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Organoborane Polymers

Universal Scaffold for Fluorescent Conjugated Organoborane Polymers**

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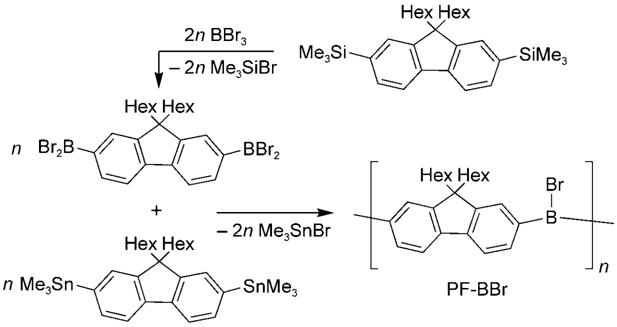
Conjugated organoboron polymers represent an attractive class of new materials with diverse potential applications, including as nonlinear optical materials, conduction and emission layers for organic light-emitting devices, and chemosensors for anions and toxic small molecules.[1] Typical methods for their synthesis are based on hydroboration polymerization techniques[2] and polycondensation reactions,[3,4] including the metal-catalyzed C−C bond formation of suitable preformed organoboron building blocks.[5,6]

An alternative highly modular approach is to prepare a universal reactive polymer scaffold that can easily be transformed into a range of other polymers with widely varying properties and applications through straightforward polymer modification procedures.[4,7,8] For instance, in the case of polyolefins the reactive poly(4-dibromoboryl styrene) is readily converted to 1) a range of polymeric Lewis acids with variable degree of Lewis acidity, 2) luminescent sensor materials with pendant anion binding sites, 3) solution-processable polymeric organoboron analogues of the well-known OLED device material tris(8-hydroxyquinolinato)-aluminum (Alq_3). Even new ligand frameworks for redox-active metallopolymers become available.[9,10] A universal fluorescent conjugated organoboron polymer scaffold would be very desirable owing to the interesting effects relating to the extended p_p–π^* conjugation[1] via the empty boron p orbital throughout the polymer main chain. Moreover, use of a single precursor polymer has the great advantage that the electronic and photophysical characteristics can more reliably be compared for polymer chains of equal length and distribution. We report herein the successful synthesis of such a novel polymer framework based on polyfluorene and demonstrate its utility as a universal scaffold for luminescent fluorene polymers that feature tricoordinate aryl borane and tetracoordinate organoboron quinolate functionalities.

The main challenge in the preparation of a reactive polymer $[ArB(X)]_n$ (Ar = arylene bridge, X = labile substituent) is the need to achieve excellent control over the condensation reaction such that the (disubstituted) linear polymer forms selectively, without conversion of the remaining labile halide substituent X on boron. We chose the poly(fluorenylborane) framework $[FlB(Br)]_n$ (Fl = 9,9-dialkyl fluorenyl) because of the high selectivity with which this reactive polymer scaffold can be prepared from simple precursor components and the high luminescence quantum efficiency typically associated with fluorene polymers.[11,12] In a first attempt, we treated the bifunctional organotin species $Fl(SnMe_3)_2$ with an equimolar amount of BBr_3. However, owing to the extremely high reactivity of BBr_3, the polymerization was difficult to control. Instead, we then decided to treat the preformed (and less reactive) aryl dibromoborane species $Fl(BBr_2)_2$ with the aryl ditin reagent $Fl(SnMe_3)_2$ in an organometallic polycondensation reaction (Scheme 1).[13] The polymerization was conducted at room temperature in CH_2Cl_2; after 4 h the volatile by-product Me_3SnBr was removed under high vacuum, and the crude product was characterized by NMR spectroscopy. The ^1H NMR spectrum showed the peak patterns that are expected for a linear polymer structure as well as an additional set of small peaks, which is likely due to fluorenyl end groups, in agreement with the MALDI-TOF mass spectrometry data discussed below. A broad signal at $\delta = 54$ ppm in the ^{11}B NMR spectrum is consistent with the incorporation of boron into the polymer backbone.



Scheme 1. Synthesis of the luminescent polymer scaffold PF-BBr.

From this universal polymer scaffold, the triaryl borane polymers PF-BM and PF-BT were readily obtained by reaction with the mild aryl transfer reagents 2,4,6-trimethylphenylcopper and 2,4,6-triisopropylphenylcopper, respectively (Scheme 2). The bulky aryl groups were chosen because of their ability to stabilize triaryl borane moieties through steric protection.[1] The polymers were purified by repeated precipitation from toluene into hexanes (PF-BM, 70%) or acetone (PF-BT, 80%) and isolated as light yellow solids. Their ^1H NMR spectra show peak patterns that reflect the

