

Charge Trapping by Anionic Quinones Electrostatically Bound to a Highly Charged Cationic Quinone–Viologen Polymer or a Cationic Poly(3-viologen–thiophene)

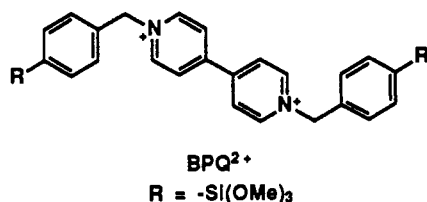
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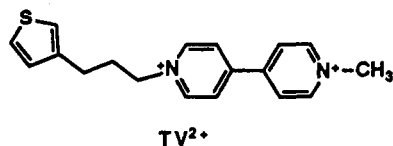
Charge associated with quinone reduction is trapped at low pH in systems composed of sulfonated anthraquinones electrostatically bound to a polymer derived from a monomer consisting of a quinone unit flanked by two viologen units. Each monomer repeat unit carries 6 equiv of positive charge which can be charge compensated by monosulfonated anthraquinone to yield a quinone:viologen ratio of nearly 7:2. At low pH, electrostatic binding is persistent, and the amount of trapped charge is 90% of the theoretical maximum. Some of the electrostatically bound quinone can be replaced with $\text{Fe}(\text{CN})_6^{3-}$ to allow mediated release of trapped charge via the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. I^- is blocked from entering the polymer and thus does not mediate release of charge. Electrostatic binding of anionic quinones to a thiophene polymer with pendant viologen units has also been demonstrated. This polymer system has the unique property of having built-in mediators for both the reduction (charge trapping) and oxidation (charge release) of the electrostatically bound anthraquinone.

In this article, we demonstrate high levels of charge trapping by an electrode-confined cationic viologen–quinone polymer that electrostatically binds water-soluble, anionic anthraquinone monomers. This work continues the characterization of viologen–quinone systems that exhibit pH-dependent charge trapping.^{1–5} In addition to studies on covalently linked viologen–quinone systems,^{1–3} we have observed charge trapping in viologen–quinone assemblies^{4,5} obtained by electrostatically binding^{4–9} anionic sulfonated anthraquinones to cationic polymers derived from the polymerization of *N,N'*-bis[*p*-(trimethoxysilyl)benzyl]-4,4'-bipyridinium, BPQ^{2+} .^{9b,10} Here we report the results of our studies



on charge trapping by sulfonated anthraquinones electrostatically bound to a more highly charged polymer derived from polymerization of BV-Q-BV^{6+} (Chart I).

We also report a new approach to mediation of both charge trapping and charge release which involves electrostatically binding anionic quinones to a polymer derived from anodic polymerization of a thiophene containing a pendant viologen unit, TV^{2+} .¹¹ This polymer, $(\text{TV}^{2+})_n$, is similar to $(\text{BPQ}^{2+})_n$ in that

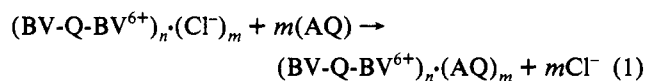


it can electrostatically bind 2-AQ to form a charge trapping “homogeneous bilayer”, yet it is unique in that each repeat unit contains functionality to mediate both charge trapping (viologen) and charge release (polythiophene).

$(\text{BV-Q-BV}^{6+})_n$ itself undergoes a $4ne^-/2n\text{H}^+$ reduction between -0.7 and $+0.2$ V vs SCE in aqueous electrolyte.^{1–3} This

corresponds to a $1e^-$ reduction for each of the $2n$ viologens and a $2e^-/2\text{H}^+$ reduction of the n quinones in the polymer. At about pH 7 and above, both reductions are reversible. However, at low pH only the viologen is reoxidized, even when the electrode potential is moved to a potential significantly positive of both the viologen and quinone redox potential. Thus, charge associated with reduction of Q to QH_2 remains “trapped” in the polymer film at low pH. We attribute this rectifying behavior in viologen–quinone films to an inherently slow self-exchange rate of the Q/ QH_2 redox system.¹² The quinone does not equilibrate directly with the electrode surface. Instead its reduction is mediated by the $\text{BV}^{2+/+}$ redox couple. At neutral pH, the redox potential of the $\text{BV}^{2+/+}$ and Q/ QH_2 coincide, and the viologen can mediate both the reduction and oxidation of the quinone. However, at low pH the redox potential of Q/ QH_2 shifts to more positive potentials so that the viologen is now capable of mediating only the reduction, but not the oxidation, of the quinone. The energetics of rectifying viologen–quinone systems are similar to polymer bilayers,^{13,14} Scheme I, but in the viologen–quinone polymers referred to as homogeneous bilayers^{1–3} there is no segregation of the components into separate layers.

