J|A|C|S
ARTICLES

Luminescent Triarylborane-Functionalized Polystyrene: Synthesis, Photophysical Characterization, and Anion-Binding Studies

Kshitij Parab, Krishnan Venkatasubbaiah, and Frieder Jäkle*

Contribution from the Department of Chemistry, Rutgers University−Newark, 73 Warren Street, Newark, New Jersey 07102

Received May 11, 2006; E-mail: fjaekle@rutgers.edu

Abstract: A new class of highly fluorescent triarylborane polymers has been prepared from trimethylsilyl-substituted polystyrene via a modular approach that involves selective polymer modification reactions with organometallic reagents. The photophysical properties, environmental stability, and the Lewis acidity of the boron sites have been tailored through modifications in the substitution pattern on boron. The photophysical properties are indicative of electronic communication between the chromophores attached to polystyrene, which has been exploited for the efficient probing of fluoride and cyanide in the micromolar concentration range.

Introduction

Recent interest in the incorporation of boron into extended organic π systems is to a large extent due to the intriguing electronic and photophysical properties that are commonly encountered.[1,2] The latter arise as a result of overlap between the empty p orbital on boron and the conjugated π system and can thus systematically be modified either through variation of the organic π system or by fine-tuning the Lewis acidity of boron itself. Materials of this kind have been extensively used, for example, in linear and nonlinear optics,[3] as emission and electron conduction layers in organic light emitting devices (OLEDs),[4] and as luminescent probes for anions.[5]

The respective polymeric analogues are particularly intriguing due to the opportunity of using solution processing techniques for device fabrication and, in the case of sensor materials, the possibility of signal amplification effects.[6] In particular, the discovery and development of hydroboration polymerization procedures by Chujo and co-workers has made organoboron polymers that contain electron-deficient boron groups in the conjugated polymer backbone readily accessible.[7] Several other techniques for the incorporation of boron moieties into the backbone of conjugated organic and organometallic polymers have also been reported.[8] Many of these polymers show very interesting photophysical properties and may even act as novel *n*-type polymers in electronic devices.[9]

---

(1) Jäkle, F. Boron: Organoboranes. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed. Wiley: Chichester, 2005.

(2) (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *652*, 3−9. (b) Entwistle, C. D.; Marder, T. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927−2931. (c) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574−4585. (d) Shirota, Y. *J. Mat. Chem.* **2000**, *10*, 1−25. (d) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75−93.

(3) (a) Branger, C.; Lequan, M.; Lequan, R. M.; Barzoukas, M.; Fort, A. *J. Mater. Chem.* **1996**, *6*, 555−558. (b) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. *J. Solid State Chem.* **2000**, *154*, 5−12. (c) Liu, Z.-Q.; Fang, Q.; Cao, D.-X.; Wang, D.; Xu, G.-B. *Org. Lett.* **2004**, *6*, 2933−2936. (d) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68−69. (e) Charlot, M.; Porres, L.; Entwistle, C. D.; Beeby, A.; Marder, T. B.; Blanchard-Desce, M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 600−606. (f) Yuan, Z.; Entwistle, C. D.; Collings, J. C.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Taylor, N. J.; Kaiser, H. M.; Kaufmann, D. E.; Poon, S.-Y.; Wong, W.-Y.; Jardin, C.; Fathallah, S.; Boucekkine, A.; Halet, J.-F.; Marder, T. B. *Chem. Eur. J.* **2006**, *12*, 2758−2771. (g) Stahl, R.; Lambert, C.; Kaiser, C.; Wortmann, R.; Jakober, R. *Chem. Eur. J.* **2006**, *12*, 2358−2370.

(4) (a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021−11022. (b) Chen, B.; Zhang, X. H.; Lin, X. Q.; Kwong, H. L.; Wong, N. B.; Lee, C. S.; Gambling, W. A.; Lee, S. T. *Synth. Met.* **2001**, *118*, 193−196. (c) Jia, W.-L.; Bai, D.-R.; McCormick, T.; Liu, Q.-D.; Motala, M.; Wang, R.-Y.; Seward, C.; Tao, Y.; Wang, S. *Chem. Eur. J.* **2004**, *10*, 994−1006. (d) Liu, Q.-D.; Mudadu, M. S.; Thummel, R.; Tao, Y.; Wang, S. *Adv. Funct. Mater.* **2005**, *15*, 143−154. (e) Jia, W. L.; Moran, M. J.; Yuan, Y.-Y.; Lu, Z. H.; Wang, S. *J. Mater. Chem.* **2005**, *15*, 3326−3333. (f) Jia, W. L.; Feng, X. D.; Bai, D. R.; Lu, Z. H.; Wang, S.; Vamvounis, G. *Chem. Mater.* **2005**, *17*, 164−170. (g) Mazzeo, M.; Vitale, V.; Sala, F. D.; Anni, M.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2005**, *17*, 34−39. (h) Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281-283.

(5) (a) Cooper, C. R.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, 1365−1366. (b) Shiratori, H.; Ohno, T.; Nozaki, K.; Osuka, A. *Chem. Commun.* **1999**, 2181−2182. (c) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372−11375. (d) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816−8817. (e) Miyata, M.; Chujo, Y. *Polym. J.* **2002**, *34*, 967−969. (f) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036−2040. (g) Solé, S.; Gabbaï, F. P. *Chem. Commun.* **2004**, 1284−1285. (h) Melaimi, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 9680−9681. (i) Koskela, S. J. M.; Fyles, T. M.; James, T. D. *Chem. Commun.* **2005**, 945−947. (j) Liu, Z.-Q.; Shi, M.; Li, F.-Y.; Fang, Q.; Chen, Z.-H.; Yi, T.; Huang, C.-H. *Org. Lett.* **2005**, *7*, 5481−5484. (k) Agou, T.; Kobayashi, J.; Kawashima, T. *Org. Lett.* **2005**, *7*, 4373−4376. (l) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495−497. (m) Hudnall, T. W.; Melaimi, M.; Gabbaï, F. P. *Org. Lett.* **2006**, *8*, 2747−2749. (n) Liu, X. Y.; Bai, D. R.; Wang, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5475−5478.

