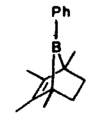
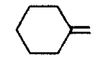
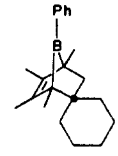
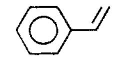
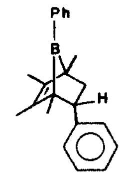
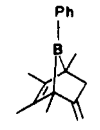
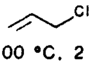
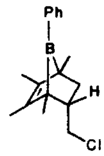
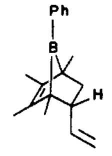
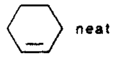
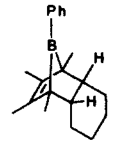
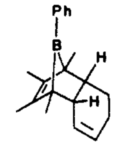
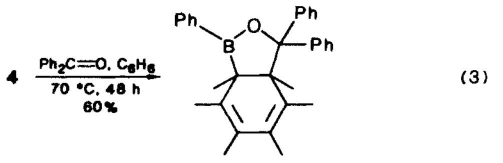
Table I. Reactions of **3** with Unactivated Alkenes

reactant	product[a]	reactant	product[a]
= 80 °C, 5 h	 **5** (82%)	 80 °C, 24 h	 **9** (91%)
 100 °C, 2 h	 **6** (92%)	=•= 70 °C, 4 h	 **10** (75%)
 100 °C, 2 h	 **7** (89%)	 80 °C, 4 h	 **11** (63%)
 120 °C, 21 h	 **8** (94%)	 100 °C, 27 h	 **12** (87%)

[a] All products were isolated as colorless oils.

one of the two possible stereoisomers is observed, and the coupling constants observed for **6** and **7** in their ^{1}H NMR spectra are again consistent with endo addition of the borole **2**.[7] Preliminary results indicate that **2** can react with both double bonds of 1,3-butadiene, which accounts for the lower yield obtained in the case of **11**.

Heating the 7-boranorbornadiene adduct **4** at 120 °C in toluene solution in a sealed tube generates hexamethylbenzene and an as yet unidentified boron-containing product. Complex **4** can be reacted with benzophenone to produce the compound **13** which was isolated as a white solid from cold (−78 °C) hexane (eq 3).[7]



13

(3)

The product **13** is expected based on the known reactivity of allylic boranes.[11] These reactions demonstrate that both removal of boron or further functionalization of the Diels-Alder adducts is possible. In some respects, the chemistry of boroles is reminiscent of the electronically related cyclopentadienylcobaltacyclopentadiene fragment which is a presumed intermediate in cobalt-mediated [2 + 2 + 2] reactions.[12] An important difference is that intermolecular reactions with alkenes proceed more readily in the case of the boroles.

Acknowledgment. We thank Ronald J. Davis for capable technical assistance.

Registry No. **1**, 84101-39-3; **3**, 113668-53-4; **4**, 113668-54-5; **5**, 113668-55-6; **6**, 113668-56-7; **7**, 113668-57-8; **8**, 113668-58-9; **9**, 113668-59-0; **10**, 113668-60-3; **11**, 113668-61-4; **12**, 113668-62-5; **13**, 113668-63-6; PhBCl$_2$, 873-51-8; Ph$_2$C=O, 119-61-9; 2-butyne, 503-17-3; ethene, 74-85-1; styrene, 100-42-5; 3-chloropropene, 107-05-1; cyclohexene, 110-83-8; methylenecyclohexane, 1192-37-6; allene, 463-49-0; 1,3-butadiene, 106-99-0; 1,3-cyclohexadiene, 592-57-4; hexamethylbenzene, 87-85-4.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, mass spectral, and analytical data for **2**–**13**; X-ray data and tables of atomic positional parameters, thermal parameters, bond distances, and bond angles for **3** (9 pages); table of observed and calculated structure factors for **3** (2 pages). Ordering information is given on any current masthead page.

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[11] (a) Negishi, E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 358–360. (b) Mikhailov, B. M. *Pure Appl. Chem.* **1974**, *39*, 505–523.

[12] Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556, and references therein.

