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ARTICLE

Redox-Active Ferrocenylboronium Polyelectrolytes with Main Chain Charge-Transfer Structure

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ABSTRACT: A cationic poly(ferrocenylboronium) derivative was prepared by postpolymerization modification reaction of poly(ferrocenylbromoborane) (**P1**) with 4,4′-dinonyl-2,2′-bipyridyl (^{R}bipy). The polymer was found to show good stability under ambient conditions and was well soluble in polar organic solvents. Dialysis in MeOH allowed for isolation of a high molecular weight fraction that was further examined. The number-average of repeat units was estimated by GPC analysis relative to PS standards to be n =17, and MALDI−TOF analysis confirmed the chemical structure of the polymer repeat units. A characteristic purple color was observed in solution, which is due to charge-transfer from the electron-rich ferrocenyl to the electron-deficient bipyridylboronium moieties along the polymer main chain.

Introduction

Ferrocene-containing polymers have been studied extensively as new materials with interesting optical, electronic, electrochemical, and magnetic properties.[1] Electronic interactions between the individual ferrocene moieties in the polymer main chain are of particular interest as they affect the ability of these materials to act as molecular wires.[2] The electronic structure of the bridge between the ferrocenyl groups is therefore of critical importance. A promising approach to promote electronic interactions is the use of electron-deficient tricoordinate organoborane bridges, in which the empty p-orbital on boron may interact with the π-systems of the ferrocene moieties.[3−5] In this respect, we have recently developed a new method for the preparation of poly(ferrocenylboranes) that takes advantage of the spontaneous polycondensation of in situ generated 1,1′-fc(BBrH)$_2$ (fc = multiply-substituted ferrocene vs Fc = mono-substituted ferrocene) with ultimate formation of B_2H_6 as a by product (Scheme 1).[6−8] The resulting polymer [1,1′-fc(BBr)]$_n$ (**A**, X = Br; Scheme 1) serves as a versatile precursor for the preparation of a variety of ferrocenylborane polymers by facile nucleophilic replacement of Br with other groups.[6,7] The related hydroborane polymer [1,1′-fc(BH)]$_n$ (**A**, X = H) is obtained through a similar mechanism and lends itself to further derivatization via hydroboration chemistries.[9]

Organoboronium-functionalized polymers such as **B** (Scheme 1), on the other hand, represent a promising new class of polyelectrolytes, in which more commonly used ammonium functionalities are replaced by isoelectronic boronium groups.[10] Related amphiphilic block copolymers, which self-assemble into well-defined micellar structures in solution have also been reported.[11] Formation of the bipyridylboronium heterocycle is easily achieved in a “click-like” reaction of diorganohaloboranes with 2,2′-bipyridyl (bipy) or its derivatives, a reaction that occurs at room temperature without the need for any catalyst.[12] Replacement of the halide on boron with chelating amines leads to formation of exceptionally stable boron−nitrogen heterocycles, in which boron is tetracoordinate, and an overall 1+ charge is balanced by the halide counterion.[13] Moreover, combination of these electron-deficient bipyridylboronium heterocycles with electron-rich ferrocenyl groups in one molecule leads to charge-transfer complexes with interesting optical and electronic properties.[3,14]

In here, we describe the preparation of a new type of ionic, redox-active ferrocenylborane polymer (**C**, Scheme 1), in which tetracoordinate boronium moieties act as the bridging groups between the ferrocenes. While in the absence of an empty p-orbital on boron strong electronic coupling of the ferrocenes as previously observed for polymers **A** with X = mesityl[7] is not expected, polyferrocenes **C** should display an interesting charge-transfer structure due to the presence of ferrocene as an electron donor and the bipyridylboronium moiety as an acceptor alternating in the polymer main chain.

Experimental Section

Materials and General Methods. Poly(ferrocenylbromoborane) (**P1**; corresponding to **A** with X = Br)[7] and diferrocenylbromoborane (**D1**)[3] were prepared according to literature procedures. All reactions involving tricoordinate bromoborane species were carried out under an inert atmosphere using Schlenk techniques or a glovebox. Solvents were freshly distilled under argon from Na/benzophenone (toluene), Na/Pb alloy (hexanes) or CaH_2 (CH_2Cl_2) prior to use.

Instrumentation. ^{1}H, ^{13}C, and ^{11}B NMR spectra were obtained on a Bruker AMX 250, AMX 400, or a Varian INOVA 500 spectrometer. Solution ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. 160.4 MHz ^{11}B NMR spectra were recorded on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA); they were acquired with boron-free quartz NMR tubes and referenced externally to $BF_3 \cdot Et_2O$ ($\delta = 0$). All NMR spectra were recorded at ambient temperature.

