functionality of 1^{3+} rather than on the Cp*Ru(phenyl) side groups. Furthermore, since the simple cation $Cp^*Ru(C_6H_6)^{+4}$ is both difficult to reduce and oxidize ($E^{ox}_{1/2}$ = 1.83 V; $E^{red}_{1/2}$ = -2.1 V in CH_3CN), it can be concluded that for 1^{4+} the primary electrochemical events are associated with the naphthacene unit. The weak reducing and oxidizing power of the naphthacene excited state relative to Cp*Ru(phenyl) would partially explain the inability of the Cp*Ru(phenyl) groups to quench totally fluorescence from the naphthacene group. That is, the rate of internal electron transfer between these groups is not sufficiently rapid to allow this potential fluorescence quenching mechanism to dominate. The relative importance of other nonradiative pathways for relaxation of the excited state cannot be assessed from the data at hand and is under study.

In conclusion, the multiple substitution of Cp^*Ru^+ on rubrene can impart novel structural, photophysical, and chemical properties to this molecule. We are investigating the effect this substitution has on the well-known electrochemical luminescent properties of rubrene[13,16] and are studying the photophysics of other related multiply metalated aromatic hydrocarbons.

Supplementary Material Available: ^1H NMR, ^{13}C NMR, and analytical data for $1^{4+}(OTf^-)_4$ and **3**, X-ray data, and tables of atomic positional parameters, thermal parameters, bond distances, and bond angles for $1^{4+}(OTf^-)_4 \cdot 2CH_3NO_2$ (6 pages); tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Verification of the "Cation-Popping" Doping Mechanism of Self-Doped Polymers

Y. Ikenoue, J. Chiang, A. O. Patil, F. Wudl,* and A. J. Heeger

Institute for Polymers and Organic Solids
Department of Physics, University of California
Santa Barbara, California 91036

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As examples of self-doped polymers[1] and water-soluble conducting polymers[2] we reported the synthesis and initial characterization of the sodium salts and acids of poly(thiophene ethanesulfonate) (P3-ETS) and poly(thiophene butanesulfonate) (P3-BTS). These polymers, in principle, can lose a proton or other monovalent cation concomitant with electron loss (oxidation) to produce self-doped polymers. The potential counterions are covalently bound via side chains to the polymer backbone; electron ejection from the polymer π-system (positive charging of the backbone) is compensated by proton (or Li^+, Na^+, etc.) migration to the electrolyte solution, leaving behind a covalently bound anion.

In this paper we present new results which confirm the validity of the self-doping principle. By using cyclic voltammetry in concert with determination of hydrogen ion or sodium ion concentration in the electrolyte, we prove that "H^+-popping" and "Na^+-popping" occur upon electrochemical oxidation of the polymer. The results demonstrate in addition, and for the first time with conducting polymers, a voltage controlled ion exchange mechanism.

Cyclic voltammetric data for polythiophene and some derivatives are known.[3,4] Typical cyclic voltammograms of a P3-BTSNa and a P3-BTSH film cast on Pt are shown in Figure 1 (parts A and B, respectively). The color changes marked on the figure[5] demonstrate that these polyelectrolytes, in nonaqueous solution,