(6) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574. See also refs 5e and 8f.

(7) (a) Chujo, Y.; Tomita, I.; Hashiguchi, Y.; Tanigawa, H.; Ihara, E.; Saegusa, T. *Macromolecules* **1991**, *24*, 345−348. (b) Chujo, Y.; Takizawa, N.; Sakurai, T. *J. Chem. Soc., Chem. Commun.* **1994**, 227−228. (c) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112−5113.

(8) (a) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776−10777. (b) Miyata, M.; Matsumi, N.; Chujo, Y. *Polym. Bull.* **1999**, *42*, 505−510. (c) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669−4672. (d) Matsumi, N.; Umeyama, T.; Chujo, Y. *Polym. Bull.* **2000**, *44*, 431−436. (e) Berenbaum, A.; Braunschweig, H.; Dirk, R.; Englert, U.; Green, J. C.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765−5774. (f) Sundararaman, A.; Victor, M.; Varughese, R.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748−13749. (g) Heilmann, J. B.; Scheibitz, M.; Qin, Y.; Sundararaman, A.; Jäkle, F.; Kretz, T.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 920−925.

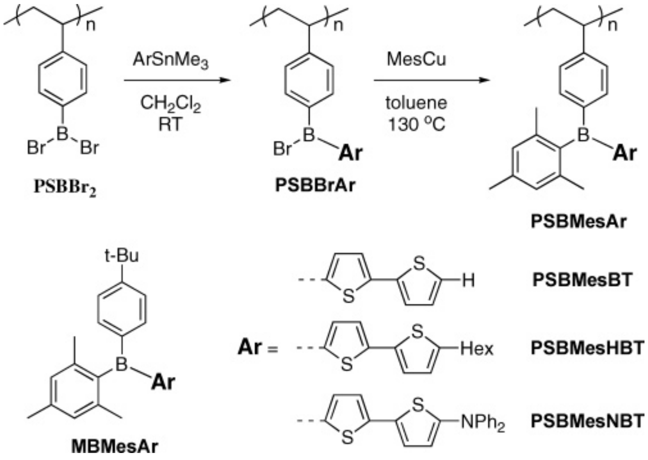
10.1021/ja063302v CCC: $33.50 © 2006 American Chemical Society

In comparison, organic polymers that contain conjugated organoborane moieties attached in a regular fashion to the polymer side chain have received far less attention. Some of the advantages of using a polymer side-chain modification approach are that high molecular weights are easily obtained and that copolymers containing different functionalities can be realized. Even block copolymer architectures are accessible through living polymerization techniques.[10] However, the side-chain functionalization of polyolefins with electro- and/or photoactive triarylborane moieties[11] has not been systematically studied, and their use in sensor applications has not been explored. We have successfully incorporated electron-deficient boryl groups into polystyrene as pendent groups using an approach that affords well-defined soluble polymers of controlled molecular weight, architecture, and degree of functionalization.[10,12,13] We have also recently demonstrated that luminescent organoboron polymers with tetracoordinated boron centers that are of interest for OLED applications can be prepared with high selectivity by substitution with 8-hydroxyquinoline ligands.[14] Herein we discuss the preparation and photophysical properties of a new class of luminescent high-molecular-weight polymers containing pendent fluorescent triarylborane moieties, in which the presence of tricoordinate boron centers provides an opportunity for the recognition of nucleophiles.