Synthesis and Unusual Properties of a Helically Twisted Multiply Metalated Rubrene Derivative[†]

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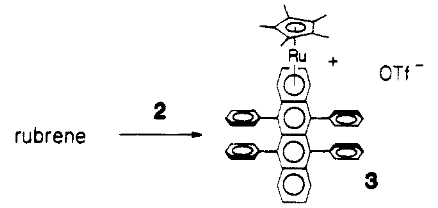
We have been interested in preparing organometallic complexes with specific shapes and distributions of charge for use in the rational preparation of solid-state materials.[1] For these studies, we have used the Cp*Ru$^+$ (Cp* = η-C$_5$(CH$_3$)$_5$) fragment for derivatization of aromatic hydrocarbons which serve as geometric templates to obtain a desired molecular shape and arrangement of positive charges. We report herein the properties of the complex $\{5,6,11,12\text{-}[\mathrm{Cp^*Ru}(\eta\text{-C}_6\mathrm{H}_5)]_4\mathrm{naphthacene}\}^{4+}(\mathrm{OTf}^-)_4$ ($\mathbf{1}^{4+}(\mathrm{OTf}^-)_4$; OTf = CF$_3SO_3$) obtained by multiple substitution of Cp*Ru$^+$ on 5,6,11,12-tetraphenylnaphthacene (rubrene). Substitution of Cp*Ru$^+$ on the phenyl groups of rubrene greatly distorts the structure such that the naphthacene core is helically twisted as determined by a single-crystal X-ray diffraction analysis. Despite the presence of the four ruthenium heavy atoms, $\mathbf{1}^{4+}$ is intensely luminescent like rubrene itself, and although significantly perturbed, the photophysical and redox properties of $\mathbf{1}^{4+}$ are essentially dominated by the naphthacene portion of the molecule.

Reaction of [Cp*Ru(CH$_3$CN)$_3$]$^+$OTf$^-$ (**2**)[2] with an equivalent of rubrene at room temperature in CH$_2$Cl$_2$ leads to formation of the blue-green derivative **3** (eq 1). The ^{1}H NMR spectral data for **3** reveal that the Cp*Ru group is bound to the outermost ring of the naphthacene functionality.[5,6] However, by repeatedly heating and removing solvent from a CH$_2$Cl$_2$ solution of rubrene



(1)

[†] Contribution No. 4592.

[1] (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C., to be submitted for publication. (b) Ward, M. D.; Fagan, P. J.; Johnson, D. C.; Calabrese, J. C., to be submitted for publication.

[2] Preparation of **2**: reduction of Cp*RuCl$_2$[3] with 1 equiv of lithium triethylborohydride in THF precipitates orange (Cp*RuCl)$_4$. Refluxing (Cp*RuCl)$_4$ in CH$_3$CN for 2 h followed by addition of AgOTf yields a solution of **2** which was filtered, and solvent was removed from the filtrate. Addition of ether and collection by filtration yields crystalline yellow-orange **2** (94%). The PF$_6^-$ salt of the cation Cp*Ru(CH$_3$CN)$_3^+$ has previously been prepared by a photochemical route.[4]

[3] Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161–1164.

[4] Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501–3504.

[5] See Supplementary Material.

[6] Related complexes have been reported: McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519–2527.

