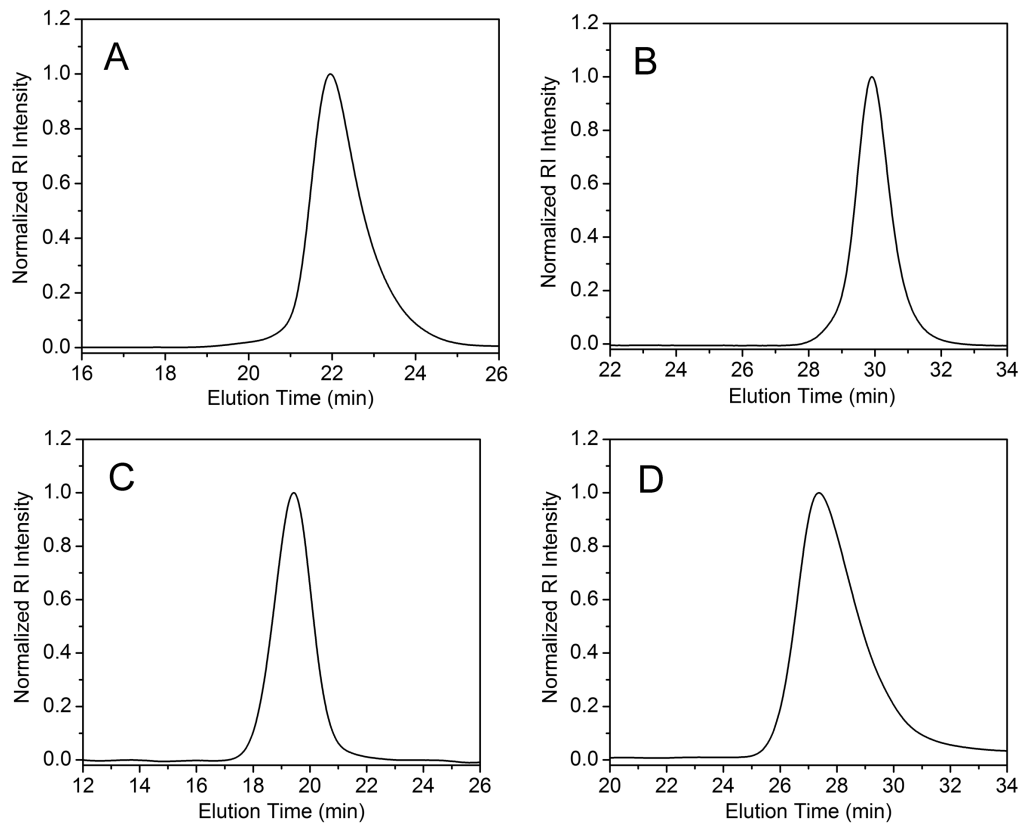
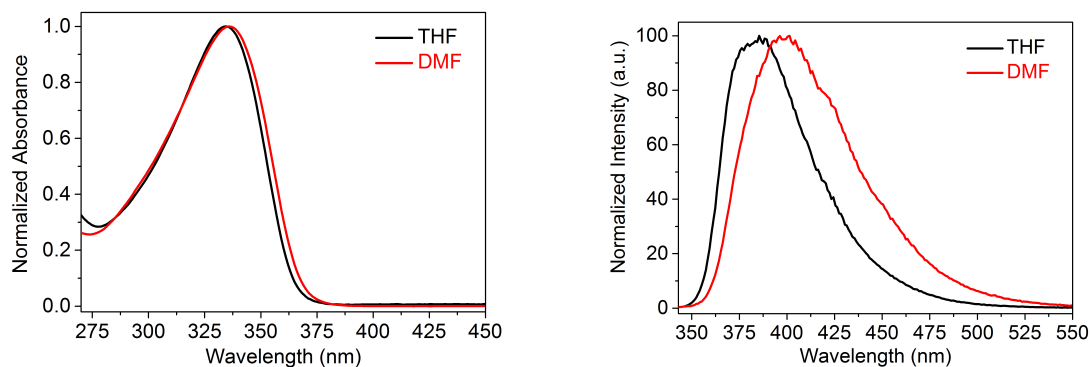
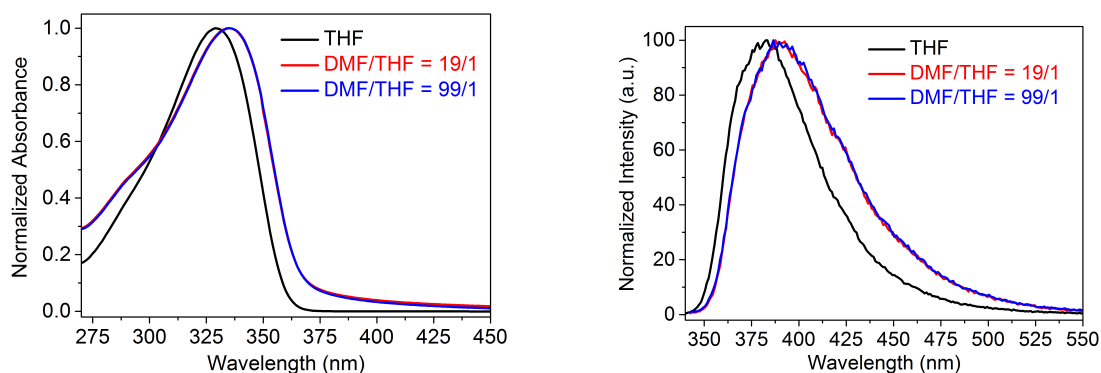