Experimental Section

Representative Experimental Procedure. Synthesis of PSBMesHBT. A solution of BBr_3 (0.88 g, 3.51 mmol) in CH_2Cl_2 (15 mL) was added dropwise to poly(4-trimethylsilylstyrene) (0.50 g, ca. 2.84 mmol of Me_3Si groups) in CH_2Cl_2 (15 mL) and stirred for 16 h. A solution of 5-trimethylstannyl-5′-hexyl-2,2′-bithiophene (1.70 g, 4.11 mmol) in CH_2Cl_2 (15 mL) was added dropwise at ambient temperature. The reaction mixture turned yellow and was allowed to stir for 12 h at room temperature. All volatile components were then removed under high vacuum. The yellow residue was taken up in toluene (30 mL), and $MesCu\cdot(C_7H_8)_{0.2}$ (0.79 g, 3.93 mmol) in toluene (15 mL) was added dropwise, leading to formation of a purple precipitate. The mixture was allowed to react for 3 h and then refluxed for 72 h. Filtration through celite gave a yellow solution, which was concentrated to ca. 3 mL and precipitated into cold hexanes (350 mL). The product was purified by repeated precipitation from toluene into hexanes and dried at 50 °C under high vacuum to give a fine yellow powder (0.84 g, 61%). ^{11}B NMR (160.386 MHz, $CDCl_3$): δ 50 ($w_{1/2} = 2000$ Hz); ^1H NMR (499.893 MHz, $CDCl_3$): δ 7.8−7.3 (br m, 4H, Ph_o and Th-H3,4), 7.1−6.9 (br m, 3H, Ph_m and Th-H3′), 6.7−6.1 (br m, 3H, Th-H4′ and Mes_m), 2.7 (br m, 2H, Hex), 2.2 (br, 3H, *p*-Me), 1.8 (br, 6H, *o*-Me), 1.62 (br m, 2H, Hex), 1.3 (br m, 6H, Hex), 0.88 (br m, 3H, Hex), the backbone protons are overlapping; ^{13}C NMR (125.69 MHz, $CDCl_3$): δ 150.4, 147.0, 143.4, 142.8 (br), 138.8 (br), 138.1, 137.0, 136.9, 134.8, 127.1, 125.2 (aromatic C), 42−40 (polymer backbone), 31.8, 31.7, 30.4, 29.0, 22.8, 14.3 (Hex), 22.8 (*o*-Me), 21.4 (*p*-Me); GPC-RI (THF vs PS standards): $M_n = 45{,}275$, $M_w = 54{,}574$, PDI = 1.15; UV−vis (CH_2Cl_2, 3.2 10^{-5} M): $\lambda_{max} = 275$ nm ($\epsilon = 18{,}220$), 380 nm ($\epsilon = 21{,}990$); fluorescence (CH_2Cl_2, 3.2 10^{-5} M): $\lambda_{em,max} = 455$ nm, $\Phi = 0.67$ ($\lambda_{exc} = 380$ nm); UV−vis (thin film): $\lambda_{max} = 301$ nm, 381 nm; fluorescence (thin film): $\lambda_{em,max} = 467$ nm ($\lambda_{exc} = 381$ nm); DSC (onset, 20 °C/min; second heating curve): $T_g = 139$ °C; TGA (20 °C/min; N_2): 39% weight loss between 242 and 358 °C and 19% between 417 and 456 °C; 12% residual mass at 800 °C; elemental analysis: calcd C 77.16, H 7.31; found C 75.92, H 7.08. Further experimental details for all other polymers and model systems are given in the Supporting Information.

Scheme 1. Synthesis of Triarylborane Polymers PSBMesAr



Results and Discussion

The key design principle for the novel fluorescent triarylborane polymers PSBMesAr (Scheme 1) is the use of one boron substituent for steric stabilization, while the second pendent group represents an extended organic π system that can effectively overlap with the empty p orbital on boron. By taking advantage of the high selectivity of tin−boron exchange reactions, we were able to replace one of the bromine substituents of $PSBBr_2$ in a controlled manner to give the substituted polymers PSBBrAr (Scheme 1). In a second step, the mesitylcopper toluene solvate $[MesCu]_5\cdot(C_7H_8)$[15] was used to attach bulky mesityl groups.[16] All polymers PSBMesAr were readily isolated by precipitation from toluene into hexanes and showed good solubility in common organic solvents such as toluene, THF, or CH_2Cl_2.

The polymers PSBMesAr and their respective molecular model compounds MBMesAr (Scheme 1) were fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy. The presence of a broad signal at about 47−50 ppm in the ^{11}B NMR spectra is typical of triarylborane moieties. However, in comparison to the model compounds, which represent one repeating unit of the polymer chain, a significant upfield shift of the ^{11}B NMR resonance of about 10−15 ppm was observed. The latter is tentatively attributed to additional shielding effects due to neighboring groups on the polymer chain.[17] The ^1H NMR spectra showed broad overlapping signals that were not very informative. However, the ^{13}C NMR spectra correlate well with those of the molecular models and thus further confirm the

---

(9) (a) Kobayashi, H.; Sato, N.; Ichikawa, Y.; Miyata, M.; Chujo, Y.; Matsuyama, T. *Synth. Met.* **2003**, *135-136*, 393−394. (b) Sato, N.; Ogawa, H.; Matsumoto, F.; Chujo, Y.; Matsuyama, T. *Synth. Met.* **2005**, *154*, 113−116.

(10) Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. *Macromolecules* **2005**, *38*, 8987−8990.

(11) (a) Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F. *Chem. Phys. Lett.* **1997**, *272*, 265−270. (b) Mutaguchi, D.; Okumoto, K.; Ohsedo, Y.; Moriwaki, K.; Shirota, Y. *Org. Electron.* **2003**, *4*, 49−59.

(12) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672−12673.

(13) Qin, Y.; Cheng, G.; Parab, K.; Achara, O.; Jäkle, F. *Macromolecules* **2004**, *37*, 7123−7131.

(14) Qin, Y.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *J. Am. Chem. Soc.* **2004**, *126*, 7015−7018.

(15) The conditions for the substitution reactions were optimized for the respective model compounds MBMesAr that are derived from 4-$^tBuC_6H_4BBr_2$. For the reaction of 4-$^tBuC_6H_4BBr_2$ with stannylated bithiophene derivatives, selectivities of >90% were realized in all cases according to ^1H NMR spectroscopy. In order to avoid the formation of any triarylborane groups in this step, a slight deficiency of the tin reagents was applied in the polymer substitution reactions.

(16) Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, *681*, 134−142.