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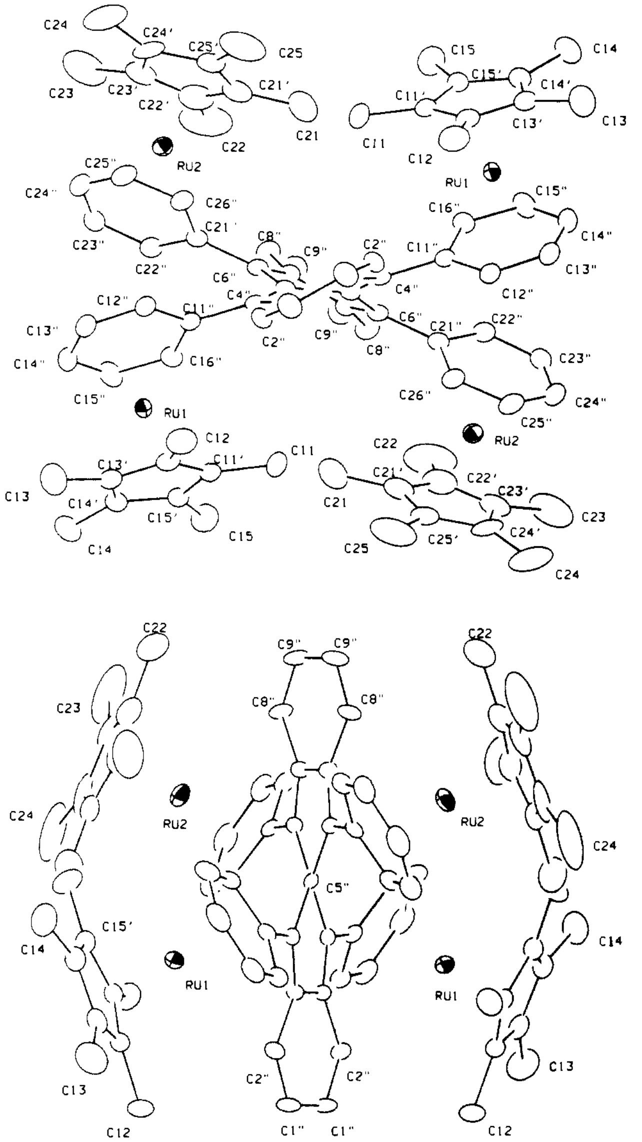
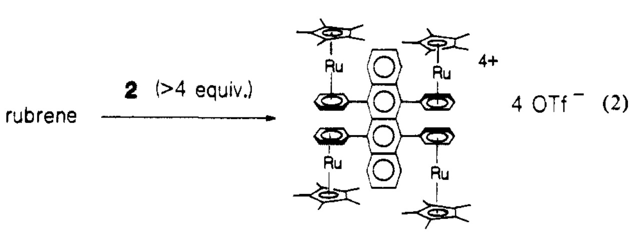


Figure 1. ORTEP drawing of the tetracation **1**$^{4+}$. Upper view: looking down the long naphthacene axis. Lower view: looking down C5″–C5″.

containing greater than 4 equiv of **2**, a dark blue precipitate of the complex **1**$^{4+}$(OTf$^-$)$_4$ was obtained in 85% yield (eq 2). The NMR spectral properties of **1**$^{4+}$(OTf$^-$)$_4$ are consistent with the substitution of four Cp*Ru groups on the phenyl rings of rubrene.[5] An X-ray diffraction study on a single crystal of **1**$^{4+}$(OTf$^-$)$_4$·2CH_3NO_2 (ether diffusion into CH_3NO_2) verifies this structural assignment.[5,7] Whereas rubrene is reported to have an essentially planar naphthacene core,[8] the naphthacene core of the tetracation **1**$^{4+}$ is helically twisted about its long axis (Figure 1). The overall twist is quite large with the torsional angle of C1″–C1″ relative to C9″–C9″ equal to 67.3°. The distortion in **1**$^{4+}$ can be attributed to the rotation of adjacent phenyl groups about the phenyl-naphthacene bonds which avoids unfavorable steric interactions between the bulky Cp*Ru groups and the naphthacene core. The resultant repulsion between adjacent phenyl groups causes the twisting of the naphthacene framework. A similar situation is observed for 1,8-bis(ferrocenyl)naphthalene,[9] and Pascal and co-workers have recently structurally characterized organic hydrocarbons with a related helical twisting of an aromatic center.[10]



(2)