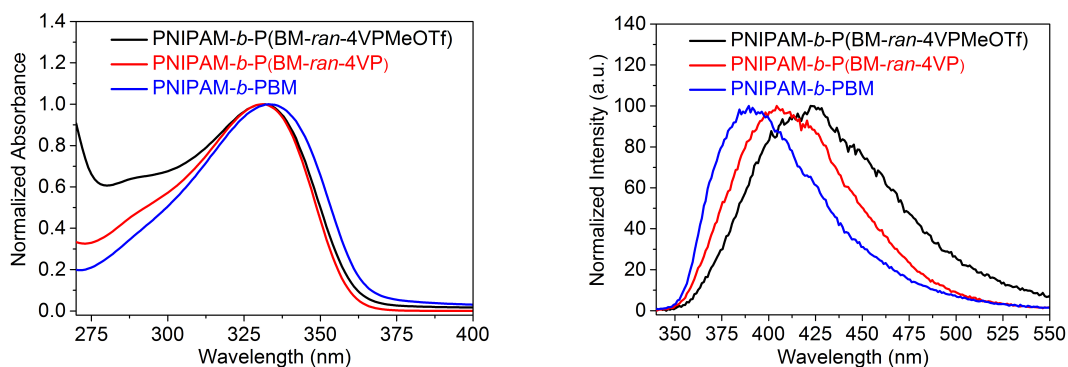
Figure S4. GPC traces of (A) PBM in THF at 1.0 mL/min; (B) PNIPAM-CTA in DMF/pyridine = 99/1 (v/v) at 0.5 mL/min; (C) PNIPAM-*b*-PBM in chloroform at 1.0 mL/min; (D) PNIPAM-*b*-P(BM-*ran*-4VP) in DMF/pyridine = 99/1 (v/v) at 0.5 mL/min.



UV-visible absorption and emission spectra (excited at λ_{\max}) of BM in THF and DMF.



UV-visible absorption and emission spectra (excited at λ_{\max}) of PNIPAM-*b*-PBM in different solvents. Solutions in DMF/THF mixtures were prepared by addition of DMF to the polymer solution in THF.



UV-visible absorption and emission spectra (excited at λ_{\max}) of block copolymers in DMF (DMF/THF = 99/1 for PNIPAM-*b*-PBM). Solutions in DMF/THF = 99/1 were prepared by addition of DMF to the polymer solution in THF.

Figure S5. Comparison of experimental absorption and emission data in different solvents.