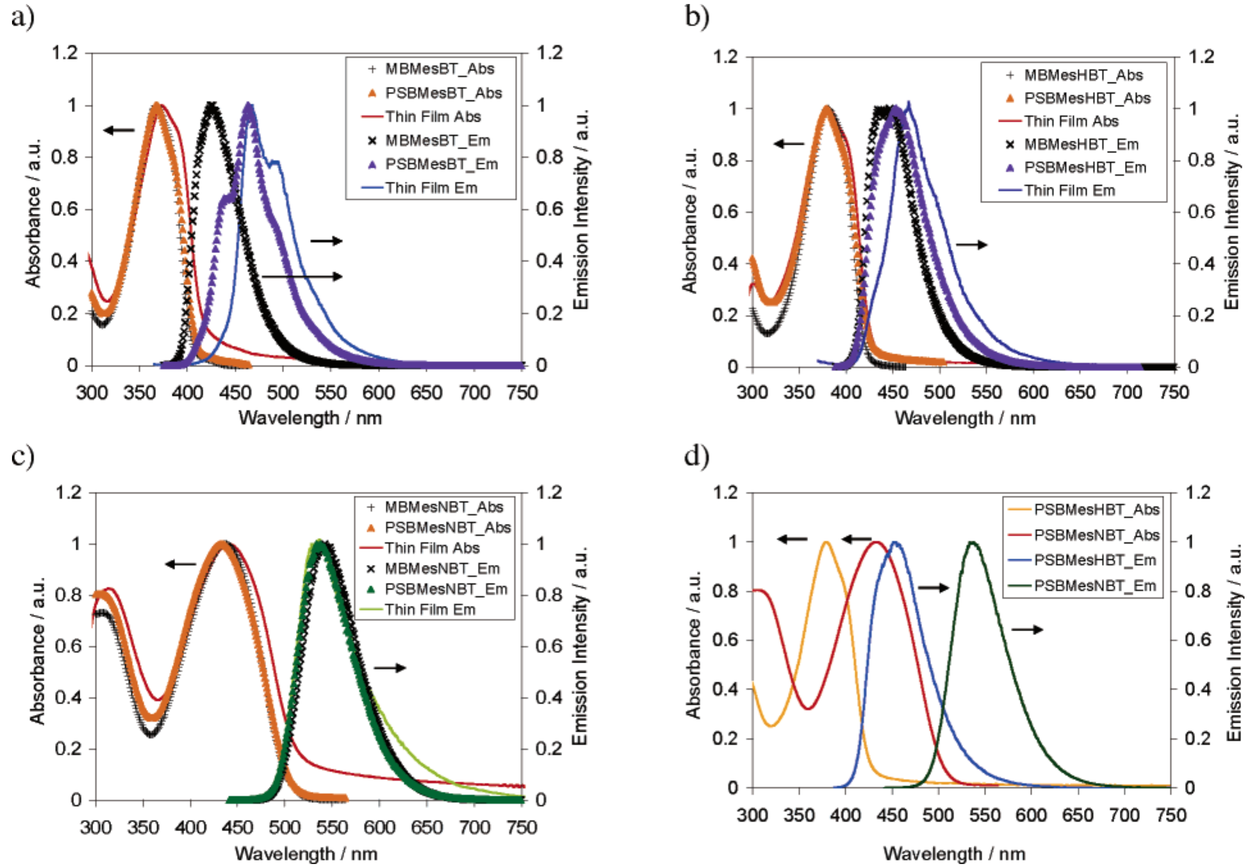


Figure 1. (a) Comparison of the absorption and emission spectra of MBMesBT and PSBMesBT in CH_2Cl_2 solution and as thin films cast from toluene. (b) Comparison of the absorption and emission spectra of MBMesHBT and PSBMesHBT in CH_2Cl_2 solution and as thin films cast from toluene. (c) Comparison of the absorption and emission spectra of MBMesNBT and PSBMesNBT in CH_2Cl_2 solution and as thin films cast from toluene. (d) Comparison of the absorption and emission spectra of PSBMesHBT and PSBMesNBT.

Table 1. Comparison of Photophysical Properties

polymer	PSBMesBT	PSBMesHBT	PSBMesNBT
λ_{abs} [nm] (lgϵ)[a]	368 (4.5)	380 (4.3)	433 (4.5)
λ_{em} [nm][b]	442,[c] 463	455	537
ϕ_F[d]	0.66	0.67	0.35
λ_{abs} film [nm]	373	381	440
λ_{em} film [nm][b]	468, 489[c]	467	536
model	MBMesBT	MBMesHBT	MBMesNBT
λ_{abs} [nm] (lgϵ)[a]	367 (4.5)	381 (4.6)	436 (4.6)
λ_{em} [nm][b]	425	437	540
ϕ_F[d]	0.72	0.76	0.74

[a] Data were acquired in CH_2Cl_2 solution (3.2×10^{-5} M of boron functional groups). [b] Excited at the absorption maxima. [c] Lower-intensity band or shoulder. [d] Anthracene was used as a standard.

structure of the polymers with borane moieties containing mesityl and bithiophene substituents.[18]

The molecular weight of the polymers was studied by GPC analysis in THF in the presence of 0.1 wt % $[Bu_4N]Br$. The molecular weights relative to PS standards were found to be in the range expected on the basis of the MW of the poly(4-trimethylsilyl)styrene precursor. However, the bands are somewhat broadened (polydispersities (PDI) from 1.15 to 1.51), presumably due to a small degree of aggregate formation and interaction with the column material that also seems to impact the retention times.

The thermal characteristics of the polymers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Polymers PSBMesBT, PSBMesHBT, and PSBMesNBT show glass transition temperatures (T_g) of 165 , 139, and 165 °C, respectively, which are slightly higher than that of polystyrene, but in a similar range as that of the related triarylborane polymer poly(4-dithienylborylstyrene) ($PS\text{-}BTh_2$, $T_g = 148$ °C).[13] The TGA plots[18] indicated that the mesityl-substituted polymers show high thermal stability with no significant decomposition up to ca. 250 °C. Above this temperature, multistep decomposition processes were observed. The residual weights at 800 °C were in the range of ca. 5−10%. The environmental stability of the polymers was considerably higher than for related sterically unprotected polymers $PSBAr_2$ (Ar = hexylbithiophene).[19] No substantial degradation was observed in the solid state over a period of 2 weeks, but additional sharp NMR signals corresponding to small molecule degradation products started to develop after ca. 2 weeks in solution.[20] In comparison, polymers $PSBAr_2$ that lack the mesityl groups decompose within 24 h under similar conditions.

