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Electronic Communication in a Novel Five-Step Redox System

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*Summary: The ansa-ferrocene complex [1,1′-fc(Bbipy)$_2$O](PF$_6$)$_2$ {[**5**](PF$_6$)$_2$; fc = (η^5-C$_5$H$_4$)$_2$Fe} has been synthesized and structurally characterized. Electronic communication between the two 2,2′-bipyridylboronium substituents was observed, suggesting the reduced forms [**5**]$^+$ and [**5**]$^-$ to be partially delocalized redox intermediates.*

Chemical systems containing electronically communicating redox-active termini have attracted recent attention due to their potential applications in the construction of electronic devices and electron storage media.[1−8] Our group has recently suggested a novel concept for the generation of charge transfer polymers[9−11] and highly efficient electron sponges[12] exploiting the spontaneous formation of boron−nitrogen and boron−oxygen bonds. Following this strategy, we have synthesized cations [**1**]$^+$−[**3**]$^{4+}$, in which up to four 2,2′-bipyridylboronium substituents, [B(Me)bipy]$^+$, are attached to a ferrocene core (Figure 1).[12]

Similar to the well-known Diquat, 2,2′-bipyridylboronium ions [**4**]$^+$ were found to be perfectly reversible two-step redox systems.[13] Consequently, [**1**]$^+$−[**3**]$^{4+}$ behave as highly redox-active species capable of storing three, five, and nine electrons, respectively. According to cyclic voltammetric measurements, however, there is only negligible electronic communication between the individual [B(Me)bipy]$^+$ fragments in [**2a**]$^{2+}$ (comproportionation constant K_{com} = 10).[12]

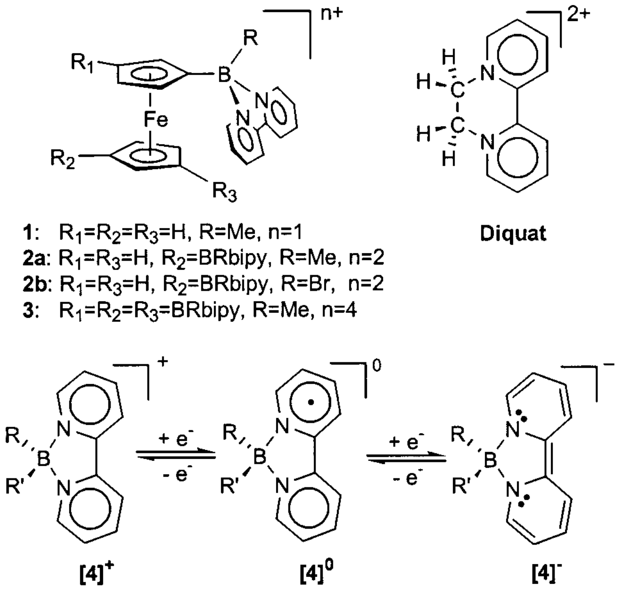

Figure 1.

Chalcogen atoms are known to be efficient transmitters of electronic and magnetic interactions. Thus, linking the 2,2′-bipyridylboronium substituents of **2** by an oxygen bridge might be helpful to attain the desired electronic communication. We report herein the facile synthesis, structural characterization, and electrochemical properties of the *ansa*-ferrocene [1,1′-fc(Bbipy)$_2$O](PF$_6$)$_2$, [**5**](PF$_6$)$_2$.

While [**2a**]Br$_2$ and [**3**]Br$_4$ can be dissolved in water without decomposition, [**2b**]Br$_2$ is rapidly hydrolyzed with liberation of ferrocene under similar conditions. However, the reaction of an acetonitrile solution of blue [**2b**]Br$_2$ with a trace amount of water in the presence of triethylamine gave [**5**]Br$_2$ in almost quantitative yield. In contrast to [**2b**]Br$_2$, [**5**]Br$_2$ is no longer sensitive to air and moisture and can be transformed into the corresponding PF$_6$ salt, [**5**](PF$_6$)$_2$, upon treatment of its aqueous solution with excess NH$_4$PF$_6$ (Scheme 1).[14]