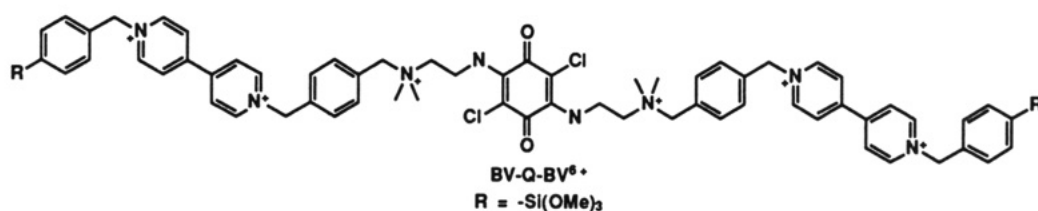
The use of electrostatic binding represents a significant simplification in the design of pH-dependent charge-trapping assemblies because the need for complex synthesis of bifunctional monomers or pinhole-free bilayer assemblies is eliminated. In the present system, we have compensated the charges on the quaternized nitrogen atoms of $(\text{BV-Q-BV}^{6+})_n$ by anthraquinone-2-sulfonate, 2-AQ, or anthraquinone-2,6-disulfonate 2,6-AQ, according to the ion-exchange reaction shown in (1). Complete



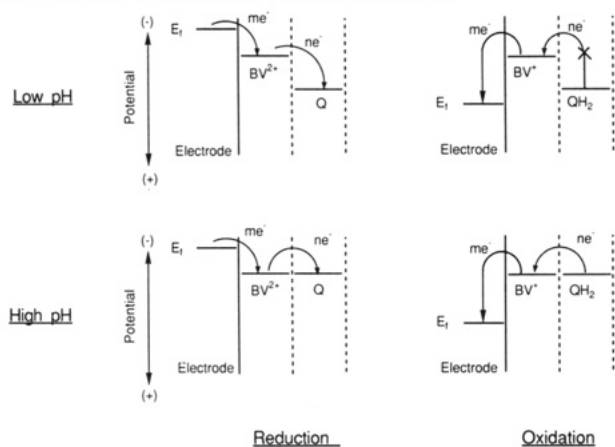
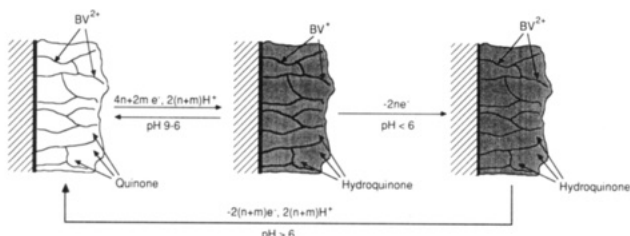
compensation of the charge on $(\text{BV-Q-BV}^{6+})_n$ by six 2-AQ molecules, together with the quinone in the polymer backbone, results in a quinone:viologen ratio of 7:2. This represents the highest ratio of charge-trapping component to charge-mediating component assembled in any homogeneous bilayer assembly. Our new results demonstrate that the viologen redox couple remains effective in shuttling charge from the electrode surface to quinone in the film even at very high loading of quinone. We view the separate sparse arrangement of viologen subunits as a network

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CHART I



SCHEME I: Energetics of Charge Trapping

SCHEME II: Representation of Charge Trapping by the (BV-Q-BV⁶⁺)_n(AQ)_m System

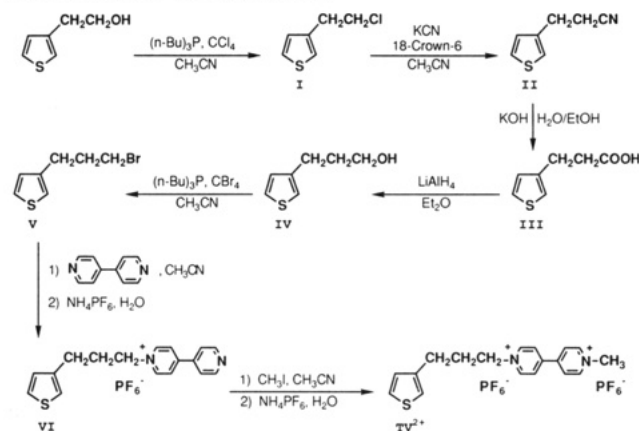
of "electronic-relay threads" that pass charge to the quinone subunits, Scheme II.

