JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication
pubs.acs.org/JACS

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

Fei Cheng,[†] Edward M. Bonder,[§] and Frieder Jäkle*,[†]

[†]Department of Chemistry, Rutgers University—Newark, 73 Warren Street, Newark, New Jersey 07102, United States
[§]Department of Biological Sciences, Rutgers University—Newark, 195 University Avenue, Newark, New Jersey 07102, United States

Ⓢ *Supporting Information*

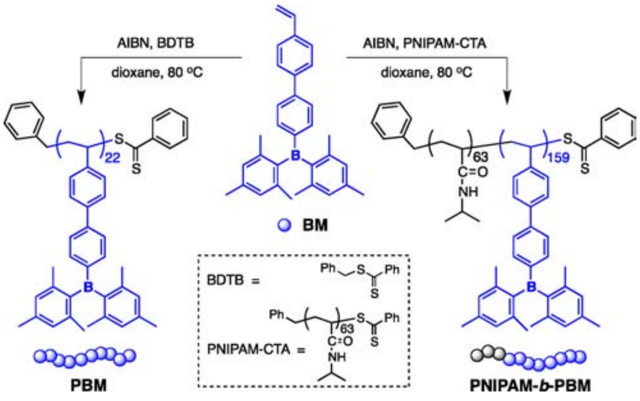
ABSTRACT: Luminescent triarylborane homo and block copolymers with well-defined chain architectures were synthesized via reversible addition−fragmentation chain transfer polymerization of a vinyl-functionalized borane monomer. The Lewis acid properties of the polymers were exploited in the luminescent detection of fluoride ions. A dual-responsive fluoride sensor was developed by taking advantage of the reversible self-assembly of a PNIPAM-based amphiphilic block copolymer. Anion detection in aqueous solution was realized by introducing positively charged pyridinium moieties along the polymer chain.

Electron-deficient conjugated organoboranes have drawn much interest as nonlinear optical materials, as luminescent and charge transport layers for organic light-emitting devices (OLEDs), and as components of other electronic devices.[1−3] As Lewis acids, they are able to interact with Lewis basic substrates, a process that typically results in marked color and/or luminescence changes and has been widely exploited in sensory schemes.[2,4,5] Triarylborane-functionalized conjugated oligomers and polymers[3] have proven especially attractive, because, different from molecular compounds, the conjugation along the polymer chain can result in higher sensitivity due to so-called sensory signal amplification effects.[6]

Compared to conjugated polymers, polyolefins tend to possess advantageous processability and fabrication properties. Moreover, well-developed controlled free radical polymerization (CFRP) techniques allow for more facile synthesis of complex architectures, such as block copolymers, polymer brushes, and star polymers.[7,8] A range of systems with luminescent chromophores that feature tetracoordinate boron centers have recently been reported.[9] However, with respect to Lewis acidic tricoordinate boranes, only boronic acid functionalities have been successfully introduced into block copolymer and other more complex architectures.[10] For instance, Sumerlin and co-workers[11] demonstrated the utility of boronic acid block copolymers as multi-responsive materials in the detection of sugars, while Kim and van Hest[12] extended this concept to systems that operate at physiological pH. In this Communication, we introduce highly electron-deficient triarylborane-functionalized polymers with well-defined architectures and discuss their application as chemical sensors for fluoride ions. The dimesitylphenylborane moiety was selected as a binding site because of its excellent stability and selectivity for fluoride over larger halide ions.[5]

The triarylborane monomer (BM) was prepared by Stille coupling of (iodophenyl)dimesitylborane and *p*-trimethylstannylstyrene in a yield of 72%. A single broad peak at 74 ppm in the ^{11}B NMR is indicative of the electron-deficient tricoordinate borane structure, while a strong blue-violet emission with a maximum of 385 nm in THF (ϕ_{Fl} = 0.52; τ = 2.19(1) ns) results from effective extension of π-conjugation to the empty p-orbital on boron. Reversible addition−fragmentation chain transfer (RAFT)[8,13] polymerization was used for the polymer synthesis because of its good compatibility with functional monomers and advantages in the synthesis of complex polymer architectures. Indeed, when mediated with benzyl dithiobenzoate (BDTB) as a chain transfer agent (CTA), the RAFT polymerization of BM proceeded with good control (Scheme 1), as evident from a narrow GPC trace for the resulting polymer, PBM. The structural integrity of the borane moieties was confirmed by the presence of a broad ^{11}B NMR signal at 65 ppm, which is slightly upfield shifted relative to that of the monomer due to neighboring group effects. Using similar methods, we also prepared PNIPAM-*b*-PBM (Scheme 1) by chain extension of a PNIPAM macro-CTA. Multinuclear NMR data and GPC analyses demonstrate that a novel