The ^{11}B NMR spectrum of [**5**](PF$_6$)$_2$ shows a signal at δ = 9.1, which lies in a range typical of tetracoordinate

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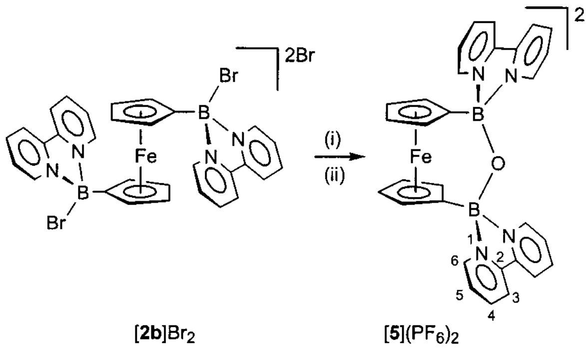
Scheme 1[a]



[a] (i) $+H_2O/NEt_3$ in CH_3CN; (ii) +exc. NH_4PF_6 in H_2O.

boron nuclei.[15] Both the ^{1}H and the ^{13}C NMR spectrum display one set of signals for the 2,2′-bipyridyl substituents, as well as for the ferrocenyl backbone, indicating a high symmetry of the molecule in solution.[15]

Single crystals were grown by gas phase diffusion of diethyl ether into an acetonitrile solution of [**5**]$(PF_6)_2$. X-ray crystallography confirmed the compound to possess the desired molecular framework (Figure 2).[16]

In contrast to the transoid configuration adopted by the unbridged [**2a**]$(PF_6)_2$,[12] the oxygen linker in [**5**]$(PF_6)_2$ forces the two 2,2′-bipyridylboronium substituents into close proximity (dihedral angle between the 2,2′-bipy planes: 73.5°). The cyclopentadienyl rings of the ferrocene backbone are only slightly tilted (dihedral angle: 7.8°), indicating, that the *ansa*-bridge does not cause any significant strain in the molecule. As a result of the rather long B(1)−O(1)−B(2) linker, the ferrocene moiety somewhat deviates from an eclipsed conformation, placing each of the cyclopentadienyl protons in its own unique chemical environment. The fact, that only two proton resonances are visible in the ferrocenyl region of the ^{1}H NMR spectrum is consistent with a mutual twisting of the cyclopentadienyl rings, giving rise to a higher average symmetry of $[\mathbf{5}]^{2+}$ in solution. This kind of bridge-reversal process is commonly observed in [3]-ferrocenophanes.[17]