Experimental Section

Equipment. Solution NMR spectra were recorded using either a Bruker WM250 (¹H 250 MHz) or AC250 (¹H 250 MHz) spectrometer; mass spectra were recorded using a Finnegan MAT System 8200; and double focusing, magnetic sector, mass spectrometer, and solution FTIR spectra were recorded using a Nicolet 60SX spectrometer. Cyclic voltammetry and potential step experiments were done using a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 programmer and recorded on a Kipp and Zonen BD91 x-y-y' or BD90 x-y recorder.

Chemicals. Electrolyte solutions were prepared from glass-distilled water and acetonitrile (Omnisolve, EM Science). Ultrapure HCl and H₂SO₄ were used throughout (Ultrex, Baker). Sulfonated anthraquinones were obtained from Aldrich Chemical Co. and used without further purification. BV-Q-BV⁶⁺ was synthesized according to a literature procedure.² TV²⁺ was synthesized according to a similar, but higher yield, route than previously reported.¹¹ Chemicals for the synthesis of TV²⁺ were commercially available (Aldrich, Alfa, etc.) and used as received, unless specified otherwise. The synthesis of TV²⁺ is outlined in Scheme III, and the details are described below.

2-(3-Thienyl)ethyl Chloride, I. A 1-L round-bottomed flask was equipped with a condenser with Ar line, addition funnel, and magnetic stirring bar. To the flask were added 20.0 g of 2-(3-thienyl)ethanol (0.156 mol), 53 mL of 85% tri-*n*-butylphosphine (0.18 mol) and 300 mL of CH₃CN. A rubber septum was then

SCHEME III: Synthesis of TV²⁺

attached and the flask purged with Ar. To the addition funnel was transferred (via cannula) a deaerated solution containing 17.4 mL of CCl₄ (0.18 mol) and 150 mL of CH₃CN. After cooling the flask in an ice/salt bath for 15 min, dropwise addition was commenced. Upon complete addition, the ice/salt bath was removed and replaced with an oil bath. The flask contents were then heated to reflux overnight. After refluxing 18 h, the flask contents were transferred to a separatory funnel along with 300 mL of Et₂O and 300 mL of H₂O. The organic layer was separated, extracted with saturated aqueous NaCl, and dried with Na₂SO₄. Rotary evaporation of solvent yielded a viscous brown liquid which was vacuum distilled to give 19.2 g of I (84% yield) as a clear liquid: bp 39 °C/0.1 Torr; ¹H NMR (CDCl₃) δ 7.31 (m, 1 H), 7.10 (m, 1 H), 7.01 (m, 1 H), 3.74 (t, *J* = 7.3 Hz, 2 H), 3.14 (t, *J* = 7.3 Hz, 2 H).

3-(3-Thienyl)propionitrile, II. To a 250-mL round-bottomed flask were added 19.2 g of I (0.129 mol), 19.5 g of KCN (0.30 mol), 2.0 g of 18-crown-6 (7.6 mmol), 150 mL of CH₃CN, and a magnetic stirring bar. After purging the flask with Ar, a condenser with Ar line was attached and the flask contents heated to reflux in an oil bath. After refluxing for 19 h, the flask was removed from the oil bath and cooled to room temperature, and the contents transferred to a separatory funnel along with 200 mL of Et₂O and 200 mL of H₂O. The organic layer was separated, extracted with saturated aqueous NaCl, and dried with Na₂SO₄. Solvent was removed via rotary evaporation to yield a light-brown liquid which was vacuum distilled to give 14.3 g of II (80% yield) as a clear liquid: bp 103–104 °C/0.9 Torr; IR (CH₂Cl₂) ν_{CN} 2246 cm⁻¹; ¹H NMR (CDCl₃) δ 7.29 (m, 1 H), 7.08 (m, 1 H), 6.97 (m, 1 H), 2.97 (t, *J* = 7.3 Hz, 2 H), 2.60 (t, *J* = 7.1 Hz, 2 H). Low-resolution EI mass spectrum contains a molecular ion peak at *m/e* 137.