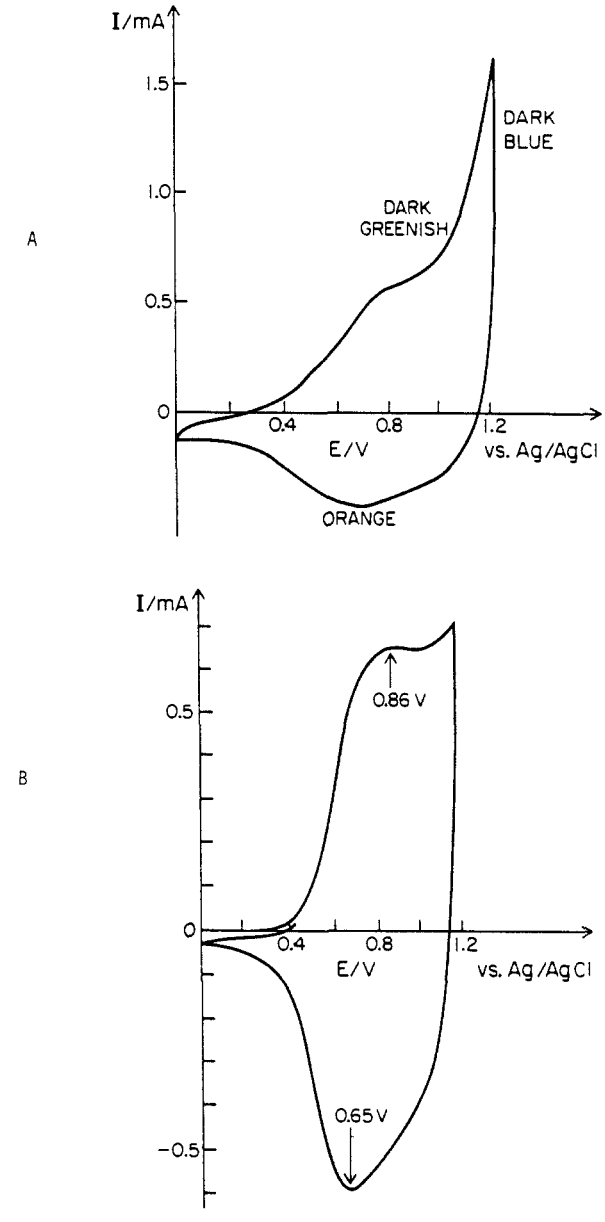
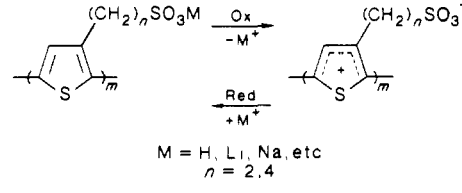


Figure 1. (A) A typical cyclic voltammogram obtained after five "break-in cycles" where the W.E. was a 3-4 μm thick P3-BTSNa film cast on a Pt foil, the C.E. was a Pt wire, the R.E. was Ag/AgCl, and the sweep-rate was 10 mV/s. The electrolyte was 0.1 N Bu_4NClO_4 in acetonitrile. (B) A typical cyclic voltammogram obtained after five "break-in cycles" where the W.E. was a 3-4 μm thick P3-BTSH film cast on ITO glass, the C.E. was a Pt wire, the R.E. was Ag/AgCl, and the sweep-rate was 100 mV/s. The electrolyte was 0.1 N Bu_4NClO_4 in acetonitrile. The same color changes recorded in Figures 1A were observed in this case.

Scheme I



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(5) The electrochromism was particularly evident for the case of P3-BTSNa only when a small amount of water was added [P3-BTSH is hygroscopic; i.e., the film surface is already coated with a layer of water (broad band at 3350 cm^{-1})].

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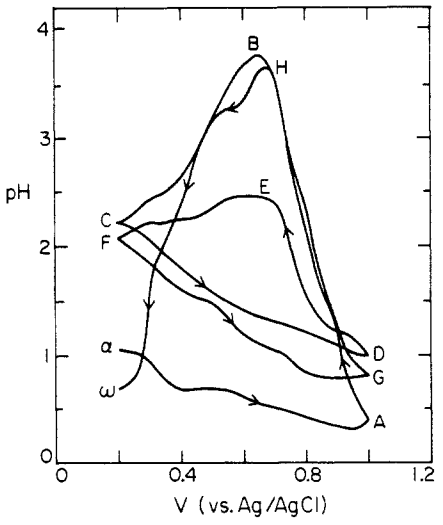

