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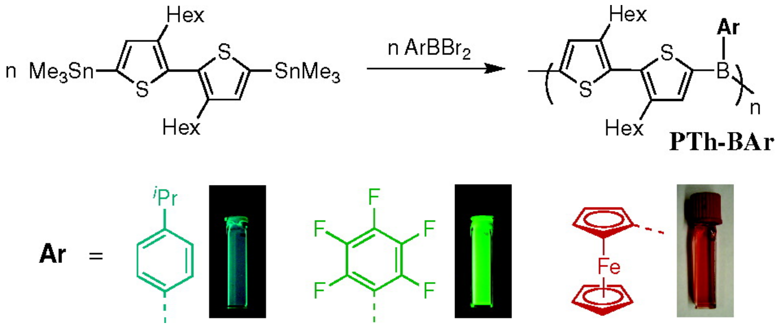

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A Family of Main-Chain Polymeric Lewis Acids: Synthesis and Fluorescent Sensing Properties of Boron-Modified Polythiophenes

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Conjugated organic polymers have emerged as an important class of new materials with numerous applications, for example, in electroluminescent devices, organic field-effect transistors, or electrochromic windows.[1] The incorporation of electron-deficient boryl groups into conjugated polymeric structures is intriguing since it is known to result in unusual photoluminescent and electron-conducting properties.[2−5] This behavior can be traced back to overlap between the empty p orbital on boron with the organic π-system, which in the case of small molecules has been corroborated through theoretical calculations and extensively exploited in device and sensor applications.[6,7] Conjugated organoboron polymers are particularly promising in this regard since recognition sites along the polymer backbone may act in a cooperative fashion, thus giving rise to sensor signal amplification. The latter is highly desirable for the design of efficient sensor systems.[8]

The hydroboration polymerization method developed by Chujo is currently the most commonly used method for the synthesis of main-chain organoboron polymers.[2] This elegant approach provides facile access to vinylene−arylene−vinylene bridged organoboron polymers. An in situ Grignard method has also been employed by Chujo for the preparation of main-chain triphenylborane polymers.[3] Intriguingly, these polymers have recently been successfully applied in fluoride anion sensing.[9] Their general use as chemosensors, however, has not been investigated in detail.

We have previously shown that Si−B exchange provides facile and selective access to polystyrene-based side-chain-functionalized polymeric Lewis acids.[10] Herein we report a new approach for the synthesis of polythiophenes with strongly Lewis acidic boryl groups embedded in the main chain, for which we take advantage of the high selectivity of tin−boron exchange. We also describe the use of these new boron-containing polythiophenes in the sensing of nucleophiles through changes in the photophysical characteristics.

Distannylated bithiophene, substituted with solubilizing hexyl substituents, serves as a versatile polymer precursor. Condensation polymerization was achieved under mild conditions by treatment with various bifunctional arylboron halides ($ArBBr_2$; Ar = 4-*i*PrPh, C_6F_5, Fc) in CH_2Cl_2 at ambient temperature (Scheme 1). The byproduct, Me_3SnBr, was removed under high vacuum, and the polymers were purified by precipitation into cold hexanes. Polymers **PTh−BAr** are highly soluble in common organic solvents; they are thermally stable to ca. 200 °C, but show some sensitivity to oxygen and were thus handled under nitrogen atmosphere.

The NMR spectra of polymers **PTh−BAr** are consistent with the proposed polymeric structures. For instance, displacement of the stannyl groups of the precursor is evident from disappearance of the $SnMe_3$ signal in the ^1H, ^{13}C, and ^{119}Sn NMR spectra and the appearance of broad signals in the ^{11}B NMR spectra in a region typical of triarylboranes (Table 1). Comparison with model compounds **M−BAr** further confirms the assignments. A slight upfield shift of the ^{11}B NMR signals of the polymers may possibly be the result of enhanced π-bonding between boron and the bithiophene moieties due to extended delocalization.[2−4]

Scheme 1. Synthesis of Boron-Modified Polythiophenes

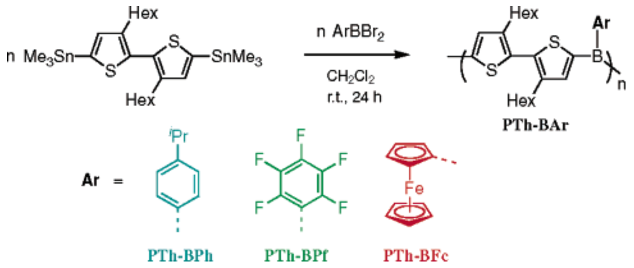
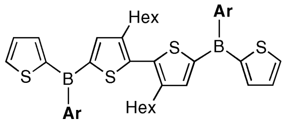


Table 1. ^{11}B NMR Data of Polymers and Model Compounds



M-BFc Ar = Ferrocenyl
M-BPh Ar = 4-(^iPr)C_6H_4
M-BPf Ar = C_6F_5

Organoboron Polymer	PTh–BPh	PTh–BPf	PTh–BFc
free acid δ [ppm]	49	46	49
Py complex δ [ppm]	1	−3	1
Bithiophene Model	**M–BPh**	**M–BPf**	**M–BFc**
free acid δ [ppm]	53	49	52
Py complex δ [ppm]	1.2	−1.8	5.0

The molecular weight and dispersity of polymers **PTh−BAr** were determined by GPC, MALDI-TOF, and NMR end-group analysis. GPC relative to PS standards gave M_n of ca. 5000−9000 and *PDI*s in the range of ca. 1.2−1.5. MALDI-TOF-TOF with benzo[*a*]pyrene/pyridine as the matrix showed peak patterns that correspond predominantly to linear polymers with the expected $-Th_2B(Ar)-$ repeating unit and bithiophene end groups (Figure 1).[11] This indicates that the polymerization is not limited by solubility but rather by a small amount of destannylated bithiophene, which may form in the presence of trace amounts of protic acids. The latter was further confirmed by ^1H NMR end-group analysis, which clearly shows the presence of two small doublets expected for adjacent protons in a terminal thiophene ring, and thus corroborates the formation of linear organoboron polymers in the molecular weight range of ca. 5000−9000.