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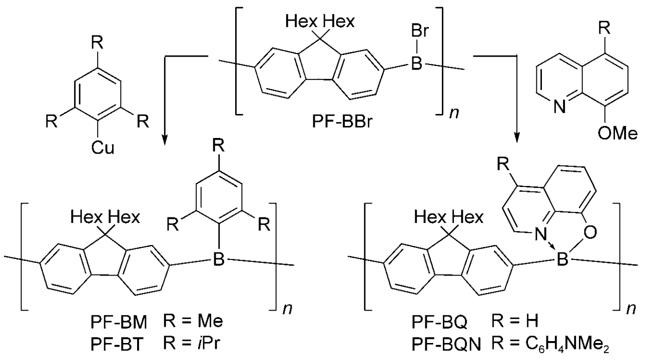

Scheme 2. Modular synthesis of fluorenylborane polymers.

replacement of the Br substituents with the aryl groups. The signals of all the protons on the fluorene rings are shifted upfield, and distinct signals for the aromatic protons on the pendant aryl groups are observed at $\delta = 6.91$ ppm for PF-BM and $\delta = 7.03$ ppm for PF-BT. Their integration is consistent with attachment of one aryl group to each fluorenylborane moiety. In the ^{11}B NMR spectrum, a single broad resonance emerged (PF-BM $\delta = 59$ ppm, PF-BT $\delta = 57$ ppm), which is slightly downfield from that of PF-BBr and in the typical region for tricoordinate aryl boranes.

Addition of 8-methoxyquinoline or 4-(8-methoxyquinolin-5-yl)-*N*,*N*-dimethylaniline to a solution of PF-BBr in CH_2Cl_2 at room temperature led to a rapid color change to bright yellow and orange-red, respectively. The polymers PF-BQ (72 %) and PF-BQN (63 %) were obtained as powdery solids by re-precipitation (Scheme 2). Compared to the precursor PF-BBr, narrower upfield-shifted signals are observed in the ^{11}B NMR spectrum at $\delta = 10.3$ ppm for PF-BQ and $\delta = 9.3$ ppm for PF-BQN, consistent with tetracoordination of boron with the quinolato ligands.

All polymers are readily soluble in common organic solvents (CH_2Cl_2, THF, toluene, etc.). Gel permeation chromatography (GPC) in THF gave number-average molecular weights in the range of 7900–10 800 g mol^{-1} with polydispersity indexes (PDIs) of 1.5–1.8, corresponding to an average degree of polymerization of $DP_n = 16–19$ for each of the four polymers. The structures of PF-BQ and PF-BQN were further confirmed by MALDI-TOF mass spectrometry, which showed two main series.[14] By comparison of the isotope patterns with calculated peak patterns, we can assign these series to polymer chains with fluorene or quinolato end groups, that is, H-[FlBQ]$_n$ and QB-[FlBQ]$_n$ (Q = 8-hydroxyquinolato).[15]

The polymers are highly stable with no significant decomposition upon exposure to air for several weeks, with the exception of PF-BM, which slowly degrades, indicating that a triisopropylphenyl group is required for optimal steric protection of the tricoordinate boron center. The onset of thermal degradation of PF-BM is observed at 212 °C and that of PF-BT at 237 °C. The thermal stability is further enhanced for the tetracoordinate boron polymers with $T_{dec} = 282$ °C for PF-BQ and $T_{dec} = 357$ °C for PF-BQN. The glass-transition temperatures T_g (onset) of 119 °C for PF-BM, 130 °C for PF-BQ, and 153 °C for PF-BQN are higher than that reported for poly(9,9-dihexylfluorene) but similar to N-bridged polyfluorenes.[16]

The absorption spectra of PF-BM and PF-BT in CH_2Cl_2 show bands with vibronic fine structure and maxima at approximately 390 nm that are red-shifted by approximately 20 nm in comparison with the related molecular species 2,7-bis(dimesitylboryl)-9,9-diethylfluorene[17] (371 nm) and by more than 80 nm relative to parent dihexylfluorene. The well-structured nature of these bands contrasts the typically broad and featureless absorptions of polyfluorenes;[12] they are attributed to π–π* transitions with a strong component of π–n_B* charge transfer. The latter is consistent with DFT calculations reported by Fang and co-workers on 2,7-bis(dimesitylboryl)-9,9-diethylfluorene.[17] Both polymers are highly emissive in the blue-violet region (PF-BM $\Phi = 84$ %, PF-BT $\Phi = 81$ % in CH_2Cl_2; Figure 1), and the bands almost perfectly mirror the absorptions with very small Stokes shifts, indicative of a highly rigid structure.[12]

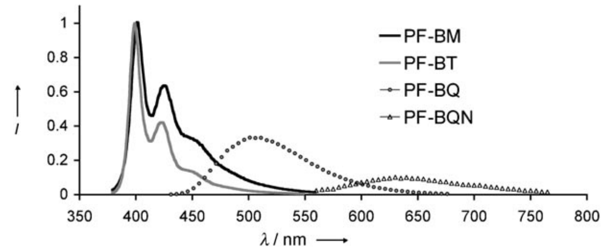

Figure 1. Comparison of polymer emission spectra, excited at absorption maxima.