Figure 2. Several cycles of an in situ hydrogen ion concentration determination, under equilibrium conditions and without stirring, during cyclic voltammetry where the W.E. was 3–4 μm thick P3-BTSH film cast on ITO glass, the C.E. was a Pt wire, the R.E. was Ag/AgCl, and the sweep-rate was 2 mV/s. The electrolyte was 0.1 N Bu_4NClO_4 in acetonitrile. The plot shows a change in "pH" versus a change in potential as the potential is cycled between 0.2 and 1.0 V relative to the R.E. First cycle, $\alpha \rightarrow A \rightarrow B \rightarrow C$; second cycle, $C \rightarrow D \rightarrow E \rightarrow F$; third cycle, $F \rightarrow G \rightarrow H \rightarrow \omega$.

are also electroactive materials.[6]

"H^+-Popping" Study of the Acid Form of Polymers and the Self-Doping Mechanism. Figure 2 shows the result of an in situ pH determination during cyclic voltammetry of P3-BTSH (W.E.); i.e., a "pH" (quotations are required; by definition, pH refers to water only, see ref 7–13, below) change in solution was dynamically observed during electrochemical cycling. Although the expected change in "pH" was observed (in accord with Scheme I) between anodic oxidation and cathodic reduction at a slow sweep rate (2 mV/s), the "pH" behavior was not stable (fluctuations of ±0.3 pH units) when the potential was not swept but moved stepwise in the range of 0.2–1.0 V versus Ag/AgCl. Since P3-BTSH is a strong acid (pK_a of most sulfonic acids is in the range of 0 to −1), a reversible cation exchange between H^+ on the polymer and Bu_4N^+ in solution is expected. Hence, a fraction (δ) of protons of the polymer will exchange to form the Bu_4N^+ salt, thereby causing a decrease in "pH" of the medium until an equilibrium value is reached (α in Figure 2) and formation of a mixed fraction of the Bu_4N^+ salt and acid form exists on the polymer before potential cycling is initiated, as indicated in eq 1.

$$\text{P-SO}_3\text{H} + \text{Bu}_4\text{N}^+ \rightleftharpoons \delta\text{P-SO}_3^-\text{Bu}_4\text{N}^+ + (1-\delta)\text{P-SO}_3\text{H} + \delta\text{H}^+ \quad (1)$$

$$\text{P = polymer} \qquad 0 < \delta < 1$$

During the electrochemical cycle, two competitive reactions take place

$$(1-\delta)\text{P-SO}_3\text{H} \underset{+e}{\overset{-e}{\rightleftharpoons}} (1-\delta)\text{P}^{n+}\text{-}(\dot{\text{SO}}_3^-)_n + n(1-\delta)\text{H}^+ \quad (2)$$

$$\delta\text{P-SO}_3^-\text{Bu}_4\text{N}^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \delta\text{P}^{m+}\text{-}(\text{SO}_3^-)_m + m\delta\text{Bu}_4\text{N}^+ \quad (3)$$

P = polymer

If reaction 2 were preferred over (3), then a noticeable decrease in "pH" would be expected. In fact that is precisely what is observed (α to A, etc., Figure 2). Thus the changes in "pH" generated during oxidation and subsequent reduction are in competition with the spontaneous ion exchange (eq 1). Because

(6) That this color change is not due to a simple equilibrium (P3-BTSNa + $H_2O \rightleftharpoons$ P3-BTSH) was demonstrated by the fact that the sodium salt changes color reversibly upon chemical oxidation (Br_2 gas) and reduction (hydrazine).

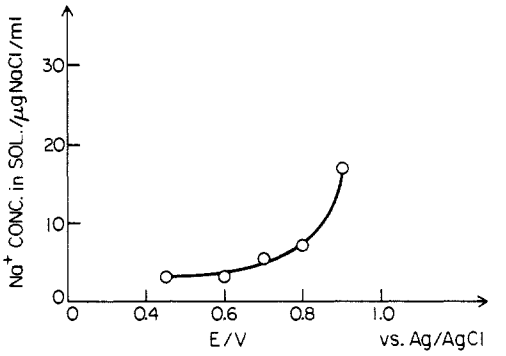

Figure 3. Sodium ion concentration as determined by atomic absorption spectroscopy versus potential (R.E., Ag/AgCl). Potential was increased from zero to the first point where a sample was withdrawn for Na analysis, from the first point to the second, where another sample was withdrawn, etc.