3-(3-Thienyl)propionic Acid, III. To a 1-L round-bottomed flask were added 14.3 g of II (0.103 mol), 56 g of KOH (1 mol), 400 mL of H₂O, 200 mL of absolute ethanol, and a magnetic stirring bar. The flask was subsequently equipped with a condenser and heated to reflux in an oil bath. The progress of the reaction was followed by monitoring NH₃ evolution via a place of moistened pH paper situated at the top of the condenser. After four days, no further NH₃ evolution was observed. Ethanol was removed via rotary evaporation, and the remaining aqueous solution was transferred to a separatory funnel and extracted

with 250 mL of Et₂O. The organic layer was discarded and the aqueous layer acidified with HCl, which resulted in the appearance of a white precipitate. After the solution was allowed to cool to room temperature, the precipitate was extracted into Et₂O and separated. The organic layer was extracted with saturated aqueous NaCl and dried with Na₂SO₄. Rotary evaporation of solvent yielded a clear oil, which solidified upon pumping in vacuo, to give 15.8 g of **III** (98% yield): mp 57 °C; ¹H NMR (CDCl₃) δ 10.5 (s, br, 1 H), 7.27 (m, 1 H), 7.01 (m, 1 H), 6.97 (m, 1 H), 2.99 (t, *J* = 7.5 Hz, 2 H), 2.71 (t, *J* = 7.5 Hz, 2 H). Low-resolution EI mass spectrum contains a molecular ion peak at *m/e* = 156.

3-(3-Thienyl)propanol, IV. A 500-mL round-bottomed flask was equipped with a condenser with Ar line, addition funnel, and magnetic stirring bar. To the flask were added 9.5 g of LiAlH₄ (0.25 mol) and 250 mL of Et₂O. A rubber septum was attached and the flask purged with Ar. To the addition funnel was transferred (via cannula) a deaerated solution containing 15.8 g of **III** (0.102 mol) and 50 mL of Et₂O. Upon completion of dropwise addition, the flask contents were heated to reflux in an oil bath for 3 h. After cooling to room temperature, unreacted LiAlH₄ was quenched with H₂O and the flask contents transferred to a separatory funnel along with 50 mL of saturated aqueous NH₄Cl. The organic layer was separated, extracted with saturated aqueous NaCl, and dried with Na₂SO₄. Rotary evaporation of solvent yielded 13.2 g of **IV** (92% yield) as a clear liquid, which was not purified further.

3-(3-Thienyl)propyl Bromide, V. A 500-mL round-bottomed flask was equipped with a condenser with Ar line, addition funnel, and magnetic stirring bar. To the flask were added 13.2 g of **IV** (0.093 mol), 35 mL of 85% tri-*n*-butylphosphine (0.12 mol), and 100 mL of CH₃CN. A rubber septum was then attached and the flask purged with Ar. To the addition funnel was transferred (via cannula) a deaerated solution containing 40 g of CBr₄ (0.12 mol) and 100 mL of CH₃CN. After the flask was cooled in an ice/salt bath for 15 min, dropwise addition was commenced. Upon complete addition, the ice/salt bath was removed and replaced with an oil bath, and the flask contents heated to reflux. After refluxing for 15 h, the flask was removed from the oil bath and cooled to room temperature. The contents were then transferred to a separatory funnel along with 200 mL of Et₂O and 200 mL of H₂O. The organic layer was separated, extracted with saturated aqueous NaCl, and dried with Na₂SO₄. Solvent was removed via rotary evaporation to yield a brown liquid which was vacuum distilled to give 13.4 g of **V** (71% yield) as a clear liquid: bp 60 °C/0.05 Torr; ¹H NMR (CDCl₃) δ 7.27 (m, 1 H), 6.99 (m, 1 H), 6.95 (m, 1 H), 3.41 (t, *J* = 6.6 Hz, 2 H), 2.82 (t, *J* = 7.2 Hz, 2 H), 2.17 (m, 2 H). Low-resolution EI mass spectrum contains a molecular ion peak at *m/e* 204 (⁷⁹Br).