Polymers **PTh−BAr** exhibit an intriguing variety of different photophysical properties. While the polymers containing phenyl and C_6F_5 groups on boron are yellow-colored materials, attachment of pendant ferrocenyl substituents leads to an intense dark red color, characteristic of d−d transitions in ferrocenylboranes (Table 2). Comparison with model compounds **M−BAr** reveals a red shift of the solution absorption bands for polymers **PTh−BPh** and **PTh−BPf**, indicative of a considerable degree of extended p−π conjugation within the polymer main chain. A similar bathochromic shift

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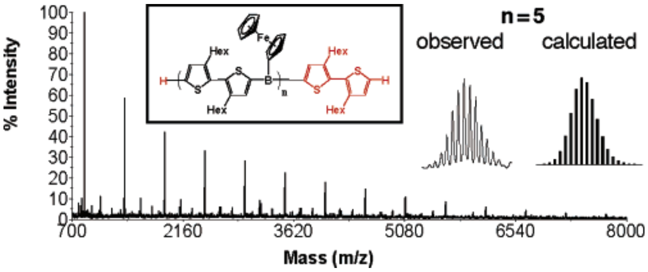

Figure 1. MALDI-TOF-TOF spectrum of **PTh−BFc** (reflectron + mode).

Table 2. Photophysical Properties of Polymeric Lewis Acids and Bithiophene Model Compounds in CH_2Cl_2 Solution

Organoboron Polymer	PTh–BPh	PTh–BPf	PTh–BFc
$\lambda_{abs,max}$ [nm]	391	413	379, 497
$\lambda_{em,max}$ [nm][a]	491	529	*d*
quantum yield ϕ[b]	0.21	0.15	*d*
Bithiophene Model	M–BPh	M–BPf	M–BFc
$\lambda_{abs,max}$ [nm]	313, 361	304, 376	350, 493
$\lambda_{em,max}$ [nm][a]	458, 482[c]	478, 508[c]	*d*
quantum yield ϕ[b]	0.19	0.18	*d*

[a] Excited at the absorption maxima. [b] Anthracene was used as a standard. [c] Shoulder. [d] Emission quenched by ferrocene.

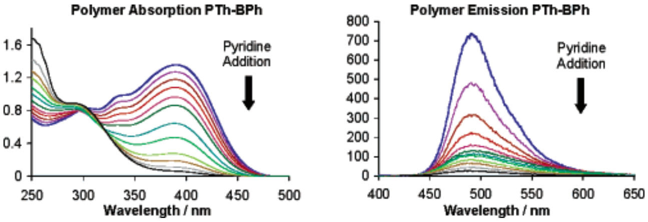

Figure 2. UV−vis absorption and fluorescence spectra (λ_{exc} = 390 nm) for the titration of a CH_2Cl_2 solution of **PTh−BPh** with pyridine.

is also observed for the solution luminescence spectra of polymers **PTh−BPh** and **PTh−BPf**. Intriguingly, the emission wavelength of these polymers is determined by the electronic effect of the pendant aryl group on boron. Thus, with phenyl groups on boron blue (thin film) to blue−green (solution) luminescence is observed, while the attachment of electron-withdrawing C_6F_5 substituents leads to bright green emission.

To investigate the potential of these organoboron polymers as sensor materials, we studied the binding of pyridine. Complexation of the boryl groups upon addition of excess pyridine is evident from a strong upfield shift of the ^{11}B NMR signal from ca. 50−60 to ca. 0 ppm, which is indicative of tetracoordinate boron (Table 1). The binding process is reversible, and in dilute solution, partial dissociation is evident. Moreover, the coordinated pyridine can effectively be removed with the stronger Lewis acid $B(C_6F_5)_3$.

The pyridine binding was further examined through titration studies using UV−vis absorption and fluorescence spectroscopy as illustrated for **PTh−BPh** in Figure 2. A gradual decrease in the visible absorption band of **PTh−BPh** at 390 nm is reflected in a color change from yellow to colorless. A single isosbestic point is not observed, which is likely due to conjugation between adjacent Lewis acid sites leading to negative cooperativity effects.[12] Effective fluorescence quenching is evident from the emission spectra, which were acquired simultaneously (Figure 2). Comparison of the Stern−Volmer plots of **PTh−BPh** and the molecular species **M−BPh** revealed a ca. 12-fold sensitivity enhancement for the polymer at low concentrations of pyridine.[13] The latter is tentatively attributed to extended conjugation through the polymer chain, leading to strong signal amplification at low analyte concentrations.[8]

A comparative binding study with different nucleophiles revealed that subtle steric and electronic effects[14] critically influence the binding to polymers **PTh−BAr** as well as the quenching of the luminescence. For instance, polymer **PTh−BPh** shows good selectivity for pyridine and 4-picoline, whereas the more strongly Lewis acidic polymer **PTh−BPf** also responds to the sterically hindered 2-picoline.

In summary, we have developed an efficient new method for the introduction of strongly Lewis acidic boron groups into the backbone of polythiophenes. The resulting linear organoboron polymers are highly soluble, form thin films from solution, and are strongly colored (Ar = Fc) or highly emissive (Ar = Ph, Pf). Their use as chemosensors is based on changes in the absorption and emission characteristics upon binding of nucleophiles to the highly Lewis acidic boron sites.

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Supporting Information Available: Additional experimental details for all polymers and model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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