the diffusion of H^+ to the polymer-electrolyte interface of the polymer electrode is the rate-determining step when the solution is not stirred, only a small change in "pH" was observed when the sweep rate was increased from 2 to 50 mV/s. Note that in the cathodic sweep shown in Figure 2, the maxima (B, etc.) appear at ca. 0.65 V versus Ag/AgCl. This implies that the ion exchange in eq 1 from H^+ to Bu_4N^+ is much faster than the H^+ resorption rate (reverse reaction in eq 2) at potentials lower than 0.65 V (corresponding to the same reduction peak potential of the cyclic voltammogram in Figure 1B). In this set of experiments, the usual doping and undoping process concomitant with anion migration from the electrolyte solution (eq 4 and 5), although possible, is nondetectable.

$$\text{SDP-SO}_3\text{H} + \text{ClO}_4^- \rightleftharpoons \text{SDP}^{n+}\text{-SO}_3\text{H(ClO}_4^-)_n \quad (4)$$

$$\text{SDP-SO}_3^-\text{Bu}_4\text{N}^+ + \text{ClO}_4^- \rightleftharpoons \text{SDP}^{m+}\text{-SO}_3\text{Bu}_4\text{N(ClO}_4^-)_m \quad (5)$$

The "pH" change noted in Figure 2 is reasonable; the "pH" range in acetonitrile solvent versus water is known[7–9] and is rather wide. An explanation was proposed by Gutmann[10,11] (the window of the pH-glass electrode in nonaqueous solvents is ca. −10.2 to more than 30 based on water[12,13]).

In a somewhat similar experiment, Okano et al.[14] reported pH changes at the counter electrode during water electrolysis at a polypyrrole (PPy) coated electrode in *aqueous* solution. If indeed there was a trace of water on the polymer surface of the P3-BTSH, its electrolysis could produce "pH" changes not related to the proton ejection mechanism. We therefore carried out the following control experiment: a PPY electrode (instead of the P3-BTSH film) coated with a thin layer of water was employed for the above H^+ ejection experiments, we found no detectable change in "pH".

In conclusion, we found that "H^+-popping" took place during cyclic voltammetry in the form of H^+ migration through the polymer in spite of the huge excess of Bu_4N^+ in the electrolyte.

"Na^+-Popping" Study and the Self-Doping Mechanism. We observed "Na^+ popping" in parallel studies; Na^+ was released from a P3-BTSNa film electrode upon oxidation during cyclic voltammetry in nonaqueous solvent as shown in Figure 3. In a control experiment, we found that there was no detectable concentration of Na^+ in the electrolyte solution after immersing the polymer film in the latter for 8 h; i.e., no spontaneous ion-exchange against Bu_4N^+ occurs. Therefore, the Na^+ concentration indicated in

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Figure 3 was released only during the oxidation of the polymer, indicative of Na^+ popping.

The experimental evidence presented above demonstrates that the self-doped polymers (P3-ETS and P3-BTS) act as cation ejectors during oxidation and proton absorbers during reduction. The proposed doping mechanisms (H^+-popping and Na^+-popping, respectively) have thus been confirmed. The acid and sodium forms of these 3-substituted polythiophene derivatives can therefore be considered as potential-dependent proton and sodium exchangers. The usefulness of the potential dependent proton exchange is currently limited by the normal ion exchange which is slower than the potential dependent one but still significant. It may be possible to control the amount of normal exchange by variations in electrolyte and medium, a part of ongoing studies.