The photophysical properties of PF-BQ and PF-BQN are very different from those of PF-BM and PF-BT. Comparatively weaker long-wavelength absorptions are found at 394 (PF-BQ) and 444 nm (PF-BQN); they are assigned to the quinolato ligands. PF-BQ emits green light with moderate quantum yield ($\Phi = 21$ %), while a weak emission in the red ($\Phi = 0.1$ %) was observed for PF-BQN (Figure 1). These findings are consistent with the results for styrene polymers that contain these boron quinolate moieties as pendant groups.[10] We therefore conclude that conjugation through the tetracoordinate boron centers is poor. However, the polymer main chain acts as an “antenna” for the quinolato chromophore, as in the case of other main-chain-type organoboron quinolate polymers.[6]

The electronic structure of the polymers was further studied by cyclic voltammetry in THF. An irreversible reduction peak was found for PF-BQ with $E_{pc} = -2.10$ V.[14] In contrast, PF-BT showed two quasi-reversible reduction waves at −2.13 and approximately −2.7 V versus ferrocene/ferrocenium. Interestingly, the first reduction corresponds to a lowest unoccupied molecular orbital (LUMO) energy level of approximately 2.8 eV, which is about 0.6 eV lower than that of fluorene homopolymers.[12] The observed enhanced electron affinity is highly desirable for applications in electronic device materials.[8,18]

Furthermore, the tricoordinate borane polymers reported herein are promising for use as chemosensor materials for anions. Of particular interest is the detection of fluoride and cyanide ions in the context of chemical warfare agent detection.[19,20] Binding studies with PF-BT indicate that both fluoride and cyanide, but not other (larger) anions such as chloride or bromide, effectively bind to PF-BT, leading to distinct changes in the absorption and emission spectra.[14] Based on the spectral titration plots for fluoride and cyanide binding to PF-BT in THF, a two-step binding process is evident. Figure 2 illustrates results for cyanide binding, and similar observations were made for the binding of fluoride.

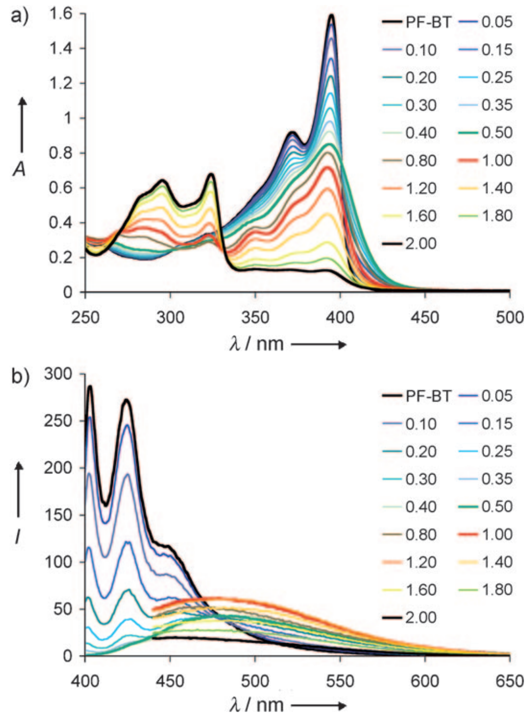

Figure 2. Spectral titration of PF-BT (2.75×10^{-5} M for boron sites in THF) with $[Bu_4N]CN$ (8.56×10^{-4} M in THF, added equivalents given relative to borane repeat units). a) Absorption spectra and b) emission spectra ($\lambda_{exc}=395$ nm).

Initial binding (up to ca. 0.5 equiv CN^-) is believed to occur at alternating boron sites. In this regime, the intensity of the longest-wavelength absorption at 395 nm strongly decreases, while the features at about 270–330 nm do not change significantly. At higher ratios of CN^- to borane, new bands develop at 295 and 323 nm, while the 395 nm absorption continues to decrease in intensity. We attribute this behavior to coordination of CN^- ions to the remaining borane sites. An interesting aspect that supports this interpretation is that the emission maxima at 403 and 425 nm initially decrease in intensity and a broad red-shifted band develops at 475 nm, which likely results from the charge-transfer structure with alternating electron-rich borate and electron-deficient borane moieties in the polymer main chain (Figure 2). In fact, this finding is consistent with a report by Müllen and co-workers that binding of one fluoride ion to a diborylated pentaphenylene ladder molecule leads to a monocomplexed species with a strongly red-shifted emission.[20] To our knowledge, this is the first observation of such a phenomenon for a polymeric system.

In conclusion, a novel poly(fluorenylborane) scaffold has been successfully developed. The preparation of a diverse range of luminescent polymers from a single precursor, including highly emissive blue, green, and red-emitting derivatives, demonstrates the broad applicability and promise in the quest for new optoelectronic materials. The suitability of PF-BT as a sensor material for anion detection has also been demonstrated. Detailed studies in this regard and efforts at further expanding the utility of PF-BBr as a universal precursor to conjugated organoboron polymers, including the development of water-soluble systems, are in progress.

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[14] See the Supporting Information for additional plots and experimental details.

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