1^{4+} (OTf$^-$)$_4$

Rubrene is known to exhibit a high quantum efficiency for fluorescence (Φ_r = 0.94 ± 10% in CH_2Cl_2; literature: 0.98 in benzene[11a]). Contrary to the expectation of quenching by the four ruthenium heavy atoms, blue solutions of **1**$^{4+}$ exhibit an intense red luminescence. The visible absorption spectrum of **1**$^{4+}$ in CH_2Cl_2 displays a band in the visible region with attendant vibrational structure (λ_{max} = 635, 585, 544, and 504 nm; $\epsilon = 2.33 \times 10^4$, 1.84×10^4, 7.95×10^3, and 2.5×10^3, respectively). Features of this band are nearly identical with the band observed in the absorption spectrum of rubrene[11b] except that the extinction coefficients for **1**$^{4+}$ are approximately twice as large, and the band is shifted 110 nm to the red. The emission spectrum of **1**$^{4+}$ has a maximum at 657 nm (cf. rubrene λ_{max}(emission) = 562 nm). The excited state lifetime for **1**$^{4+}$ is 11.6 ± 0.5 ns with Φ_r = 0.45 ± 10% ($k_r = 3.87 \times 10^7$ s^{-1}; $k_{nr} = 4.73 \times 10^7$ s^{-1}) compared with 12.5 ± 0.5 ns measured for rubrene in CH_2Cl_2 (literature: 16.5 ns in benzene[11]).[12] These data characterize the emission from **1**$^{4+}$ as a fluorescent process associated primarily with the naphthacene core of the molecule. In contrast to rubrene, solutions of **1**$^{4+}$ are resistant to photochemical air oxidation. For example, an aqueous solution of **1**$^{4+}$ stored in air and exposed to room light shows no evidence of decomposition after 6 months.

Cyclic voltammetry of **1**$^{4+}$ in CH_2Cl_2 (0.1 M (n-$C_4H_9)_4NBF_4$) reveals a reversible one-electron oxidation at $E°_{ox}$ = 1.30 V and two reversible one-electron reductions at $E°_{red(1)}$ = −0.53 V and $E°_{red(2)}$ = −0.84 V. These values are shifted to more positive potential compared to rubrene ($E°_{ox}$ = 0.97 V; $E°_{red(1)}$ = −1.48 V in dimethylformamide[13]) which is the expected trend for the inductive effect in the more highly charged species **1**$^{4+}$. In addition, the difference between the first oxidation and reduction potentials of **1**$^{4+}$ (1.83 V) is smaller than the corresponding difference for rubrene (2.45 V) which is consistent with the red shift observed for the visible absorption spectrum of **1**$^{4+}$ relative to rubrene.

By reduction of **1**$^{4+}$ with Na/Hg in CH_3CN, the radical trication **1**$^{3+}$ can be generated and isolated as the complex **1**$^{3+}$(OTf$^-$)$_3$ after recrystallization from CH_2Cl_2/ether.[14] In solution, **1**$^{3+}$ can be converted back to **1**$^{4+}$ by air oxidation. The EPR spectrum of **1**$^{3+}$ in CH_2Cl_2 at 25 °C exhibits a single resonance (g = 1.9992; lw = 3.1 G) with no hydrogen hyperfine splitting and is identical with the spectrum of **1**$^{3+}$ generated electrochemically. Frozen solutions of **1**$^{3+}$ at −170 °C similarly display a single resonance (g = 1.9992; lw = 11 G) indicating a nearly isotropic g tensor. For comparison, the rubrene radical anion[15] (generated in THF with sodium naphthalide) displays a single absorption at −170 °C (lw = 4.3 G) with g = 2.00256. It can be concluded that the majority of the unpaired spin density resides on the naphthacene

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(7) Crystal data: monoclinic, $C2/c$ (no. 15), a = 26.206 (8) Å, b = 13.123 (6) Å, c = 27.126 (4) Å, β = 108.31 (2)°, T = −70 °C, V = 8856.4 Å^3, Z = 4, R = 0.034, R_w = 0.041.[5]

(8) Bulgarovskaya, I.; Vozzhennikov, V.; Alekesandrov, S.; Bel'skii, V. *Latv. PSR Zinat. Akad. Vestis, Fiz. Teh. Zinat. Ser.* **1983**, 53–59.

(9) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *3*, 539–547.

(10) (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665. (b) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653.

(11) (a) Stevens, B.; Algar, B. E. *J. Phys. Chem.* **1968**, *72*, 2582–2588. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971; p 374.

(12) (a) Fluorescent quantum yields were determined relative to both rubrene (Φ_r = 0.98[11a]) and bis(4-dimethylaminophenyl)squaraine (Φ_r = 0.65)[12b]. (b) Law, K.-Y., *J. Phys. Chem.* **1987**, *91*, 5184–5193.

(13) (a) Faulkner, L. R.; Bard, A. J. *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, 1977; Vol. 10, pp 1–95. (b) Faulkner, L. R.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 691–699.