All polymers PSBMesAr are strongly fluorescent in solution, and their thin films also show bright emission (Table 1, Figure 1). For instance, in CH_2Cl_2 solution, the polymers PSBMesBT

---

(17) Partial coordination of nucleophilic impurities, which would also explain this phenomenon, is unlikely since addition of small amounts of the strong Lewis acids BBr_3 or $B(C_6F_5)_3$ did not lead to a significant downfield shift of the ^{11}B NMR resonances.

(18) See the Supporting Information for details.

(19) Parab, K.; Qin, Y.; Jäkle, F. *Polym. Mater. Sci. Eng. Prepr.* **2005**, *93*, 422−423.

(20) The environmental stability of the polymers in the solid state is slightly higher than that of the molecular species; in solution, similar stabilities were observed for molecular species and polymers. Attempts to further improve the steric protection of the boron sites to allow for applications under ambient conditions are currently under way.

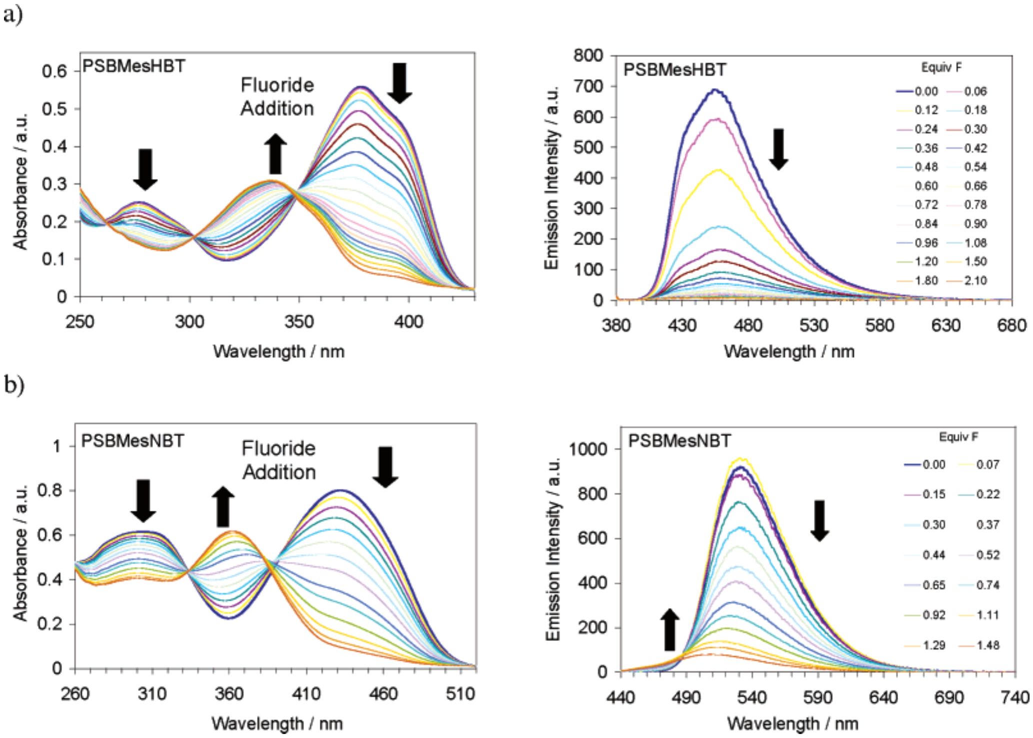


Figure 2. Absorption and emission spectra for the titrations of (a) PSBMesHBT (1.8×10^{-5} M boron sites, $\lambda_{exc} = 378$ nm) and (b) PSBMesNBT (2.9×10^{-5} M boron sites, $\lambda_{exc} = 432$ nm) with Bu_4NF (3.2×10^{-4} M) in THF.

and PSBMesHBT absorb at $\lambda_{abs} = 368$ and 380 nm, respectively, and emit bright blue light at $\lambda_{em} = 463$ and 455 nm. In contrast, the polymer PSBMesNBT has a yellow appearance due to an absorption at $\lambda_{abs} = 433$ nm and displays a yellow-green emission at $\lambda_{em} = 537$ nm, consistent with a bathochromic shift due to the donor−π−acceptor structure of the aminobithiophene substituents.[2] The absorption data for the respective molecular model compounds are quite similar to those of the polymers, while the emission data differ significantly (Figure 1). This trend is most pronounced in the case of the unsubstituted bithiophene derivative, for which a single emission maximum of $\lambda_{em} = 425$ nm was determined in CH_2Cl_2 solution. In contrast, the polymeric material shows a broad red-shifted emission band at $\lambda_{em} = 463$ nm that appears to consist of multiple components. This indicates that intrapolymer aggregation is encountered in the case of the parent bithiophene group, while the presence of the bulky diphenylamino substituents renders aggregate formation less favorable. Molecular mechanics calculations on a model trimer of PSBMesHBT indicate that conformations in which the bithiophene moieties are aligned with respect to each other are possible and energetically favorable.[18] A further bathochromic shift was observed for thin films that were cast from toluene solution. Such an effect has also been reported for the luminescence of the respective vinylbithiophene polymers and been attributed to interpolymer aggregate formation.[21] The polymers PSBMesBT and PSBMesHBT show high quantum yields of 66% and 67% in CH_2Cl_2 solution, respectively, which are in a similar range to those of the molecular model compounds. However, a notably lower quantum yield of 35% was determined for PSBMesNBT in comparison to MBMesNBT (74%) (Table 1).