1-(3-Thienyl)propyl-4,4'-bipyridinium Hexafluorophosphate, VI. To a 200-mL round-bottomed flask were added 2.68 g of **V** (0.013 mol), 5.66 g of freshly sublimed 4,4'-dipyridyl (0.036 mol), 80 mL of dry CH₃CN (distilled from CaH₂, stored over activated Al₂O₃ under Ar), and a magnetic stirring bar. After purging the flask with Ar, a condenser with Ar line was attached and the flask contents heated to reflux in an oil bath overnight. After refluxing 14 h, the flask volume was reduced to ~10 mL via rotary evaporation. The addition of 50 mL of Et₂O to the flask resulted in the appearance of an off-white precipitate, which was collected via filtration, dissolved in 125 mL of H₂O, and reprecipitated as the hexafluorophosphate salt upon addition of a solution containing 4.1 g of NH₄PF₆ and 35 mL of H₂O. The solid was collected via filtration, washed with H₂O and Et₂O, and dried in vacuo. Recrystallization from H₂O afforded 4.50 g of **VI** (80% yield) of analytically pure product: ¹H NMR (CD₃SOCD₃) δ 9.20 (d, *J* = 7.2 Hz, 2 H), 8.87 (m, 2 H), 8.59 (d, *J* = 7.2 Hz, 2 H), 8.02 (m, 2 H), 7.45 (m, 1 H), 7.19 (m, 1

H), 6.99 (m, 1 H), 4.67 (t, *J* = 7.1 Hz, 2 H), 2.69 (t, *J* = 7.2 Hz, 2 H), 2.31 (m, 2 H).

1-Methyl-1'-(3-thienyl)propyl-4,4'-bipyridinium Bis(hexafluorophosphate), TV²⁺. To a 100-mL round-bottomed flask were added 1.50 g of **VI** (3.52 mmol), 1.1 mL of iodomethane (0.018 mol), 35 mL of dry CH₃CN (distilled from CaH₂, stored over activated Al₂O₃ under Ar), and a magnetic stirring bar. After purging the flask with Ar, a condenser with Ar line was attached and the flask contents heated to reflux in an oil bath overnight. The reaction was discontinued after refluxing 14 h, and the flask volume was reduced to ~10 mL via rotary evaporation. Upon addition of 50 mL of Et₂O to the flask, an orange precipitate formed. The solid was collected via filtration, dissolved in H₂O (required ~500 mL), and reprecipitated as the bis(hexafluorophosphate) salt upon addition of a solution containing 3.5 g of NH₄PF₆ and 20 mL of H₂O. The off-white solid was collected via filtration, washed with H₂O and Et₂O, and dried in vacuo. We collected 1.25 g of TV²⁺ (61% yield): ¹H NMR (CD₃SOCD₃) δ 9.49 (d, *J* = 6.8 Hz, 2 H), 9.42 (d, *J* = 6.8 Hz, 2 H), 8.90 (m, 2 H), 8.87 (m, 2 H), 7.65 (m, 1 H), 7.35 (m, 1 H), 7.16 (m, 1 H), 4.87 (t, *J* = 7.1 Hz, 2 H), 4.58 (s, 3 H), 2.86 (t, *J* = 8.0 Hz, 2 H), 2.64 (m, 2 H).

Electrochemistry. Indium tin oxide, ITO, electrodes were fabricated by contacting Cu wire to ITO-coated glass (Delta Technologies) with Ag epoxy and encapsulating the contact with white epoxy (Epoxy-Patch). Commercial glassy carbon, GC, electrodes with an area of ~0.071 cm² (Bioanalytical Systems) were initially polished with progressively smaller grades of diamond paste. Between uses, the electrodes were repolished with 1-μm diamond paste and sonicated in MeOH for 15 min. A 1–2 mM solution of BV-Q-BV⁶⁺ in 0.2 M KCl/0.1 M K₂HPO₄ was used for modifying electrodes with (BV-Q-BV⁶⁺)_{*n*}. The solution was prepared by first dissolving the BV-Q-BV⁶⁺ in a drop of DMSO and then diluting with electrolyte. All solutions were rigorously degassed with Ar prior to electrochemical measurements. Electrodes were modified by holding the electrode potential at –0.7 V vs SCE for a period sufficiently long to deposit the desired amount of polymer. Usually 20–30 min of deposition time resulted in coverages of ~10^{–8} mol of monomer/cm². After derivatization, the electrodes were soaked overnight in 5.0 M KCl to facilitate polymer cross-linking.² Electrodes modified in this way were further modified with sulfonated anthraquinones by soaking in an unbuffered saturated aqueous solution of the quinone. In most cases, maximum charge compensation was complete in 30 min. Derivatization of GC electrodes with (TV²⁺)_{*n*} was achieved by oxidative polymerization of a 0.1 M solution of TV²⁺ in 0.1 M (*n*-Bu₄N)PF₆ in CH₃CN. GC electrodes were cycled from 0 to +2.1 V vs a Ag wire quasi-reference electrode until the desired coverage was obtained (usually one to three cycles). The electrodes were characterized in 0.1 M (*n*-Bu₄N)PF₆ in CH₃CN before being soaked in a saturated solution of 2,6-AQ. The coverage of polymer was determined by integrating the charge under the cyclic voltammetric wave associated with the first one-electron reduction of the pendant viologen groups.