Scheme 1. RAFT Polymerization of Triarylborane Monomer (BM)



Received: September 14, 2013
Published: November 5, 2013

triarylborane block copolymer with well-defined chain architecture and narrow molecular weight distribution was successfully obtained (Table 1, Figures S1−S4). The borane

Table 1. Polymer Molecular Weight Data[a]

polymer	$M_{\mathrm{n,\,GPC}}$[b]	PDI	m, n_{GPC}[b]	m, n_{NMR}[c]
PBM	9770	1.25	22	–[d]
PNIPAM-CTA	9630	1.09	82	63[e]
PNIPAM-*b*-PBM	57470	1.20	82, 111	63,[e] 159

[a] *m* and *n* refer to the average degree of polymerization of the first and second block, respectively. [b] Determined by GPC-RI vs PS standards. [c] Based on ^{1}H NMR integration. [d] Not determined due to signal overlap of the end group and repeating units. [e] Based on ^{1}H NMR end group analysis.

polymers PBM and PNIPAM-*b*-PBM are strongly fluorescent at ca. 385 nm, with similar lifetimes (ca. 1.9 ns) as the respective monomer. The quantum yields (PBM, 0.22; PNIPAM-*b*-PBM, 0.30) are somewhat lower than for the monomer BM (0.52), possibly because of the neighboring group effect of the boron chromophores along the polymer chain (bimolecular quenching) or the heavy atom quenching effect of the CTA end group.[8,14] Of note is a more bathochromic emission for PNIPAM-*b*-PBM with increased solvent polarity (see Figure S5). A similar observation was made for the monomer, which suggests a solvatochromic effect as a result of significant charge transfer character, rather than an aggregation effect.[15]

With well-defined triarylborane-functionalized polymers in hand, we next examined their application as chemical sensors for fluoride ions. Fluoride ions play an important role in human health. As an additive in drinking water and toothpaste, fluoride is known to be beneficial to dental health. On the other hand, over-absorption of fluoride can cause dental or skeletal fluorosis.[16] Therefore, the development of new sensitive and accurate fluoride sensors has drawn much attention.[5] We first compared the fluoride binding behavior of BM, PBM, and PNIPAM-*b*-PBM in THF. The spectral data of the monomer and polymers upon titration with $[\mathrm{Bu_4N}]\mathrm{F}$ (TBAF) in THF are illustrated in Figure 1. For the titration of PBM and the corresponding block copolymer PNIPAM-*b*-PBM the absorption band at ca. 330 nm decreased with the addition of TBAF, and a higher energy band at ca. 278 nm developed. The new absorption band of the borate complex is slightly different from that of the corresponding BM monomer complex (312 nm), because the vinyl group of BM is replaced by the saturated polymer backbone in PBM. A binding constant of ca. $\lg\beta = 7.3$ was determined in all cases, which is typical of triarylboranes.[4,17] A completely different picture emerged from the corresponding emission spectra. While the fluorescence of the borane monomer very gradually disappeared upon fluoride addition (Figure 1A), enhanced quenching was clearly evident for the polymers. Addition of only 0.18 equiv (1.6 μM; 0.13 ppm) of TBAF led to about 60% fluorescence quenching of PBM, and the emission was almost completely quenched at 0.70 equiv of TBAF (Figure 1B).[18] A similar phenomenon was observed for the block copolymer PNIPAM-*b*-PBM (Figure 1C), indicating that the presence of the PNIPAM block does not affect fluoride binding in THF. In contrast, for the random copolymer PNIPAM-*b*-P(BM-*ran*-4VP) (vide infra), in which the chromophores are diluted, no enhanced fluorescence quenching was observed (Figure S6). The enhanced quenching for PBM and PNIPAM-*b*-PBM is therefore likely due to exciton migration along the polymer chain to lower energy quenching sites that are generated upon F$^-$ binding.[19,20]