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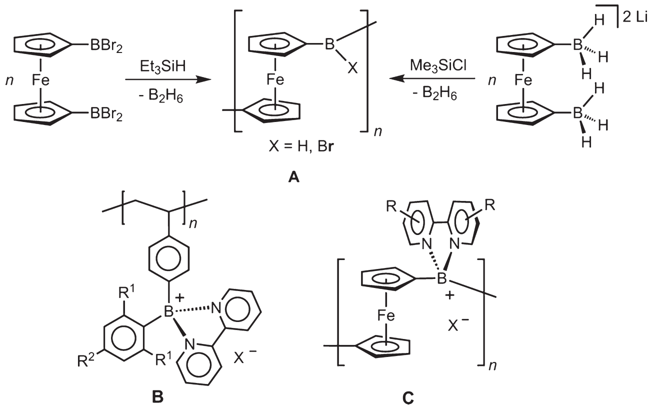
Scheme 1



UV−visible measurements were performed in CH_2Cl_2 using a Perkin-Elmer Lambda 16 UV/vis spectrometer with a 1 cm quartz cuvette. Cyclic voltammetry was carried out on an EG&G Princeton Applied Research 263A potentiostat. The three-electrode system consisted of a Pt wire as working electrode, a Pt wire as secondary electrode, and an Ag wire as the pseudo-reference electrode. The voltammograms were recorded on ca. 10^{-3} to 10^{-4} M solutions in CH_2Cl_2 containing $[Bu_4N]PF_6$ (0.1 M) or $[Bu_4N][B(C_6F_5)_4]$ (0.1 M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of decamethylferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple (for decamethylferrocene vs ferrocene: −548 mV in CH_2Cl_2 containing $[Bu_4N]PF_6$ (0.1 M) and −614 mV in CH_2Cl_2 containing $[Bu_4N][B(C_6F_5)_4]$ (0.1 M)). Elemental analyses were carried out by the microanalytical laboratory at the University of Frankfurt.

Gel permeation chromatography (GPC) analyses were performed in DMF/20 mM $[NH_4]PF_6$ (0.5 mL/min) using a Waters Breeze system equipped with a 717 plus auto sampler, a 1525 binary HPLC pump, a 2414 refractive index detector, and a 2487 dual λ absorbance detector (measurement at $\lambda = 339$ nm). A series of Shodex Asahipak columns (GF-510 HQ, GF-310 HQ), which were kept in a column heater at 60 °C, were used for separation. The columns were calibrated with PS standards (Polymer Laboratories). MALDI−TOF measurements were performed on an Applied Biosystems 4800 Proteomics Analyzer in (+)-ion reflector mode with delayed extraction. Benzo[a]pyrene was used as the matrix. Samples were prepared in methanol (10 mg/mL), mixed with the matrix in a 1:10 ratio, and then spotted on the wells of a sample plate inside a glovebox. Peptides were used for calibration.

Synthesis of Polymer P2-Br. At −78 °C, a solution of 4,4′-dinonyl-2,2′-bipyridyl (1.788 g, 4.374 mmol) in CH_2Cl_2 was added dropwise to a suspension of polymer **P1** (1.092 g, 3.975 mmol repeat units) in CH_2Cl_2 (10 mL) under stirring. The reaction mixture was allowed to come to room temperature and kept stirring overnight. The resulting mixture was filtered, and the solvent was removed from the filtrate under high vacuum. The residue was extracted with toluene (10 mL) to remove any excess of 4,4′-dinonyl-2,2′-bipyridyl. The solid was then redissolved in CH_2Cl_2 (2 mL) and precipitated by addition of hexanes (20 mL). The product was obtained as a gray-purple powdery solid, which was dried at room temperature under high vacuum. Yield: 2.179 g (80%).