Results and Discussion

Charge Trapping in Electrostatically Bound Quinones. The charge trapping ability of the (BV-Q-BV⁶⁺)_{*n*}(2-AQ)_{*m*} system at low pH is demonstrated by the cyclic voltammetry shown in Figure 1A. The first negative potential scan shows a large cathodic wave corresponding to 1e[–] reductions of the 2*n* viologen subunits and 2e[–]/2H⁺ reductions of the *n* + *m* quinone subunits in the polymer assembly. The return scan of the first cycle shows a small anodic wave at –0.5 V vs SCE corresponding to only the 1e[–] oxidation of the 2*n* viologen subunits. A small broad anodic wave appears at ~+0.2 V, which we believe represents oxidation of the small amount of quinone that exchanges electrons directly with the electrodes surface. Importantly, most of the quinone

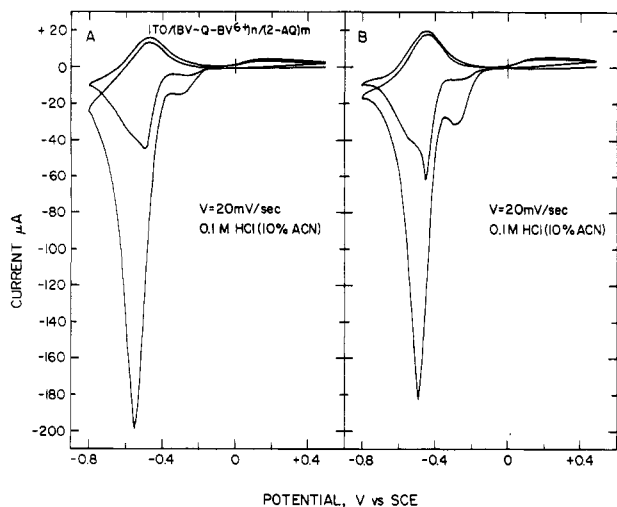


Figure 1. Cyclic voltammetry of an ITO/(BV-Q-BV⁶⁺)_n electrode after ion exchange with 2-AQ. The electrode area was 0.32 cm², and the coverage of BV-Q-BV⁶⁺ was $\sim 5 \times 10^{-9}$ mol/cm². Initially the polymer was 90% charge compensated with 2-AQ. In each case the second scan was taken immediately after the first scan: (A) Cyclic voltammetry of the modified electrode in pH 1 HCl (with 10% acetonitrile) immediately after modification with 2-AQ; (B) cyclic voltammetry in the same electrolyte solution after allowing the reduced quinone to reoxidize air. In both (A) and (B) the first scan is the one with large cathodic peak at ~ -0.6 V corresponding to quinone reduction.

remains in the reduced hydroquinone form and therefore traps 2 equiv/mol of quinone in the polymer film. The second scan illustrates that only the viologen subunits are reduced (along with a small amount of quinone that did not remain trapped as QH₂). The second return scan is essentially identical to the first one.

The (BV-Q-BV⁶⁺)_n(2-AQ)_m system differs from the (BPQ²⁺)_n(2-AQ)_m system⁴ in two ways. First, in the (BV-Q-BV⁶⁺)_n(2-AQ)_m system, nearly all of the positive charges on the polymer are charge compensated by the sulfonated anthraquinone, while in the (BPQ²⁺)_n(2-AQ)_m system, complete charge compensation did not always occur. The lower degree of cross-linking in the (BV-Q-BV⁶⁺)_n polymer apparently results in a more open structure, facilitating nearly 100% charge compensation by 2-AQ. When all charged groups on the viologen polymer are compensated, the ratio of quinone to viologen is 7:2. Since the quinone is a 2e⁻ redox couple, the maximum ratio of trapped charge to viologen mediator is 14:2. Based on integration of the cyclic voltammetric peaks in Figure 1A, the (BV-Q-BV⁶⁺)_n polymer is at least 90% charge compensated by 2-AQ.