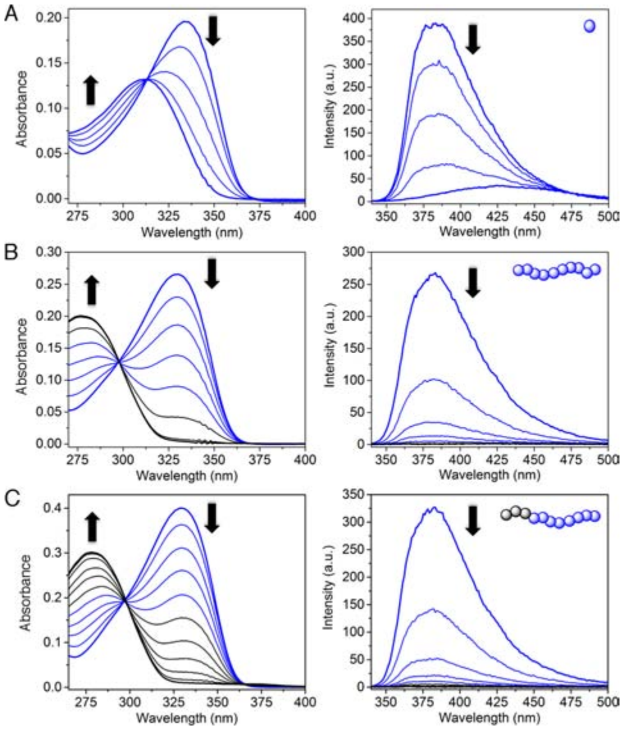


Figure 1. Titration data in THF. (A) Spectra of BM upon titration with TBAF ($[\mathrm{B}]^0 = 7.07 \times 10^{-6}$ M, $[\mathrm{F}^-] = 3.30 \times 10^{-4}$ M in THF, 0−1.35 equiv, step = 0.27 equiv). (B) Spectra of PBM upon titration with TBAF ($[\mathrm{B}]^0 = 9.32 \times 10^{-6}$ M, $[\mathrm{F}^-] = 3.30 \times 10^{-4}$ M in THF, 0−1.23 equiv, step = 0.175 equiv). (C) Spectra of PNIPAM-*b*-PBM upon titration with TBAF ($[\mathrm{B}]^0 = 1.43 \times 10^{-5}$ M, $[\mathrm{F}^-] = 2.20 \times 10^{-4}$ M in THF, 0−1.24 equiv, step = 0.12 equiv). $[\mathrm{B}]^0$ and $[\mathrm{F}^-]$ correspond to the initial borane chromophore and F$^-$ concentration, respectively.

Given its amphiphilic structure, the block copolymer PNIPAM-*b*-PBM is expected to self-assemble in polar solvents, which are selective for the PNIPAM block and non-solvents for the borane-functionalized block. We hypothesized that fluoride binding to the boron-containing block should affect its solubility characteristics. This may in turn lead to a morphology change that could be used as a second response mechanism, in addition to the observed fluorescence quenching. PNIPAM-*b*-PBM aggregate solutions were prepared by adding DMF into the block copolymer solution in THF (0.25 mg/g in DMF/THF = 99/1; $[\mathrm{B}] = 5.0 \times 10^{-4}$ M). According to dynamic light scattering (DLS) analysis, particles with an average hydrodynamic diameter of $\langle D_\mathrm{h}\rangle = 93 \pm 24$ nm formed (Figure 2). These particles are expected to feature the boron chromophores in the core, surrounded by a solubilizing PNIPAM shell. Interestingly, upon addition of only ∼0.2 equiv (8 ppm) of TBAF, the opalescence due to the block copolymer micelles disappeared and the solution turned completely clear (Figure 2). DLS revealed a significantly reduced size of $\langle D_\mathrm{h}\rangle = 10.5 \pm 3.0$ nm, which is close to that of the block copolymer in the good solvent THF ($\langle D_\mathrm{h}\rangle = 9.2 \pm 2.7$ nm). In a control experiment, the same amount of THF was added without TBAF, and no visible change was observed. This suggests that after F$^-$ binding, the charged borate-containing block turned soluble in DMF, which in turn led to micelle dissociation into single chains.