Table S1. Summary of photophysical data [a]

Sample	Solvent	$\lambda_{\max, \text{abs}}$ (nm)	$\lambda_{\max, \text{em}}$ (nm)	ϕ_{Fl}	τ [c] (ns)
BM	THF	335	385	0.52	2.19(1)
	DMF	336	398	--	1.20(3) (48%); 3.43(1) (52%)
PBM	THF	330	384	0.22	1.92(1) [d]
	DMF	[b]	[b]	[b]	[b]
PNIPAM-<i>b</i>-PBM	THF	330	384	0.30	1.90(1)
	DMF/THF=19/1	334	391	--	1.22(2) (83%); 2.47(2) (17%)
	DMF/THF=99/1	334	391	--	--
PNIPAM-<i>b</i>-P(BM-<i>ran</i>-4VP)	THF	330	394	0.20	1.98(1)
	DMF	332	404	--	2.55(1)
PNIPAM-<i>b</i>-P(BM-<i>ran</i>-4VPMeOTf)	THF	[b]	[b]	[b]	[b]
	DMF	332	423	0.08	1.81(1) (89%); 5.98(4) (11%)

[a] All samples excited at λ_{\max} . [b] Not soluble. [c] Measured at emission maximum. [d] After addition of a small amount of $[\text{Bu}_4\text{N}]\text{F}$ the emission lifetime decreased to 1.70(1) ns (21%) / 0.65 (13) ns (79%).

Note: Relative to the other polymers and the monomer in DMF, PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) displays a similar absorption maximum at 332 nm, but a significantly red-shifted emission maximum at 423 nm and a lower quantum yield of 0.08. The red shift of the emission may be related to the more polar environment provided by the quaternized 4VP units. The emission of PNIPAM-*b*-P(BM-*ran*-4VP) in THF is also ~ 7 nm red-shifted relative to that of PBM.

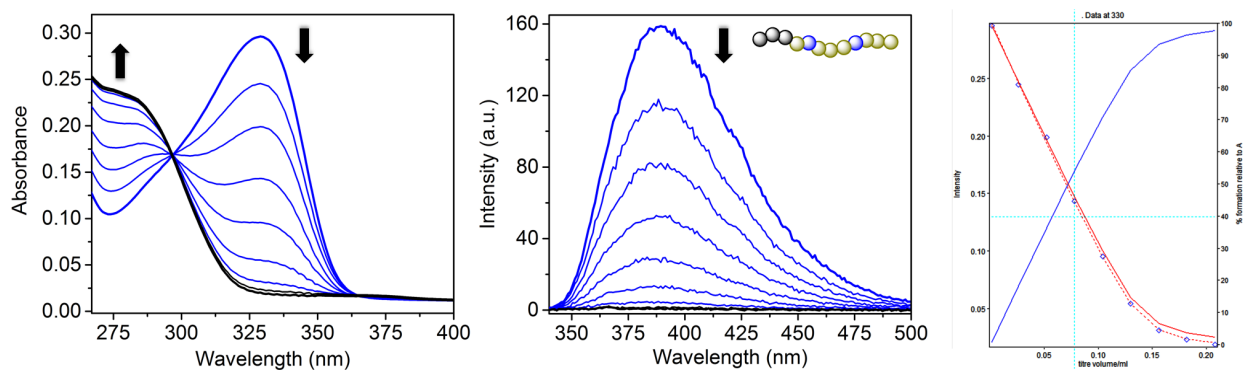


Figure S6. Titration data for PNIPAM-*b*-P(BM-*ran*-4VP) in THF as the solvent. TBAF in THF: $[\text{F}^-] = 2.20 \times 10^{-4}$ M; $[\text{B}]^0 = 9.87 \times 10^{-6}$ M, 0~1.48 equiv F^- , step = 0.185 equiv. $[\text{B}]^0$ corresponds to the initial concentration of the boron chromophore). Fit for $\lg\beta = 6.9$.

No enhanced quenching effect is observed for the pyridine copolymer system, in which the boron chromophores are “diluted”.