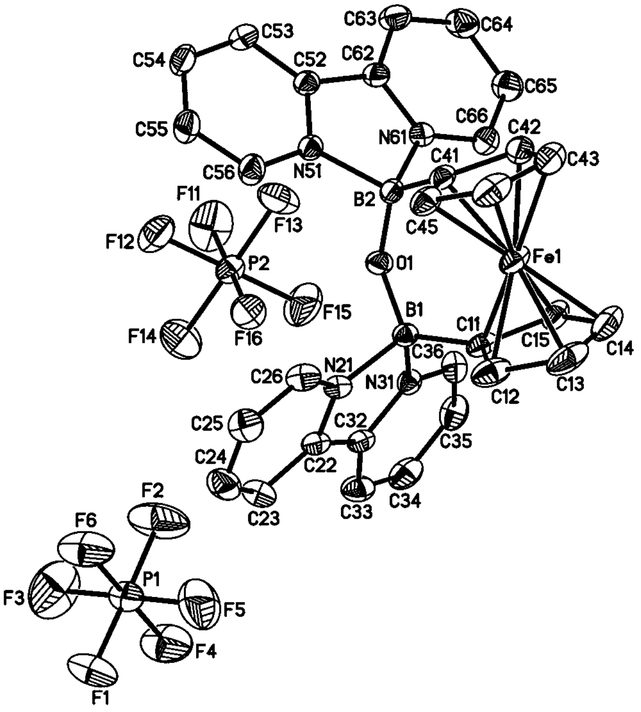


Figure 2. Structure of [**5**]$(PF_6)_2$ in the crystal. Selected bond lengths (Å) and angles (deg): B(1)−O(1) 1.398(3), B(2)−O(1) 1.389(3), B(1)−C(11) 1.591(3), B(1)−N(31) 1.621(3), B(1)−N(21) 1.625(3), B(2)−C(41) 1.596(3), B(2)−N(51) 1.627(3), B(2)−N(61) 1.627(3); B(1)−O(1)−B(2) 136.21(19), C(11)−B(1)−O(1) 119.55(19), C(41)−B(2)−O(1) 120.89(19), N(21)−B(1)−N(31) 93.62(15), N(51)−B(2)−N(61) 93.37(15).

It is noteworthy that the two 2,2′-bipyridylboronium cations form a bowl-shaped cavity, hosting one PF_6^- anion (distance between P(2) and O(1): 3.921 Å). This provides an important hint for a possible application of $[\mathbf{5}]^{2+}$ in the molecular recognition of anionic guests.

The cyclic voltammetric profile exhibited by $[\mathbf{5}]^{2+}$ in DMF solution[18] displays one oxidation and two doubly split reduction processes, all of them possessing features of chemical reversibility on the cyclic voltammetric time scale (Figure 3).

Controlled potential coulometric measurements (E_w = +1.0 V), followed by cyclic voltammetric tests, show the oxidation process ($E^{\circ\prime}$ = +0.57 V) to involve one electron per molecule and the electrogenerated trication $[\mathbf{5}]^{3+}$ to be quite stable. As a consequence of the one-electron removal, the original violet solution ($\lambda_{max} = 531$ nm) assumes the blue color ($\lambda_{max} = 628$ nm) typical of ferrocenium species. Coulometry also reveals the overall consumption of two electrons per molecule in the first split reduction wave ($E_w = -1.3$ V), suggesting the electron addition to take place in two sequential one-electron processes ($E^{\circ\prime} = -0.80$ and -0.93 V). Step-by-step cyclic voltammetric inspection proves the electrogenerated green monocation $[\mathbf{5}]^{+}$ and the neutral congener $[\mathbf{5}]^{0}$ to be stable species in DMF solution. In

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(14) Synthesis of [**5**]$(PF_6)_2$: Neat Et_3N (0.10 mL, 0.72 mmol) was added to a solution of [**2b**]Br_2 (0.29 g, 0.35 mmol) in 45 mL of CH_3CN in the presence of a trace amount of H_2O. The solution gradually changed its color from deep blue to purple, and a small amount of precipitate formed. The mixture was stirred at ambient temperature for 3 days and filtered, and the remaining solid was extracted into CH_3CN (3 × 10 mL). The extracts were combined and evaporated to dryness. The deep purple residue was dissolved in 30 mL of H_2O and then added dropwise to an aqueous solution of NH_4PF_6 (0.25 g, 1.53 mmol), whereupon [**5**]$(PF_6)_2$ precipitated as a purple microcrystalline solid. Yield: 0.24 g (83%).

(15) Data for [**5**]$(PF_6)_2$ are as follows: ^{11}B NMR (64.2 MHz, CD_3CN): δ 9.1 ($h_{1/2}$ = 180 Hz). ^{1}H NMR (250.1 MHz, CD_3CN): δ 9.26 (d, 4H, $^{3}J(HH)$ = 5.8 Hz, bipy-6,6′), 8.59 (m, 8H, bipy-3,3′,4,4′), 8.23 (m, 4H, bipy-5,5′), 4.42, 4.30 (2 × vtr, 2 × 4H, $^{3}J(HH)$ = 1.8 Hz, C_5H_4). ^{13}C NMR (62.9 MHz, CD_3CN): δ 146.4 (bipy-4,4′), 145.4 (bipy-2,2′), 144.2 (bipy-6,6′), 130.4 (bipy-5,5′), 124.2 (bipy-3,3′), n.o. (C_5H_4-*ipso*), 73.2, 72.2 (C_5H_4). Anal. Calcd for $C_{30}H_{24}B_2F_{12}FeN_4OP_2$ (823.94): C, 43.72; H, 2.94; N, 6.80. Found: C, 43.65; H, 3.21; N, 6.68.