The second difference between the (BV-Q-BV⁶⁺)_n(2-AQ)_m and (BPQ²⁺)_n(2-AQ)_m systems is that electrostatic binding of 2-AQ to the (BV-Q-BV⁶⁺)_n polymer is less persistent at neutral pH compared to the (BPQ²⁺)_n polymer, again reflecting a more open structure for the (BV-Q-BV⁶⁺)_n polymer. Reduction at neutral pH apparently causes movement of sulfonate anions out of the film at a rate that is competitive with movement of cations into the film. This situation is in contrast to that at low pH, where compensation of charge associated with reduction of the film movement is by rapid movement of H⁺ into the films.¹⁷

Charge trapping indicates that diffusion of quinone within the polymer film is limited. When the sulfonated quinone alizarin red S is electrostatically bound to a non-redox-active fluorocarbon polymer with fixed cationic sites, it is electroactive, implying that the quinone can diffuse through the polymer to the electrode surface.⁶ Charge trapping in the (BV-Q-BV⁶⁺)_n(2-AQ)_m system, however, implies that the quinone does not diffuse through the polymer to the electrode surface on the electrochemical time scale, presumably due to formation of distinct ion pairs between the anionic quinones and the cationic viologens.

Evidence that the electrochemical response at low pH is due

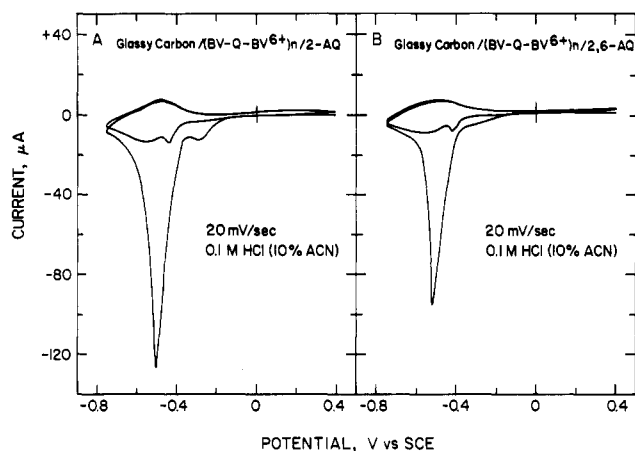
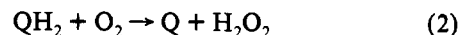


Figure 2. Comparison of 2-AQ and 2,6-AQ electrostatically bound to a GC/(BV-Q-BV⁶⁺)_n-modified electrode. The coverage of BV-Q-BV⁶⁺ was $\sim 1 \times 10^{-8}$ mol/cm². In both cases the polymer is essentially 100% charge compensated with quinone: (A) cyclic voltammetry for the 2-AQ-modified electrode; (B) cyclic voltammetry after the 2-AQ has been removed by repeated cycling of the electrode in 0.1 M KCl/0.1 M Tris buffer, pH 7, and replaced with 2,6-AQ by soaking in a saturated solution of 2,6-AQ for 45 min. All scans are at 20 mV/s in 0.1 M HCl (10% ACN). In both (A) and (B) the first scan is the one with large cathodic peak at ~ -0.6 V corresponding to quinone reduction.

to rectification rather than loss of quinone from the film is shown in Figure 1B. After initial trapping of charge, the electrode was removed from solution and exposed to atmospheric O₂. This results in reoxidation of the hydroquinone by reaction with O₂, as shown in eq 2.¹⁸ Allowing the electrode film to completely air



dry is an effective method for releasing all of the trapped charge from the (BV-QH₂-BV⁶⁺)_n(2-AQH₂)_m film. When the electrode is placed into fresh electrolyte at low pH, nearly the same amount of the initial trapped charge can again be trapped in the polymer film, as shown in Figure 1B, indicating that little quinone is lost from the film.