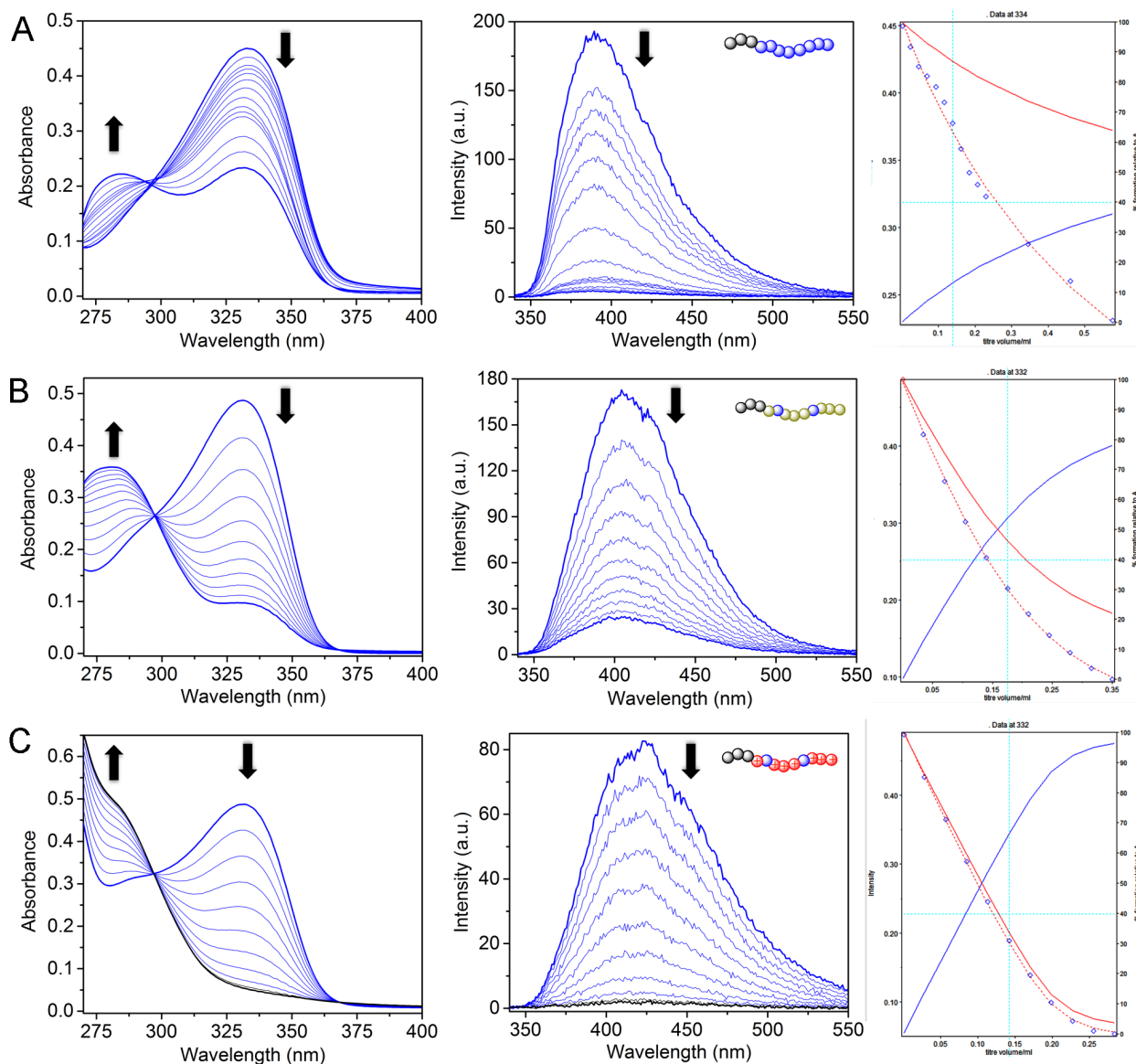
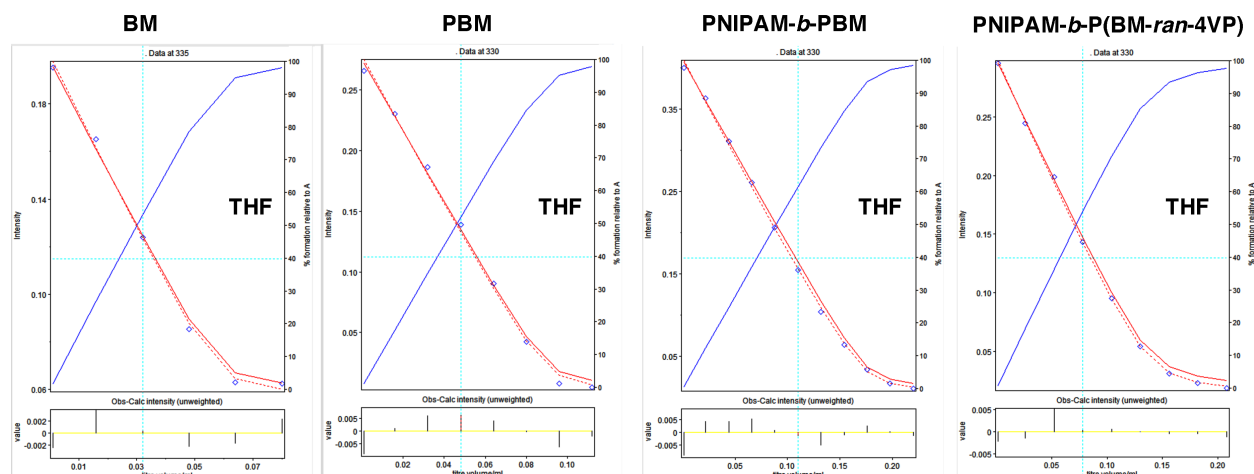