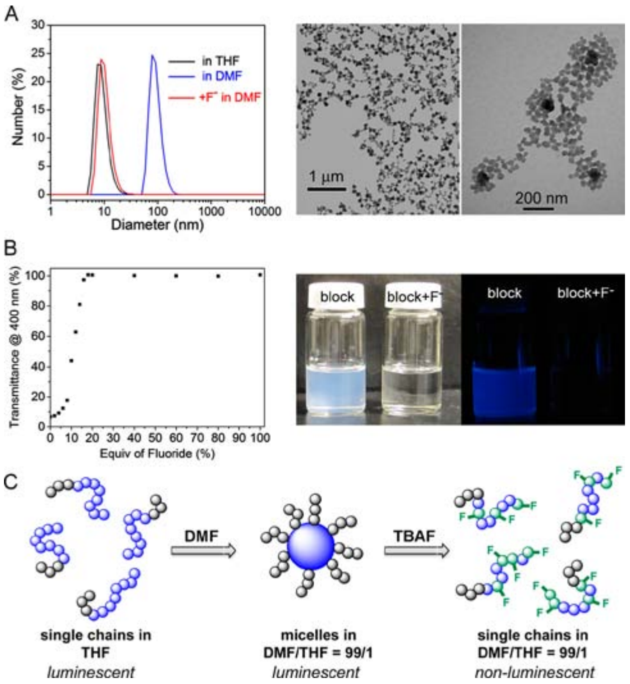
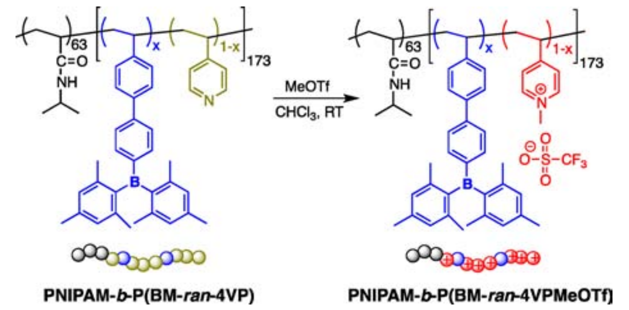


Figure 2. (A) Size distribution histogram of PNIPAM-*b*-PBM in THF (black, $\langle D_h \rangle$ = 9.2 ± 2.7 nm), micelles in DMF/THF = 99/1 (blue, $\langle D_h \rangle$ = 93 ± 24 nm), and block copolymer/fluoride complex in DMF/THF = 99/1 upon TBAF addition (red, $<D_h>$ = 10.5 ± 3.0 nm). TEM images from solutions in DMF/THF = 19/1. (B) Plot showing the decrease in turbidity upon fluoride addition and photographs of PNIPAM-*b*-PBM micelles in DMF/THF = 99/1 before and after addition of 1 equiv of TBAF in natural light (left) and with UV irradiation (right). (C) Schematic illustration of dual-responsive fluoride sensor based on PNIPAM-*b*-PBM micelles in DMF/THF = 99/1.

Scheme 2. Synthesis of Quaternized P4VP Copolymer



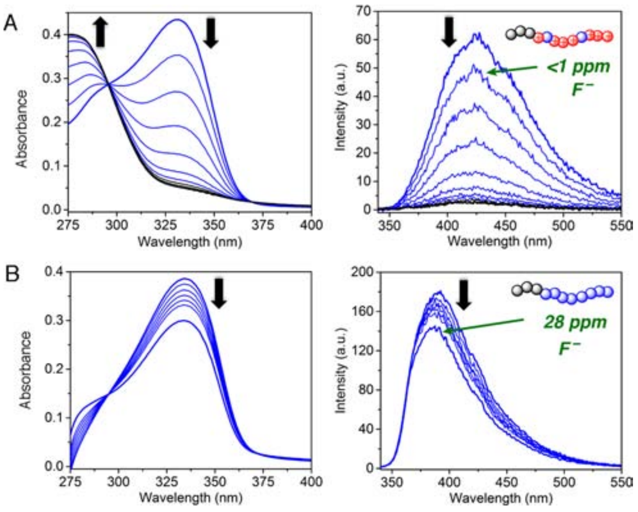


Figure 3. Titration data in DMF/water = 9/1 (w/w) as the solvent. (A) Spectra of PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) upon titration with TBAF ($[B]^0 = 1.38 \times 10^{-5}$ M, 0−2.1 equiv, step = 0.21 equiv). (B) Spectra of PNIPAM-*b*-PBM upon titration with TBAF ($[B]^0 = 1.45 \times 10^{-5}$ M, 0−5.0 equiv, step = 1.0 equiv, and 20.0 equiv). $[F^-] = 2.20 \times 10^{-4}$ M in THF; $[B]^0$ corresponds to the initial concentration of the boron chromophore.