(16) Crystal and structure determination data for [**5**]$(PF_6)_2$: $C_{30}H_{24}B_2F_{12}FeN_4OP_2$, M = 823.94, monoclinic, space group $P2_1/n$, a = 15.180(1) Å, b = 12.287(1) Å, c = 18.093(1) Å, β = 110.20(1)°, V = 3167.1(4) Å^3, Z = 4, D_c = 1.728 g cm^{-3}, $F(000)$ = 1656, Siemens SMART-CCD area detector diffractometer, Mo Kα radiation (λ = 0.71073 Å), T = 173(2) K; crystal size 0.40 × 0.20 × 0.18 mm, ω-scan mode, measurement range 1.52° ≤ θ ≤ 29.13°, 8529 independent reflections, 6490 reflections with $I > 2\sigma(I)$, μ = 0.684 mm^{-1}. The structure was solved by direct methods and full-matrix least-squares refinement was carried out against F^2 using the SHELXTL/PC package, 469 parameters, R1 = 0.0705 (all data), wR2 = 0.1208 (all data), max/min residual electron density +0.726/−0.614 e Å^{-3}.

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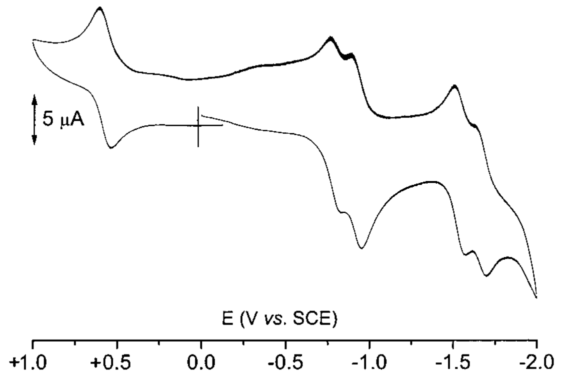

Figure 3. Cyclic voltammogram recorded at a platinum electrode on a DMF solution containing $[NEt_4](PF_6)$ (0.1 mol dm^{-3}) and $[\mathbf{5}][PF_6]_2$ (0.6×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

both cases, two strong absorption bands appear in the UV/vis spectrum ($\lambda_{max} = 850$ and 920 nm). Controlled potential electrolysis in correspondence with the most cathodic processes leads to the decomposition of the material. However, on the basis of relative peak heights in the cyclic voltammogram, it is reasonable to assume that the second cathodic couple also involves two subsequent one-electron additions ($E°' = -1.55$ and -1.67 V). In agreement with previous findings,[12] we assign the two couples of reductions as centered on the two bipyridylboronium groups. In contrast to $[\mathbf{5}]^{2+}$, the reduction of the unbridged analogue $[\mathbf{2a}]^{2+}$ occurs through two single stepped two-electron processes ($E°' = -0.98$ and -1.71 V), which excludes the presence of electrochemically detectable through-space interactions. The B−O−B bridge in $[\mathbf{5}]^{2+}$ apparently causes the electrons to enter the two electronically communicating bipyridylboronium groups stepwise and in an alternating way. The separation $\Delta E°'$ of the two redox potentials inside each couple provides a quantitative picture of the through-bond electronic interaction. Values of the comproportionation constant K_{com} of 160 and 110, respectively, allow us to classify $[\mathbf{5}]^{+}$ and $[\mathbf{5}]^{-}$ as partially delocalized (on the electrochemical time scale) Robin-Day class II systems.

In conclusion, electrochemical measurements on $[\mathbf{5}](PF_6)_2$ showed its oxygen bridge to exert a pronounced effect on the degree of electronic communication between the two 2,2′-bipyridylboronium units. To understand the nature of this phenomenon, the effect of a systematic variation of the bridging element (e.g., substitution of O by NR, S, Se) on the electrochemical behavior of the complex is currently under investigation.

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Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complex $[\mathbf{5}](PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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