Figure S7. Titration data in DMF as the solvent (TBAF in THF: $[F^-] = 2.20 \times 10^{-4}$ M; $[B]^0$ corresponds to the initial concentration of the boron chromophore).

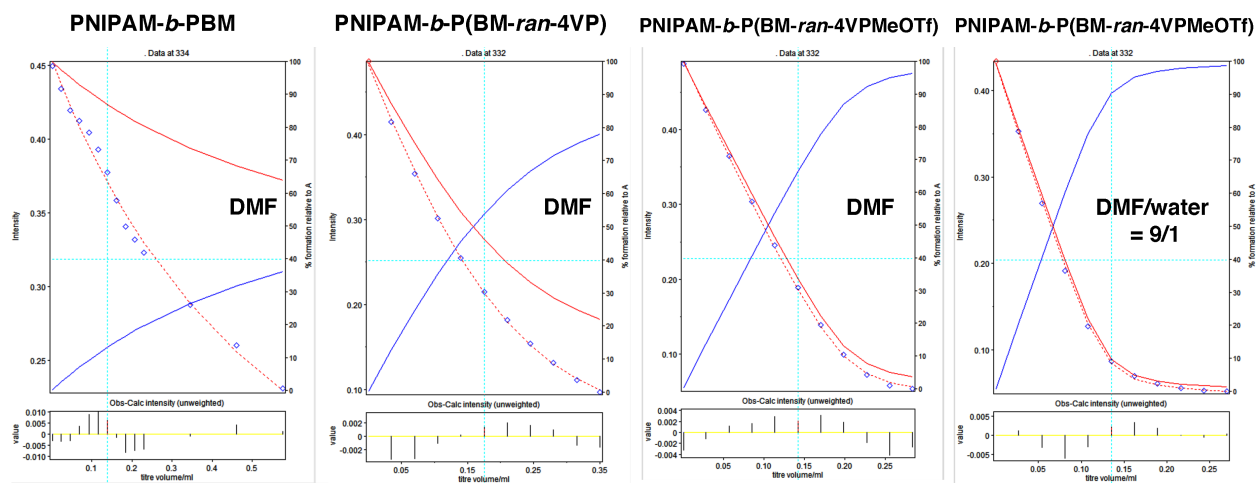
(A) Absorption and emission spectra of PNIPAM-*b*-PBM ($[B]^0 = 1.44 \times 10^{-5}$ M, 0~1.6 equiv, step = 0.16 equiv F⁻, 1.6~4.0 equiv., step = 0.8 equiv.). Note that the data are affected by self-assembly in DMF as the solvent. Note also the enhanced quenching effect, which is not visible for the pyridine copolymer systems, in which the boron chromophores are “diluted”. Fit for $\lg\beta = 4.2$.

(B) Absorption and emission spectra of PNIPAM-*b*-P(BM-*ran*-4VP) ($[B]^0 = 1.59 \times 10^{-5}$ M, 0~1.6 equiv F⁻, step = 0.16 equiv). Fit for $\lg\beta = 5.5$.