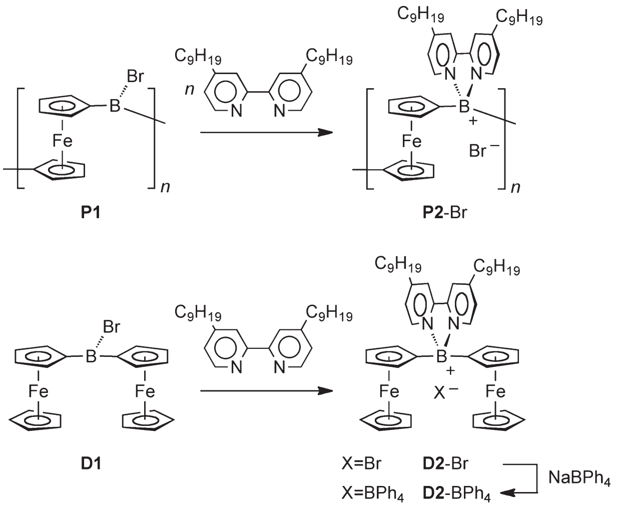
Further Purification and Isolation of a High Molecular Weight Fraction of $[1,1'\text{-fc}(B(^{R}bipy))]_nBr_n$ (P2-Br). Polymer **P2**-Br (185 mg) was dissolved in 15 mL of methanol to give a purple-colored solution. This solution was transferred into a dialysis tube (Fisherbrand regenerated cellulose membrane with 6000 to 8000 Da molecular weight cutoff), which had been washed thoroughly with deionized water prior to use. The tubing was then closed and placed in a beaker containing 500 mL of methanol. Upon slow stirring, the MeOH solution outside the tubing gradually took on the purple color. After 2 days, the solution was collected, exchanged with fresh methanol, and dialysis was continued for one additional day. The solution inside the dialysis tubing was transferred to a new dialysis tube, and the procedure was repeated once again. The solvent was then evaporated separately from the different dialysates and the remaining solution in the tube, respectively, yielding the products as brown solids with a purple tint. The isolated yield of the purified polymer left behind inside the dialysis tubing was ca. 20 mg. **For P2-Br:** ^1H NMR (499.9 MHz, DMSO-d_6) $\delta = 9.20$, 9.11, 8.24 (br, bipy), 3.61, 3.10 (br, Cp), 3.00, 1.74, 1.27, 1.14, 0.77 (br, nonyl). ^{13}C NMR (125.7 MHz, methanol-d_4) $\delta =$ 164.3, 146.4, 145.0, 130.0, 124.0 (bipy), 83.8 (Cp_{ipso}), 71.4 (2 × Cp), 37.2, 33.2, 31.5, 30.8, 30.7, 30.5 (2 × intensity), 23.9, 14.7 (nonyl). ^{11}B NMR (160.4 MHz, methanol-d_4) $\delta = 4.2$ ($w_{1/2} =$ 1360 Hz). UV−vis (CH_2Cl_2): $\lambda_{max} = 532$ nm ($\varepsilon = 570\ M^{-1}cm^{-1}$ for each repeat unit), $\Delta\nu = 6280\ cm^{-1}$, $\sigma = 0.016$. GPC−RI (DMF/20 mM $[NH_4]PF_6$, 60 °C): $M_n = 10.6 \times 10^3$, $M_w = 14.1 \times 10^3$, PDI = 1.32; GPC−UV (DMF/20 mM $[NH_4]PF_6$, 60 °C): $M_n = 10.1 \times 10^3$, $M_w = 14.1 \times 10^3$, PDI = 1.39.

Synthesis of $[Fc_2B(^{R}bipy)]Br$ (D2-Br). A solution of 4,4′-dinonyl-2,2′-bipyridyl (0.710 g, 1.737 mmol) in toluene (10 mL) was added dropwise to a solution of Fc_2BBr (**D1**) (0.727 g, 1.579 mmol) in toluene at −78 °C under stirring. The reaction mixture was allowed to come to room temperature, toluene (10 mL) was added, and the mixture was kept stirring overnight. The resulting suspension was filtered, and the solid was extracted with toluene (20 mL). The combined toluene-soluble fractions were concentrated to ca. 2 mL. The product was precipitated by addition of hexanes (20 mL) and washed with hexanes (10 mL). The product was obtained as a dark purple powdery solid, which was dried at room temperature under high vacuum. Yield: 0.894 g (65%). ^1H NMR (250.1 MHz, DMSO-d_6) $\delta = 9.30$ (d, $J = 5.9$ Hz, 2H, bipy), 9.09 (s, 2H, bipy), 8.18 (d, $J = 5.9$ Hz, 2H, bipy), 4.23, 4.08 (br, 2 × 4H, Cp), 3.62 (s, 10H, Cp), 3.05 (t, $J = 7.0$ Hz, 4H, nonyl-CH_2), 1.82, 1.33, 1.21, 0.82 (m, 34H, nonyl). ^1H NMR (250.1 MHz, methanol-d_4) $\delta = 9.18$ (d, $J = 6.0$ Hz, 2H, bipy), 8.91 (s, 2H, bipy), 8.09 (d, $J = 6.0$ Hz, 2H, bipy), 4.26, 4.03 (br, 2 × 4H, Cp), 3.62 (s, 10H, Cp), 3.10 (t, $J = 7.5$ Hz, 4H, nonyl-CH_2), 1.89, 1.40, 1.25, 0.85 (m, 34H, nonyl). ^{13}C NMR (62.9 MHz, methanol-d_4) $\delta = 164.3$, 146.7, 144.8, 129.5, 123.7 (bipy), 71.7, 70.9, 69.2 (Cp), 37.0, 33.0, 31.2, 30.6, 30.5, 30.4, 30.3, 23.7, 14.5 (nonyl), not observed (Cp_{ipso}). ^{11}B NMR (128.4 MHz, $CDCl_3$) $\delta = 6.6$ ($w_{1/2} = 510$ Hz). **Conversion to $[Fc_2B(^{R}bipy)][BPh_4]$ (D2-BPh4).** A solution of **D2**-Br (0.150 g, 0.173 mmol) in ethanol (12 mL) was added dropwise to a solution of $NaBPh_4$ (0.296 g, 0.865 mmol) in ethanol (10 mL). A purple precipitate formed, which was collected by filtration and washed first with ethanol (10 mL) and then with distilled water (30 mL). The solid was taken up in CH_2Cl_2 (10 mL), the resulting solution was dried over $MgSO_4$, and the solvent was then removed under high vacuum. Yield: 0.145 g (76%). Anal. Calcd for $C_{72}H_{82}N_2B_2Fe_2$ (1108.77): C, 78.00; H, 7.45; N, 2.53. Found: C, 77.49; H, 7.52; N, 2.64.