At the same time, the fluoride binding gave rise to fluorescence quenching. In DMF the fluoride binding is much weaker than in THF (Figure S7). The binding constant was estimated to be $\lg \beta \approx 4$,[21] which is about 3 orders of magnitude lower than that of the block copolymer in THF. However, because of the enhanced fluorescence quenching effect, which is also observed in DMF, the presence of ca. 2.4 equiv (1.9 ppm) of TBAF led to almost complete quenching of the emission. PNIPAM-*b*-PBM thus serves as an effective dual-responsive fluoride sensor. The proposed sensing mechanism is illustrated in Figure 2C.

For practical applications it is desirable to develop a sensory system that operates in aqueous media. However, due to the high hydration enthalpy of the fluoride anion, the binding to boron tends to be relatively weak. To overcome this issue, the Gabbaï group introduced a series of positively charged (molecular) boranes, in which electrostatic interactions further enhance anion binding to boron.[5] Taking advantage of our modular synthetic approach, we prepared the charged block-random copolymer PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) (Scheme 2; x = 0.14) and compared the fluoride binding properties to the neutral block copolymer PNIPAM-*b*-PBM.

In DMF solution, the binding constant for the quaternized block copolymer PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) ($\lg \beta$ = 6.6) proved to be more than 2 orders of magnitude larger than that of PNIPAM-*b*-PBM (Figure S8).[22] Encouraged by these results we also attempted fluoride detection in aqueous solution (DMF/water = 9/1 (w/w), Figure 3).[23] The fitted binding constant for PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) of $\lg \beta$ = 6.7 is essentially identical to that in pure DMF and a significant response is observed even at <1 ppm F⁻ relative to the water content. In stark contrast, fluoride binding to neutral PNIPAM-*b*-PBM under similar conditions proved to be so weak that even 20 equiv of F⁻ (28 ppm) led to only a small degree of complexation. These results clearly demonstrate that, indeed, the positively charged pyridinium moieties strongly enhance F⁻ binding in aqueous solution.

In summary, successful controlled free radical polymerization of a highly electron-deficient borane monomer gave a well-defined homopolymer and the first examples of luminescent triarylborane amphiphilic block copolymers. These polymers were used as effective chemical sensors for fluoride ions. As illustrated in Figure 4, our systematic studies demonstrate that: (1) The distribution of borane chromophores along the polymer chain critically influences the fluoride binding response. In THF, both the homo and block copolymer showed enhanced fluorescence quenching, which is attributed to effective exciton migration to lower energy non-emissive sites generated upon F⁻ binding. (2) The block copolymer acts as a dual-responsive chemical sensor for fluoride in the polar solvent DMF; F⁻ binding gave rise to a sharp decrease in the scattering of light and simultaneous fluorescence quenching,

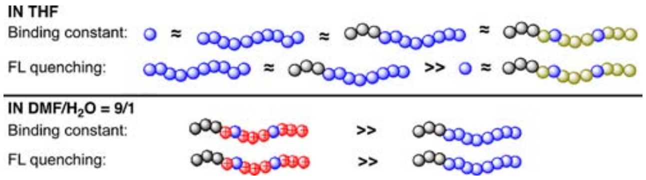


Figure 4. Polymer-architecture effect on the F$^-$ binding constant and fluorescence quenching in different solvents.

which can be easily detected by naked eye. (3) Introduction of positive charges along the polymer chain enhanced the anion binding strength and enabled F$^-$ recognition in highly polar solvents and even in aqueous solution.

We expect our results to have significant impact on the practical applications of luminescent boron-containing polymers for anion sensing. In addition, electron-deficient block copolymers such as the ones reported in here could prove useful as self-assembled luminescent materials for biological imaging and in the area of organic electronics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

fjaekle@rutgers.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This Communication is based upon work supported by the National Science Foundation under Grants No. CHE-0809642 and CHE-1112195. We thank Dr. Xiaodong Yin for assistance with fluorescence liftetime measurements.