To explore their potential use in anion recognition, the polymers were first subjected to complexation with fluoride in THF solution. Fluoride binding upon addition of a 5-fold excess of Bu_4NF was evident from the ^{11}B NMR spectra, which display strongly upfield shifted signals at $\delta = 1-2$ in ca. 20 mM solution in THF (for PSBMesAr, $\delta = 47-50$). The complexation of PSBMesHBT and PSBMesNBT with fluoride was further investigated by UV−vis and fluorescence spectroscopy in THF (Figure 2). Upon addition of aliquots of the fluoride source to a solution of PSBMesHBT, a gradual decrease in intensity of the absorption band at 378 nm was evident, and a new band at 338 nm developed, which can be assigned to bithiophene groups with coordinated boron sites, $[B(Mes)ArF]^-$ (Figure 2).[22] Similarly, fluoride addition to PSBMesNBT led to a new band at 362 nm that is blue-shifted by 70 nm relative to the absorption maximum of the uncomplexed polymer.[22]

These results are consistent with TD-DFT calculations (Gaussian03)[23] that were performed on the closely related molecular tricoordinate bithiopheneborane species PhBMesMeBT and PhBMesNBT and their respective fluoride complexes (Table 2, Figure 3).[18] For both compounds, the calculations predict the distinct blue-shift of the absorption upon fluoride binding that is experimentally observed. This effect may be rationalized by inspection of the molecular orbitals involved in the transitions (Table 2). The lowest energy absorption in the case of the tricoordinate species PhBMesMeBT corresponds to

---

(21) Melucci, M.; Barbarella, G.; Zambianchi, M.; Benzi, M.; Biscarini, F.; Cavallini, M.; Bongini, A.; Fabbroni, S.; Mazzeo, M.; Anni, M.; Gigli, G. *Macromolecules* **2004**, *37*, 5692−5702.

(22) The absorption and emission bands for the fluoride-complexed polymers PSBMesHBT and PSBMesNBT are similar in energy to those of 2-trimethylstannyl-2′-hexyl-5,5′-bithiophene ($\lambda_{abs} = 317$ nm; $\lambda_{em} = 379$ nm) and 2-trimethylstannyl-2′-diphenylamino-5,5′-bithiophene ($\lambda_{abs}= 364$ nm; $\lambda_{em} = 450$ nm), respectively.

(23) DFT calculations were performed with the Gaussian03 program (Revision C. 02, Frisch, M. J.; et al.; Gaussian, Inc.: Wallingford CT, 2004). Geometries and electronic properties were calculated by means of the hybrid density functional B3LYP with the basis set of 6-31G(d). The input files and orbital representations were generated using Gaussview. Excitation data were calculated using TD-DFT (B3LYP) methods.

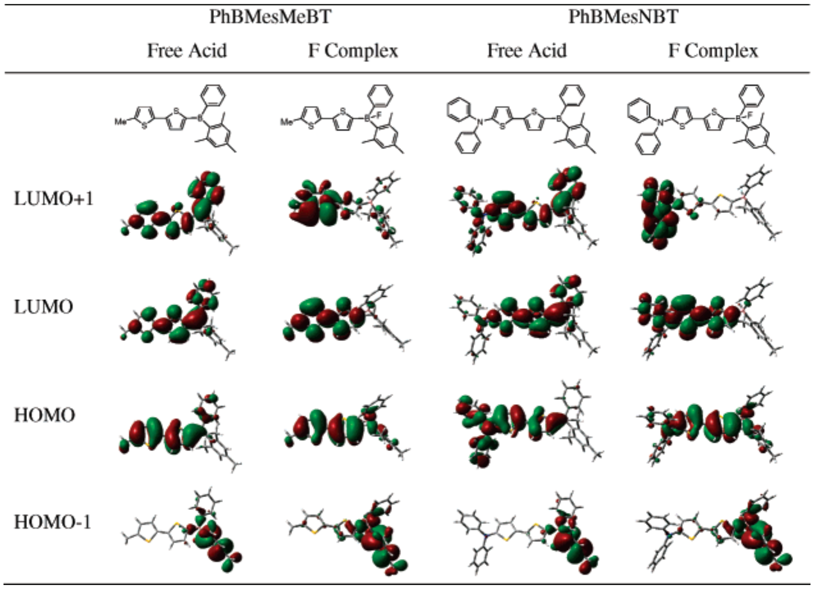


Figure 3. Computed (Gaussian03) orbital plots for the model systems of PSBMesHBT and PSBMesNBT.

Table 2. Calculated Electronic Transitions for PhBMesMeBT, PhBMesNBT, and Their Respective Fluoride Complexes from TD-DFT (B3LYP) Calculations

compound	transition	MO contributions	energy gap eV (nm)	oscillator strength/*f*
PhBMesMeBT	$S_0 \rightarrow S_1$	HOMO-1→LUMO HOMO→LUMO	3.19 (388)	0.3452
	$S_0 \rightarrow S_2$	HOMO-1→LUMO HOMO→LUMO	3.27 (379)	0.4387
[PhBMesMeBT]F$^-$	$S_0 \rightarrow S_1$	HOMO→LUMO	3.53 (351)	0.6596
PhBMesNBT	$S_0 \rightarrow S_1$	HOMO→LUMO	2.65 (468)	1.2544
[PhBMesNBT]F$^-$	$S_0 \rightarrow S_1$	HOMO→LUMO HOMO→LUMO+1	3.22 (386)	0.3125
	$S_0 \rightarrow S_2$	HOMO→LUMO HOMO→LUMO+1	3.23 (384)	0.5713

transitions from the HOMO and HOMO-1 orbitals to the LUMO orbital, while the absorption of PhBMesNBT can be assigned to a HOMO−LUMO excitation. For both PhBMesMeBT and PhBMesNBT, the LUMO orbital shows significant overlap between the p orbital on boron and the bithiophene system, while the HOMO is primarily centered on the bithiophene moieties and shows only a minor contribution from boron (Figure 3). For PhBMesMeBT, the HOMO-1 is found on the mesityl group, indicating that the transition involves also charge transfer from the mesityl to the bithiophene moiety. In the case of the aminobithiophene model, PhBMesNBT, the HOMO−LUMO transition entails charge transfer from the amino group to the borane center.