Results and Discussion

The generation of positive charges upon formation of boronium groups on each of the repeating units of a polymer results in formation of a polyelectrolyte that is soluble only in highly polar organic solvents. For the preparation of the targeted ferrocenylboronium polymers, we reasoned that the use of solubilizing alkyl groups attached to the bipy moiety would be beneficial, not only in terms of obtaining a well-soluble product that can easily be analyzed, but also to facilitate quantitative substitution, which can be difficult to achieve if precipitation of the product occurs from the moderately polar, aprotic solvents typically employed (toluene, CH_2Cl_2). Hence, we decided to utilize 4,4′-dinonyl-2,2′-bipyridyl (^{R}bipy) with its long alkyl side

Scheme 2. Synthesis of Polymer P2-Br and Diferrocene Model Systems D2-Br and D2-BPh$_4$



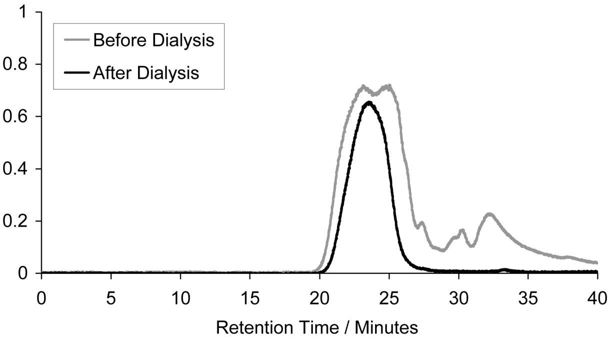


Figure 1. GPC−UV traces of [1,1′-fc(B(^{R}bipy))]$_n$Br$_n$ (**P2**-Br) before and after purification by dialysis (DMF, 20 mM [NH$_4$]PF$_6$, 60 °C).

chains for the preparation of bipyridylboronium-functionalized redox-active ferrocene polymers. Addition of ^{R}bipy to a suspension of poly(ferrocenylbromoborane) (**P1**) in CH$_2$Cl$_2$ led to an immediate color change from red to dark purple, which is characteristic[14] for the formation of ferrocenylboronium-type charge-transfer complexes (Scheme 2). After 12 h, the soluble fraction was isolated by filtration, evaporated to dryness under high vacuum, and any excess of ^{R}bipy was then removed by extraction with toluene. The product (**P2**-Br) was obtained as a greyish-purple powdery solid after precipitation by addition of hexanes to a solution in CH$_2$Cl$_2$. Using similar synthetic procedures, we also prepared a dimeric model system (**D2**-Br) that features two ferrocenyl groups connected by a dinonylbipyridylboronium moiety and as such represents a fragment of the anticipated polymer chain in **P2**-Br. Compound **D2**-Br was further converted to the tetraphenylborate salt (**D2**-BPh$_4$), because the latter was found to display better reversibility in the cyclic voltammetry measurements.