(14) Anal. Calcd for $C_{85}H_{88}F_9O_9Ru_4S_3$: C, 53.03; H, 4.61. Found: C, 52.76; H, 4.62.

(15) Wheeler, L. O.; Bard, A. J. *J. Phys. Chem.* **1967**, *13*, 4513–4517.

J. Am. Chem. Soc. **1988**, *110*, 2983-2985

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: ^{1}H 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$^-$)$_4$·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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(16) Brilmyer, G. H.; Bard, A. J. *J. Electrochem. Soc.* **1980**, *127*, 104–110 and references therein.

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

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Received December 21, 1987
Revised Manuscript Received February 29, 1988

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,

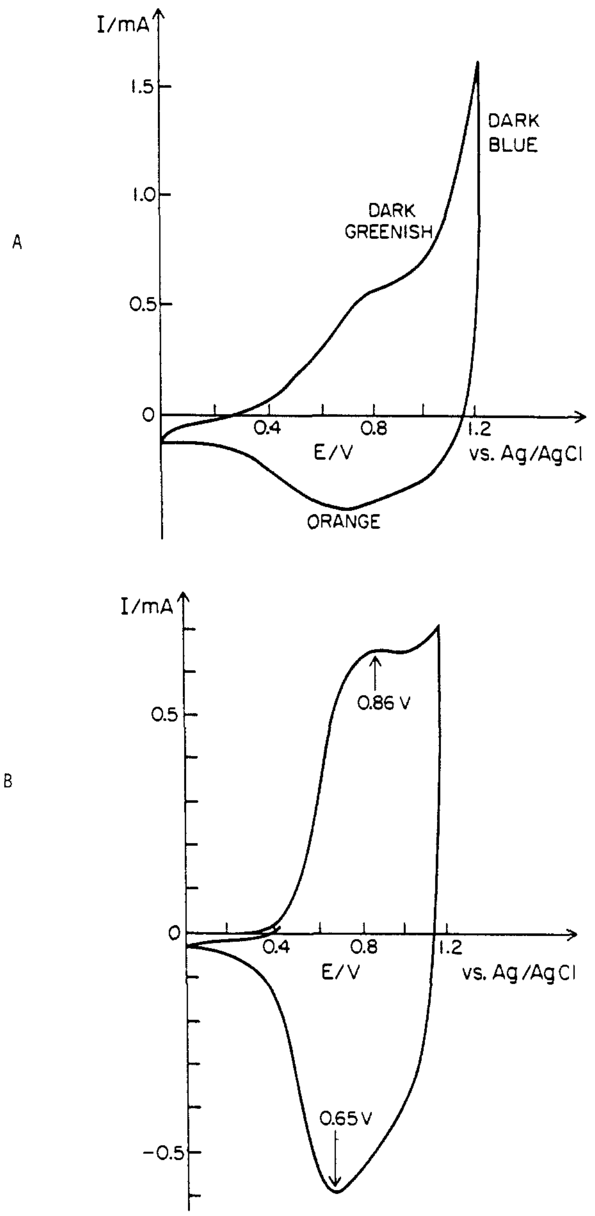
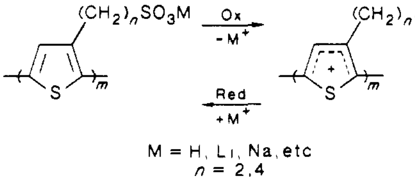


Figure 1. (A) A typical cyclic voltammogram obtained after five "break-in cycles" where the W.E. was a 3–4 μm thick P3-BTSNa film cast on a Pt foil, the C.E. was a Pt wire, the R.E. was Ag/AgCl, and the sweep-rate was 10 mV/s. The electrolyte was 0.1 N Bu_4NClO_4 in acetonitrile. (B) A typical cyclic 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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(1) Patil, A. O.; Ikenoue, Y.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.

(2) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858. (b) Havinga, E.; van Horsen, L.; ten Hoeve, W.; Wynberg, H.; Meijer, *Polymer Bull.* **1987**, *18*, 277. (c) Tsai, W.; Jang, G. W.; Rajeshwar, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1776.

(3) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51.

(4) Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459.

(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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