Upon fluoride complexation, the extended conjugation through the boron center is interrupted, and the boron p orbital neither contributes to the HOMO nor the LUMO level of the borate complexes.[24] While for the fluoride complex of PhBMesMeBT the lowest energy absorption corresponds to a bithiophene $\pi-\pi^*$ transition, in the case of the fluoride complex of PhBMesNBT, an additional charge-transfer contribution to the diphenylamino group (LUMO+1) is also present.

Further analysis of the fluoride titration data for PSBMesHBT assuming independent binding sites provided an estimate of the binding constant of lgK = 6.9.[18] The slightly lower binding constant in comparison to the model system MBMesHBT (lgK = 7.4)[18] most likely is due to neighboring group effects that are expected to play a significant role at the later stages of the titration (formation of a polyelectrolyte). Very similar binding constants were determined for PSBMesNBT (lgK = 6.9) and the respective model compound MBMesNBT (lgK = 7.6).

Upon fluoride addition, the emission intensity of PSBMesHBT at $\lambda = 461$ nm strongly decreased (Figure 2).[25] The luminescence quenching at low fluoride concentrations is considerably more effective for the polymer than for the molecular analog MBMesHBT, for which the changes in emission intensity correlate with the decrease in absorption intensity.[18] Stern−Volmer analysis revealed an estimated 8-fold amplification effect for the polymeric material. In contrast, similar pronounced signal amplification was not observed for PSBMesNBT that contains diphenylamino groups attached to the bithiophene moieties.

We tentatively attribute the different behavior of PSBMesHBT to efficient exciton migration along the polymer chain (and possibly also between polymer chains) with subsequent trapping at lower energy aggregate states that are weakly or non-emissive.[26] In agreement with this interpretation is the lack of signal amplification for PSBMesNBT, which as discussed above does not show any spectroscopic evidence of aggregate formation in the excited state. To provide additional support we prepared a *random* copolymer that contains both hexylbithiophene and diphenylaminobithiophene substituents on boron (60:40). The absorption spectrum of this polymer reflects the presence of both chromophores with absorption maxima at λ_{abs} = 384 and 433 nm (shoulder).[18] However, the fluorescence spectrum clearly shows emission from only the lower energy states of the boron-bound diphenylaminobithiophene moiety at

---

(24) Similar changes in the HOMO and LUMO levels of arylboranes upon nucleophile binding have been reported by Yamaguchi and co-workers. See refs 2a and 5.

(25) For a review on optical halide sensing, see: (a) Geddes, C. D. *Meas. Sci. Technol.* **2001**, *12*, R53−R88. See also: (b) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443−448. (c) Bianchi, A.; Bowman-James, K.; García-España, E., Eds. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997. (d) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 487−516.

(26) The different behavior of PSBMesNBT indicates that the amplification effect is not simply due to dynamic exchange of fluoride between neighboring boron sites.