The crude product **P2**-Br was studied by GPC using DMF with 20 mM [NH$_4$]PF$_6$ as the eluent at 60 °C. The GPC−UV trace showed a bimodal molecular weight distribution with $M_{\mathrm{n}} = 5.5 \times 10^3$, $M_{\mathrm{w}} = 17.4 \times 10^3$, and a polydispersity index (PDI) of $M_{\mathrm{w}}/M_{\mathrm{n}} = 3.2$ (Figure 1). To further purify the polymeric material and to isolate a high molecular weight fraction we subjected **P2**-Br to dialysis in MeOH using tubing with a 6000−8000 Da molecular weight cutoff. The progress of the dialysis could be easily monitored, as the MeOH solution on the outside of the tube gradually took on the characteristic purple color of the polymer solution of **P2**-Br. The procedure was repeated once again by transferring the solution that remained inside the tube into a new piece of dialysis tubing. The solvent was finally evaporated from the solution that remained inside the dialysis tube, yielding the purified product as a brownish solid with a purple tint. Most importantly, after dialysis the GPC−UV plot of **P2**-Br showed a monomodal size distribution with $M_{\mathrm{n}} = 10.1 \times 10^3$, $M_{\mathrm{w}} = 14.1 \times 10^3$ and a considerably lower polydispersity of PDI = 1.39 (Figure 1). This corresponds to a number-average degree of polymerization of $DP_n = 17$. The absence of any UV intensity at higher retention times suggests that the small oligomeric components were successfully removed by dialysis and that the purified sample consists primarily of relatively high molecular weight material. This is consistent with the GPC results for the dialysates, which show the presence of low molecular weight oligomers that have passed through the tubing (see Figure S2).

The purified sample was further studied by multinuclear NMR spectroscopy, high-resolution MALDI−TOF mass spectrometry, UV−visible spectroscopy and cyclic voltammetry. A single resonance is observed in the ^{11}B NMR spectrum at $\delta = 4.2$ (Figure 2a), which is in the expected region for ferrocenyl(bipyridyl)boronium moieties and only slightly shifted relative to that of **D2**-Br ($\delta = 6.6$). The ^{1}H NMR spectrum in DMSO-d_6 shows one set of broadened peaks as expected for a well-defined polymer, further confirming the successful removal of oligomeric species and other impurities (Figure S1). The main peaks in the aromatic region at $\delta = 9.20, 9.11, 8.24$ are readily assigned to the ^{R}bipy moieties and their shifts are consistent with those of the respective molecular species. In the Cp region two broad signals are observed at $\delta = 3.61, 3.10$, which is upfield in comparison to the chemical shifts of the diferrocene model compound [Fc$_2$B(^{R}bipy)]Br (**D2**-Br, $\delta = 4.23, 4.08$; Fc = ferrocenyl). However, the observed shifts correlate quite well with data for the internal 1,1′-ferrocenediyl (fc) moiety in the trimeric species [Fc−B(bipy)−fc−B(bipy)−Fc](PF$_6$)$_2$ ($\delta = 3.62, 3.57$ in CD$_3$CN),[3] further supporting the polymeric nature of **P2**-Br. The ^{13}C NMR data are also consistent with the structure of the polymer; most notably, a broad signal at $\delta = 83.8$ ppm can be assigned to the boron-bound *ipso*-Cp carbon atoms and a large resonance at $\delta = 71.4$ ppm corresponds to all other Cp carbon atoms (Figure 2b). All signals correlate well with those of compound **D2**-Br (Figure 2c). It should be noted that some smaller peaks are still observed in the Cp region of the ^{1}H NMR spectrum and as shoulders to the main peaks in the ^{13}C NMR spectrum. They are tentatively attributed to polymer end groups, which are expected to be observable for an average degree of polymerization of $DP_n = 17$.

To gain further insight into the structure of the polymer, we studied the purified sample by high resolution MALDI−TOF mass spectrometry in positive-ion reflector mode. The spectrum shown in Figure 3 clearly reveals the presence of two series of peaks. The difference between peaks of 603.4 mass units in each series corresponds to the expected repeating unit of {C$_{38}$H$_{52}$B$_1$Fe$_1$N$_2$} for **P2**-Br. Notably, this repeating unit does not include the bromide counterion and the individual peak patterns are consistent with the presence of singly charged species. This suggests that for the observed species all but one of the cationic bipyridylboronium moieties are reduced to the corresponding radical under the laser desorption/ionization conditions. In light of these observations, it is very likely that the relatively low molecular weight ions observed correspond to fragments of larger polymer chains.[15]

We examined several peaks for each series more closely and compared them with calculated peak patterns assuming a 10000:1 resolving power. We find that one of the series with peak maxima of 1022.73, 1626.17, 2229.61, 2832.07, 3434.55, and 4039.03 fits reasonably well to a series of polymer fragments of the formula (^{R}bipy)B-[1,1′-fcB(^{R}bipy)]$_n^{+}$ (n = 1−6), suggesting the presence