(C) Absorption and emission spectra of PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) ($[B]^0 = 1.69 \times 10^{-5}$ M, 0~1.4 equiv F⁻, step = 0.14 equiv). Fit for $\lg\beta = 6.6$.



Monomer BM	Polymer PBM	PNIPAM- <i>b</i> -PBM	PNIPAM- <i>b</i> -P(BM- <i>ran</i> -4VP)
<i>THF</i>	<i>THF</i>	<i>THF</i>	<i>THF</i>
$\lg\beta = 7.3$	$\lg\beta = 7.3$	$\lg\beta = 7.3$	$\lg\beta = 6.9$
1st Step: 1.9 μM	1st Step: 1.6 μM	1st Step: 1.8 μM	1st Step: 1.8 μM
1st Step: 0.15 ppm	1st Step: 0.12 ppm	1st Step: 0.14 ppm	1st Step: 0.14 ppm



PNIPAM- <i>b</i> -PBM	PNIPAM- <i>b</i> -P(BM- <i>ran</i> -4VP)	PNIPAM- <i>b</i> -P(BM- <i>ran</i> -4VPMeOTf)	PNIPAM- <i>b</i> -P(BM- <i>ran</i> -4VPMeOTf)
<i>DMF</i>	<i>DMF</i>	<i>DMF</i>	<i>DMF/H₂O = 9/1</i>
$\lg\beta = 4.2$	$\lg\beta = 5.5$	$\lg\beta = 6.6$	$\lg\beta = 6.7$
1st Step: 2.0 μM	1st Step: 2.5 μM	1st Step: 2.3 μM	1st Step: 3.3 μM
1st Step: 0.15 ppm	1st Step: 0.19 ppm	1st Step: 0.18 ppm	1st Step: 0.6 ppm vs H ₂ O content

Figure S8. Fit of absorption data (HyperquadTM software) at the absorption maxima of the uncomplexed species (red) using the given binding constants $\lg\beta$. The binding constants were determined using multiple wavelengths (global fit).

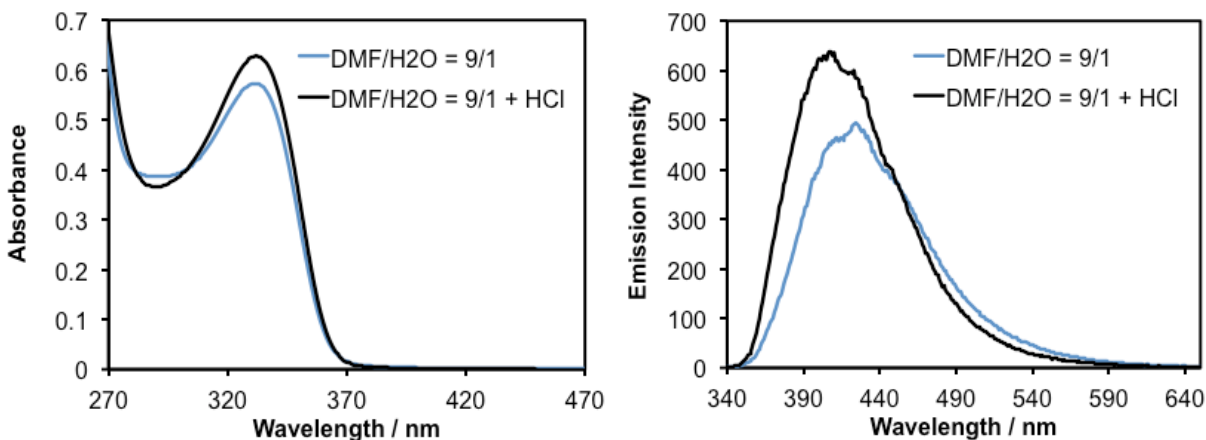


Figure S9. Absorption and emission spectra of PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) in DMF/H₂O = 9/1 before and after addition of a drop of 0.5N HCl.

The slight enhancement of absorption and emission upon HCl addition suggests some extent of OH⁻ binding to the polymer in DMF/H₂O = 9/1 as the solvent. Based on the absorption data the extent of binding is ca. 5%. This is consistent with prior studies by the Gabbai group on hydroxide binding to highly electron-deficient boranes in aqueous solutions.

References:

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