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Evidence for Water Coordinated to the Active Site Iron in Soybean Lipoxygenase-1[1]

Mark J. Nelson

Central Research and Development Department
E. I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware 19898

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In this communication I report evidence for the existence of at least one iron-coordinated water in the active site of soybean lipoxygenase-1. Lipoxygenases are atypical mononuclear nonheme iron dioxygenases that catalyze the peroxidation by dioxygen of fatty acids containing a 1,4-diene unit.[2] In contrast to the more familiar intradiol catechol dioxygenases, soybean lipoxygenase-1 contains an iron with a relatively high reduction potential[3] and no phenolate ligands. Although the fatty acid may bind very close to the iron,[4] there is no evidence for coordination of either the fatty acid or dioxygen to the metal.[5] Available data are consistent with a mechanism involving oxidation and deprotonation of the diene, yielding a radical species that may react directly with dioxygen.[6] This oxidation reaction would not require coordination of the substrate to the iron; however, the observed regio- and stereospecificity of the reaction might imply the existence of an iron–alkyl intermediate.[7] Thus, it is of considerable interest to know if the iron in lipoxygenase contains ligands that might be displaced by the substrate, an intermediate, or an appropriately designed inhibitor.

Mammalian lipoxygenases are the targets of active inhibitor design programs by virtue of their importance in the biosynthesis of leukotrienes.[8] One approach to such inhibitors is via substrate analogues with potentially iron-coordinating moieties.[9] Detailed structural information to support this approach has been lacking; it has been known only that the iron in ferrous soybean lipoxygenase-1 is six-coordinate,[10] probably with four imidazole ligands,[11] and that the protein-derived ligands in ferric lipoxygenase–catecholate complexes likely are three neutral and one anionic.[12] By comparison, the more thoroughly characterized active site iron in the intradiol catechol dioxygenases is known to contain water ligands that are displaced by substrate.[13]

Table I. Line Widths in the EPR Spectrum of Ferric Lipoxygenase at pH 7

		FWHH[a]		
	feature (g_y)	$H_2{}^{16}O$	$H_2{}^{17}O$	broadening
no addition[b]	7.3	71.9 ± 0.6	75.0 ± 0.7	3.1 ± 1.0
	6.4	65.8 ± 0.9	71.3 ± 0.3	5.5 ± 0.9
ethanol[c]	6.3	63.8 ± 1.1	70.6 ± 1.1	6.8 ± 1.5
HCN	6.4	72.6 ± 0.3	77.0 ± 0.3	4.4 ± 0.5

[a] Full width at half-height in g ± standard deviation in multiple measurements. [b] Four samples. [c] Three samples.

The EPR spectrum of ferric soybean lipoxygenase-1[14,15] at pH 7 comprises two major components, each typical of high-spin Fe^{3+} and each representing a ground-state Kramer's doublet of an $S = 5/2$ system: one shows features at $g = 7.3$, approximately 4.5, and 2 ($E/D \approx 0.06$),[16] while the other has features at $g = 6.4$, 5.7, and 2 ($E/D \approx 0.01$). In samples prepared in $H_2{}^{17}O$, the low field features of each component (g_y and g_x) show line-broadening that presumably arises from unresolved hyperfine coupling between the ^{17}O nucleus of bound water and the electronic spin (Table I).[17] Thus the iron sites represented by each of these components apparently have at least one exchangeable water ligand.

Unresolved hyperfine broadening from $H_2{}^{17}O$ is also observed in samples of ferric lipoxygenase-1 treated with either 8 mM ethanol or 5 mM cyanide at pH 7 (Table I). Addition of ethanol or KCN (at pH 7, effectively HCN) results in the appearance of a single major component in the EPR spectrum,[12] with features corresponding to $g = 6.3$, 5.8, and 2 or 6.4, 5.8, and 2, respectively, although neither of these species is thought to coordinate the iron.[18] Thus, although both ethanol and cyanide bind to lipoxygenase and affect the electronic structure of the iron, neither appears to cause the loss of all (if any) of the water from the iron.[19]

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(19) The magnitude of the line broadening depends not only on the number of ^{17}O nuclei coupled to the spin system but also the electronic structure of the complex as manifested in the spin density at the ^{17}O nucleus. Consequently it is not fruitful to make quantitative conclusions about the number of bound waters from these experiments.

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