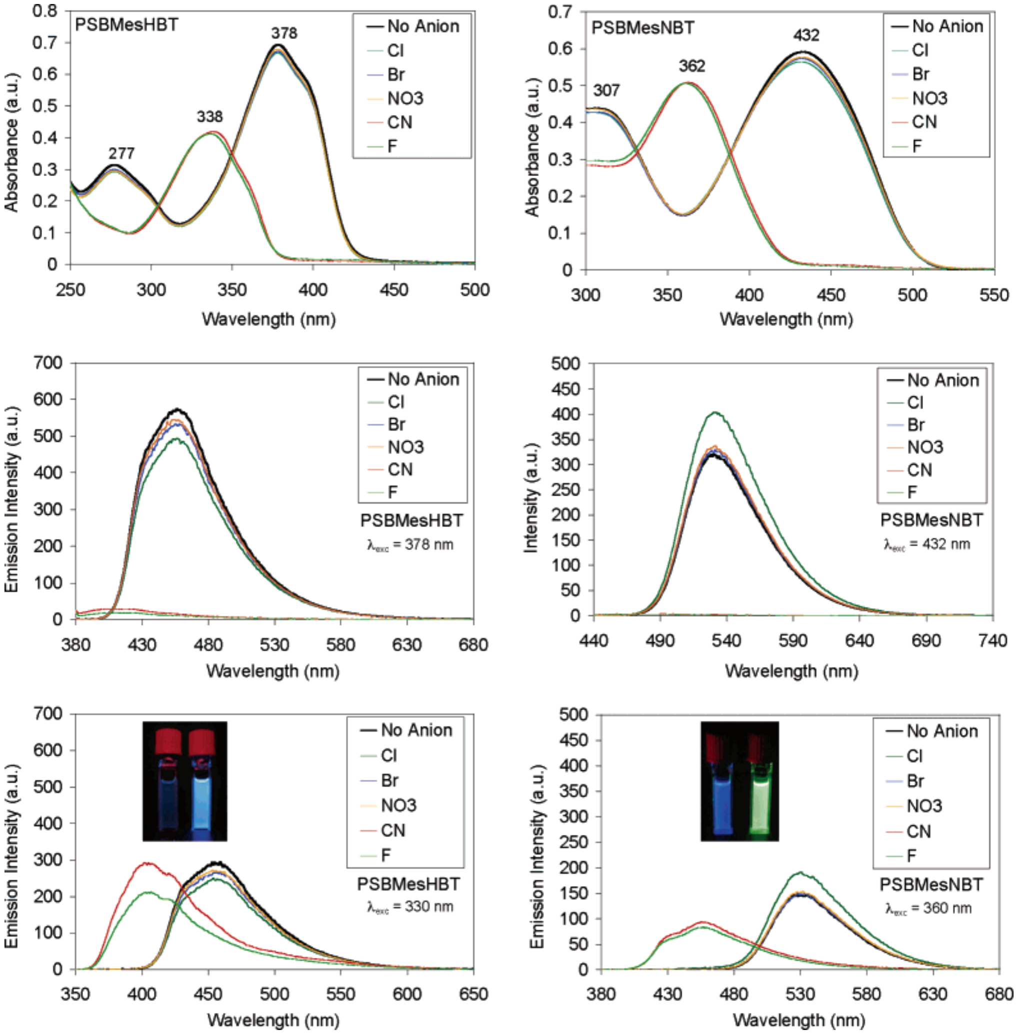


Figure 4. Absorption (top) and emission spectra (middle, excited at absorption maxima of free acids: $\lambda_{exc} = 378/432$ nm; bottom, excited at absorption maxima of complexes: $\lambda_{exc} = 330/360$ nm) for the exposure of PSBMesHBT and PSBMesNBT (3×10^{-5} M boron sites) to different anions in THF (3×10^{-4} M). The solutions in the photographs were excited with black light at 360 nm.

$\lambda_{em} = 532$. This suggests that exciton migration along the polymer chain indeed is a fast process that likely is responsible for the enhanced emission quenching of PSBMesHBT upon addition of small amounts of a fluoride source.[27]

To determine the substrate selectivity of PSBMesHBT and PSBMesNBT, we performed a comparative study in which a solution of each polymer was treated under identical conditions with a 10-fold excess of fluoride, chloride, bromide, nitrate, and cyanide, respectively. The photophysical response was monitored by UV−visible absorption and emission spectroscopy. From examination of the absorption and emission data, it is evident that fluoride and cyanide bind strongly to the boron polymers, while the other anions showed no significant response (Figure 4).[28−30] Interestingly, when PSBMesHBT was excited at 330 nm, the decrease in emission intensity of the blue band at 461 nm upon nucleophile binding was accompanied by the development of a (weaker) new band at ca. 405 nm that reaches into the UV region, and can be attributed to emission from the bithiophene moieties with nucleophile-bound boron sites.[31] This desirable feature of a "turn-on" sensor is clearly evident by visual observation for the green emissive PSBMesNBT, which upon fluoride addition shows a new blue emissive band at 457 nm with a shoulder at ca. 430 nm. These observations suggest that, while no signal amplification is found for PSBMesNBT, the polymer (and the respective model system) may serve as wavelength-ratiometric probes for fluoride or cyanide.

Conclusions

We have demonstrated that organotin and organocopper compounds may serve as convenient aryl-transfer reagents in the preparation of new fluorescent triarylboron polymers that are derived from poly(4-dibromoborylstyrene). The photophysical properties, environmental stability, and the Lewis acidity of the boron sites have been tailored through modifications in the substitution pattern on boron. Anion binding studies indicate

---

(27) The phenomenon of exciton migration in non-conjugated polymers is more commonly observed for thin films. See: Broadwater, S. J.; Hickey, M. K.; McQuade, D. T. *J. Am. Chem. Soc.* **2003**, *125*, 11154−11155 and references therein.

(28) Cyanide-sensitive fluorescent probes based on boronic acids have recently been reported: Badugu, R.; Lakowicz, J. R.; Geddes, C. D. *Dyes Pigm.* **2005**, *64*, 49−55.

(29) The slight emission enhancement of PSBMesNBT in the presence of excess chloride is likely due to changes in solvent polarity.

(30) Similar anion selectivity was observed for the respective model systems.

(31) Emission from tetracoordinate species is observed throughout the titrations of the polymers and model compounds with fluoride, but in the case of PSBMesHBT, energy transfer leads to emission only from the lower energy states at relatively low fluoride concentrations. This is consistent with the results described for the copolymer emission.

that the presence of Lewis acidic tricoordinate organoboron groups in these polymers can be exploited for the recognition of nucleophiles based on changes in the absorption and emission characteristics. The observation of strong sensitivity enhancement for PSBMesHBT in comparison to the model MBMesHBT suggests that highly functionalized polyolefins offer an interesting alternative to conjugated polymers as efficient sensor materials. We are currently pursuing applications of these and related polymers with further enhanced steric stabilization as sensors and as components of polymer light emitting devices (PLEDs).

Acknowledgement is made to the National Science Foundation (CAREER award CHE-0346828 to F.J. and MRI 0116066), to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Rutgers Research Council for support of this research. F.J. is an Alfred P. Sloan Research Fellow. We are grateful to Prof. Piotr Piotrowiak for stimulating discussions and help with luminescence measurements.

Supporting Information Available: Experimental procedures and data for all polymers and model compounds described, TGA plots, additional absorption and emission plots, details of the binding studies, Stern−Volmer plots, computational studies, and the full reference 23. This material is available free of charge via the Internet at http://pubs.acs.org.

JA063302V