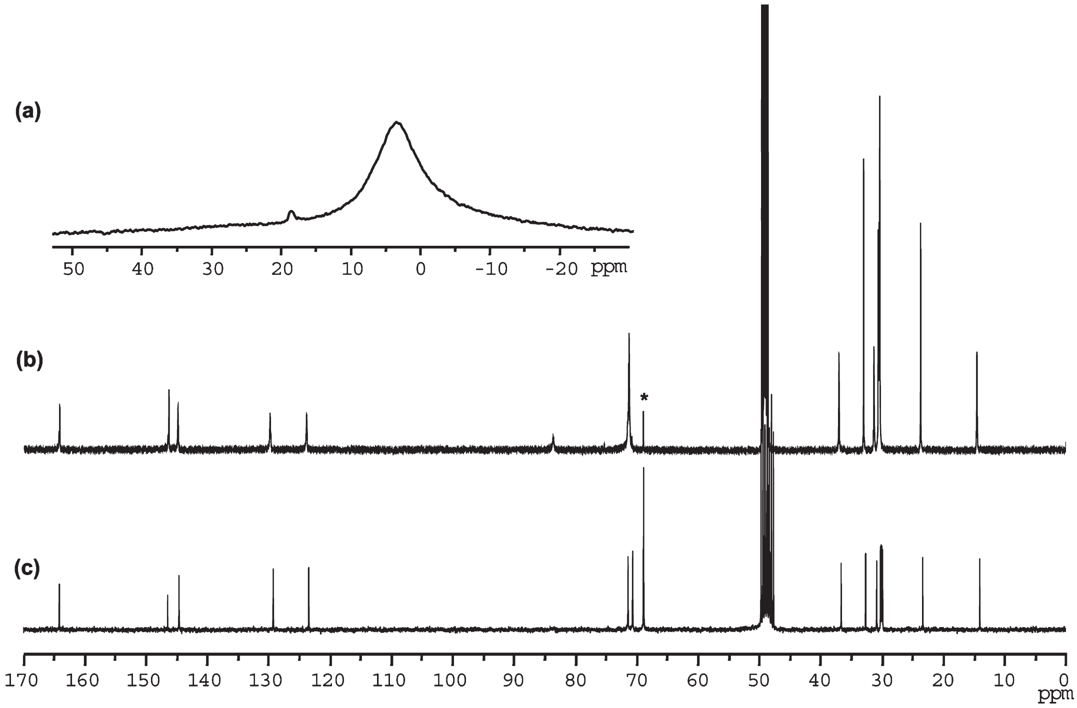


Figure 2. (a) ^{11}B NMR spectrum of the dialyzed polymer $[1,1'\text{-fc}(B(^{R}\text{bipy}))]_nBr_n$ (**P2**-Br) in methanol-d_4 and comparison of the ^{13}C NMR spectrum of **P2**-Br (b) with that of the model compound **D2**-Br (c) in methanol-d_4. The signal that is indicated with an asterisk corresponds to an unsubstituted Cp ring at the polymer chain end or to a trace of ferrocene.

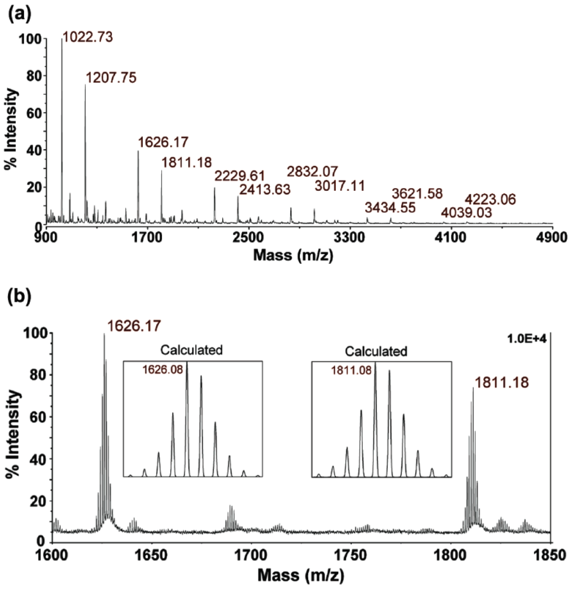


Figure 3. (a) MALDI−TOF mass spectrum of the dialyzed polymer $[1,1'\text{-fc}(B(^{R}\text{bipy}))]_nBr_n$ (**P2**-Br) acquired in (+)-ion reflector mode. (b) Comparison of the observed and calculated peak patterns for $(^{R}\text{bipy})B\text{-}[1,1'\text{-fcB}(^{R}\text{bipy})]_n^+$ ($n = 2$, 1626 Da) and $H\text{-}[1,1'\text{-fcB}(^{R}\text{bipy})]_n^+$ ($n = 3$, 1811 Da).

of $-B(^{R}\text{bipy})$ moieties at both chain ends. The second series with peak maxima at 603.34 (not shown), 1207.75, 1811.18, 2413.63, 3017.11, 3621.58, and 4223.06 closely matches the peak positions expected for polymer fragments containing only one $(^{R}\text{bipy})B$ end group, $H\text{-}[1,1'\text{-fcB}(^{R}\text{bipy})]_n^+$ ($n = 1-7$).