■ REFERENCES

(1) (a) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927. (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (c) Lorbach, A.; Hübner, A.; Wagner, M. *Dalton Trans.* **2012**, *41*, 6048.

(2) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584.

(3) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985.

(4) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372.

(5) (a) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbaï, F. P. *Chem. Rev.* **2010**, *110*, 3958. (b) Zhao, H.; Leamer, L. A.; Gabbaï, F. P. *Dalton Trans.* **2013**, *42*, 8164.

(6) (a) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339. (b) Miyata, M.; Chujo, Y. *Polym. J.* **2002**, *34*, 967. (c) Sundararaman, A.; Victor, M.; Varughese, R.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748. (d) Li, H.; Jäkle, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 2313. (e) Chen, P. K.; Jäkle, F. *J. Am. Chem. Soc.* **2011**, *133*, 20142. (f) Sung, W. Y.; Park, M. H.; Park, J. H.; Eo, M.; Yu, M.-S.; Do, Y.; Lee, M. H. *Polymer* **2012**, *53*, 1857. (g) Cai, M.; Daniel, S. L.; Lavigne, J. J. *Chem. Commun.* **2013**, *49*, 6504.

(7) (a) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317. (b) Shipp, D. A. *J. Macromol. Sci., Polym. Rev.* **2005**, *45*, 171.

(8) Moad, G.; Chen, M.; Haussler, M.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Chem.* **2011**, *2*, 492.

(9) Cheng, F.; Jäkle, F. *Polym. Chem.* **2011**, *2*, 2122.

(10) Cambre, J. N.; Sumerlin, B. S. *Polymer* **2011**, *52*, 4631.

(11) (a) Cambre, J. N.; Roy, D.; Gondi, S. R.; Sumerlin, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 10348. (b) Roy, D.; Sumerlin, B. S. *ACS Macro Lett.* **2012**, *1*, 529.

(12) (a) Kim, K. T.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; van Hest, J. C. M. *J. Am. Chem. Soc.* **2009**, *131*, 13908. (b) Kim, H.; Kang, Y. J.; Kang, S.; Kim, K. T. *J. Am. Chem. Soc.* **2012**, *134*, 4030.

(13) (a) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993. (b) Barner, L.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Aust. J. Chem.* **2004**, *57*, 19.

(14) The higher quantum yield for PNIPAM-*b*-PBM relative to PBM is consistent with a smaller end group effect due to the much higher molecular weight.

(15) The slight bathochromic shift of the absorption of PNIPAM-*b*-PBM in DMF relative to THF could also be due to enhanced π-interactions between side-chain chromophores. However, no concentration dependence of the monomer or polymer absorption was observed.

(16) Carton, R. J. *Fluoride* **2006**, *39*, 163.

(17) All measurements were performed under ambient conditions in the presence of air, but using freshly distilled anhydrous THF. Similar binding constants were observed for other arylboranes in anhydrous solvents, while somewhat lower binding constants are typically obtained in the presence of traces of water. See: Schmidt, H. C.; Reuter, L. G.; Hamacek, J.; Wenger, O. S. *J. Org. Chem.* **2011**, *76*, 9081.

(18) Enhanced fluorescence quenching is frequently observed in conjugated polymers. See ref 6.

(19) (a) For exciton migration in non-conjugated polymers, see: Ghosh, D.; Nandi, N.; Chattopadhyay, N. *J. Phys. Chem. B* **2012**, *116*, 4693. and references therein (b) Related studies on borane polymers: Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879.

(20) Consistent is a decrease in the fluorescence liftetime to <1 ns upon partial complexation with fluoride; see Table S1.

(21) The lower accuracy is due to the light scattering effect of block copolymer aggregates on the titration spectra.

(22) Relative to the other polymers and the monomer, PNIPAM-*b*-P(BM-*ran*-4VPMeOTf) displays a similar $\lambda_{\mathrm{max,abs}}$ = 332 nm, but a red-shifted $\lambda_{\mathrm{max,em}}$ = 423 nm and a lower ϕ = 0.08. The red shift of the emission could be related to the more polar environment provided by the quaternized 4VP units.

(23) A shoulder at 290 nm in the spectrum of the initial solution indicates a small extent of OH$^-$ binding in DMF/H$_2$O (ca. 5%; see Figure S9).