Next, we studied the redox properties of polymer **P2**-Br and compared them with those of diferrocene **D2**-BPh_4 (Figure 4). For **D2**-BPh_4, three reversible redox waves are found in $CH_2Cl_2/[Bu_4N]PF_6$ as the supporting electrolyte. The redox wave at −1470 mV vs FcH/FcH$^+$ can be assigned to reduction of the bipyridylboronium fragment, which is slightly harder to reduce than boronium salts[3] derived from the parent bipy ligand. Only one reversible reduction process is resolved in CH_2Cl_2, while more polar solvents such as CH_3CN or DMF typically reveal a second reduction process at more cathodic potentials. The redox events at −20 and +140 mV on the other hand are assigned to successive oxidation of the two boron-bridged ferrocene moieties. From these data it is clear that the attachment of $B(^{R}\text{bipy})^+$ as a pendant group does not very strongly affect the redox potential of the ferrocene moieties. Moreover, the redox splitting of $\Delta E = 160$ mV between the first and second oxidation is modest and most likely the result of Coulombic effects only. The results for polymer **P2**-Br are similar, although the oxidation waves are not as well resolved.[15] Again, the redox splitting of ca. $\Delta E = 250$ mV is relatively small and comparable to that of 230 mV found between the terminal and internal ferrocenes in $[Fc{-}B(\text{bipy}){-}fc{-}B(\text{bipy}){-}Fc](PF_6)_2$.[3] On the basis of the observation of two redox waves, we conclude that Coulombic interactions disfavor

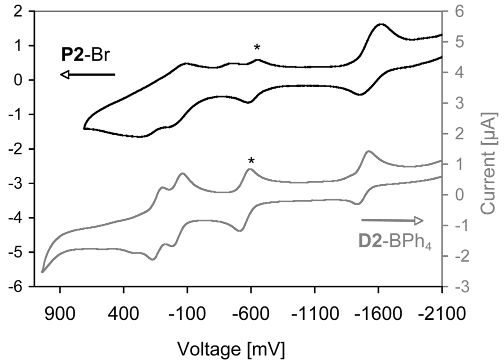
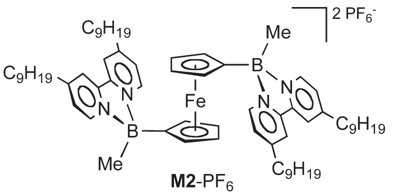


Figure 4. Cyclic voltammograms of **P2**-Br (ca. 1×10^{-3} M with 0.1 M $[Bu_4N][B(C_6F_5)_4]$ in CH_2Cl_2 as the supporting electrolyte; scan rate $\nu = 200$ mV/s) and **D2**-BPh_4 (ca. 1×10^{-3} M with 0.1 M $[Bu_4N]PF_6$ in CH_2Cl_2 as the supporting electrolyte; scan rate $\nu = 150$ mV/s). The asterisk denotes decamethylferrocene used as a reference.

Chart 1



M2-PF_6

Table 1. Comparison of UV−Visible and Cyclic Voltammetry Data

	P2-Br	**D2**-BPh_4	**M2**-PF_6
λ_{max} (nm)[a]	532	499	516
ε_{max} (M^{-1} cm^{-1})[a]	570	790	840
$\Delta\nu$ (cm^{-1})	6280	7070	5900
$E^{0\prime}(1)$ (mV)	ca. +230[b]	+140[c]	d
$E^{0\prime}(2)$ (mV)	−20[b]	−20[c]	d
$\Delta E(2-1)$ (mV)	ca. 250[b]	160[c]	d
$E^{0\prime}(3)$ (mV)	−1540[b]	−1470[c]	d

[a] Data were acquired in CH_2Cl_2 at room temperature; molar absorptivities are reported per ferrocene unit. [b] In CH_2Cl_2/0.1 M $[Bu_4N][B(C_6F_5)_4]$. [c] In CH_2Cl_2/0.1 M $[Bu_4N]PF_6$. [d] Not determined.

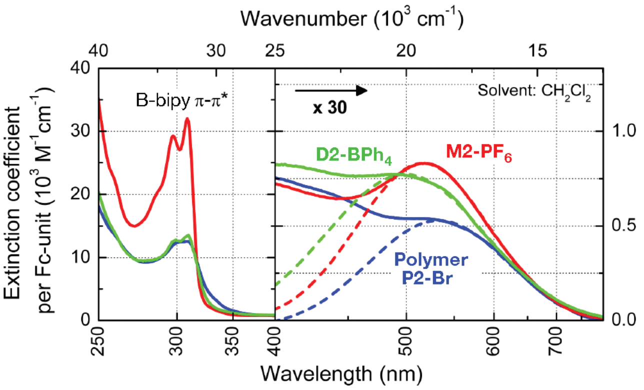


Figure 5. UV−visible absorption spectra of polymer **P2**-Br in comparison with those of the diferrocene species **D2**-BPh_4 and the monoferrocene **M2**-PF_6 in CH_2Cl_2.

oxidation of neighboring ferrocene moieties leading initially to a polymer in which alternating ferrocenes are oxidized, while the remaining ferrocenes are only oxidized at higher potential. This interpretation is consistent with detailed studies by Manners et al. on the redox behavior of silyl-bridged oligo- and polyferrocenylenes, which show redox splittings of similar magnitude in their cyclic voltammograms.[17] In comparison to polymer **A** (X = mesityl; ΔE = 705 mV)[7] with its tricoordinate organoborane moieties, the electronic interaction between adjacent ferrocene moieties in polymer **P2**-Br is much less pronounced, which is clearly an attribute to the fact that boron is in a tetracoordinate form.

A characteristic feature of ferrocenyl(bipyridyl)boronium cations is the observation of metal-to-ligand charge-transfer (MLCT) bands in the visible region, which are responsible for the observation of characteristic colors in solution and the solid state.[3,14] We acquired UV−visible absorption data for the ferrocenylboronium polymer **P2**-Br, the diferrocene species **D2**-BPh_4, and a related diborylated monoferrocene compound **M2**-PF_6[14g] (Chart 1, Table 1). A comparison of the spectra is provided in Figure 5. In all three cases, an MLCT band is clearly observed with a maximum around 500−530 nm. The fact that the MLCT absorptions of **M2**-PF_6 and **P2**-Br are found at slightly longer wavelength in comparison to that of **D2**-BPh_4 is consistent with previous findings on the series of non-alkylated bipy complexes $[FcB(bipy)Me]PF_6$, $[1,1'\text{-}fc(B(bipy)Me)_2](PF_6)_2$, and $[1,1',3,3'\text{-}fc\text{-}(B(bipy)Me)_4](PF_6)_4$, which revealed a continuous red shift of the MLCT band with increasing number of bipyridylboronium substituents attached to the ferrocene unit (λ_{max} in CH_3CN: 505, 514, 540 nm, respectively).[14b] We refrain from a more detailed interpretation of the UV−visible absorption data of **M2**-PF_6, **D2**-BPh_4, and **P2**-Br, because, for the following reasons,[14] we regard it as too speculative at this point: (i) The B(bipy)Me-fragment has a net positive inductive effect. With regard to the ferrocene redox potential/HOMO energy, this works against the positive charge associated with this substituent thereby rendering concrete predictions of the net result difficult. (ii) Ferrocenyl(bipyridyl)boronium cations generally show a pronounced solvatochromism and the position of the MLCT band is strongly dependent on counterion effects. (iii) The polarity of the microenvironment in the polymer coil is likely different from that experienced by the molecular species in solution.

In conclusion, we have successfully prepared the first boronium cation-bridged polyferrocene. Dialysis of this polyelectrolyte proved to be an effective method for purification and isolation of a high molecular weight polymer fraction. GPC and MALDI−TOF analysis confirmed the polymeric structure with an average of 17 repeat units based on GPC−UV detection relative to PS standards. Polymer **P2**-Br acts as a redox-active polyelectrolyte, which not only contains ferrocene moieties that undergo quasi-reversible oxidation at moderate potentials, but also features redox-active bipyridylboronium heterocycles which can be reversibly reduced. Charge-transfer between the electron-rich ferrocene and the electron-poor bipyridylboronium groups results in an intense purple color in solution, which is characteristic of this class of compounds.

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Supporting Information Available: Figures showing ^1H NMR comparison of the crude and purified sample of polymer **P2**-Br in DMSO-d_6 and additional GPC−UV traces for the dialysis of **P2**-Br. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) This conclusion is further supported by (a) the absence of a second organyl group at the terminal borons and (b) the observation of fragments in the low molecular weight region of the mass spectrum that can be assigned to cleavage products (e.g. [Cp-B-(^{R}bipy)]$^+$, [Cp-B(^{R}bipy)-Cp]$^+$, [Cp-B(^{R}bipy)-CpFe]$^+$ [Cp-B(^{R}bipy)-Fc]$^+$, [FeCp-B(^{R}bipy)-Fc]$^+$).

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