Figure 2 compares the degree of charge trapping when 2-AQ or 2,6-AQ is used to charge compensate the polymer. When 2,6-AQ is used to charge compensate the polymer, the amount of charge trapped in the polymer is approximately 60% of the charge trapped when 2-AQ is used, suggesting that half as much quinone has been exchanged into the polymer. Such experiments establish that the quinone anions used are electrostatically bound to the cationic polymer. The amount bound is consistent with essentially complete charge compensation of the cationic centers in the polymer by the anionic quinones.

Controlled Release of Trapped Charge. We have previously demonstrated that trapped charge can be instantaneously released from viologen-quinone systems by a rapid pH jump experiment.^{3,4} The results of this experiment are shown in Figure 3 for the (BV-Q-BV⁶⁺)_n(2-AQ)_m system. Briefly, the experiment involves trapping charge in a viologen quinone assembly by stepping to a negative potential to reduce both the viologen and quinone redox units, and then stepping to a positive potential to oxidize only the viologen subunits, leaving the quinones reduced as QH₂. Addition of strong base raises the pH, shifting the thermodynamic potential for quinone oxidation negative, so that the viologen can mediate the release of charge to the electrode surface. The electrochemical response is a sharp anodic peak in the current-time response (Figure 3B), corresponding to QH₂ → Q + 2H⁺ + 2e⁻. The release of charge upon raising the pH indicates that charge has been stored in the polymer film.

The cyclic voltammetry of a (BV-Q-BV⁶⁺)_n(2-AQ)_m-modified electrode that has been subsequently modified by partial exchange (~ 1 Fe(CN)₆³⁻ per BV-Q-BV⁶⁺ repeat unit) of 2-AQ by

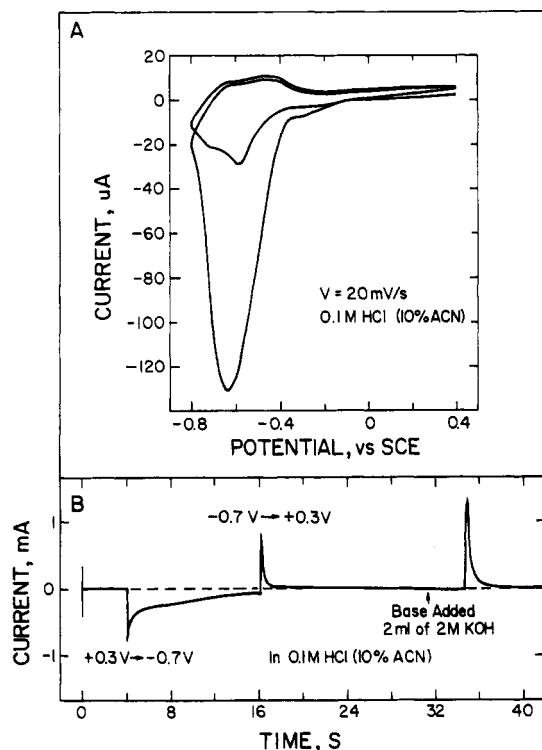


Figure 3. Demonstration of charge release by a pH jump. The coverage of BV-Q-BV⁶⁺ was $\sim 1 \times 10^{-8}$ mol/cm², and there is nearly 100% charge compensation with 2-AQ: (A) cyclic voltammety of a glassy C/(BV-Q-BV⁶⁺)_n/(2-AQ)_m electrode in the starting pH 1 HCl (10% ACN) solution, demonstrating that the electrode shows rectification; (B) current-time profile for a pH jump experiment. The electrode was rotated at 1000 rpm in 10 mL of 0.1 M HCl. The electrode was initially held at +0.3 V and then stepped to -0.7 V to fully reduce both the quinone and viologen. After 12 s, the electrode was stepped to +0.3 V to reoxidize the viologen, leaving the quinone trapped in the reduced form. At the time indicated by the arrow, 2 mL of 2 M KOH was added to raise the pH and release the trapped charge.

Fe(CN)₆³⁻ is shown in Figure 4. The partial exchange was monitored by cycling a (BV-Q-BV⁶⁺)_n/(2-AQ)_m-modified electrode from 0 to +0.6 V vs SCE in a 5 μM Fe(CN)₆³⁻ solution until the desired amount of Fe(CN)₆³⁻ was incorporated into the film as deduced from the cyclic voltammety response of the electrostatically bound Fe(CN)₆^{3-/4-}. As shown in Figure 4, the Fe(CN)₆^{3-/4-} couple brings about the mediated release of charge that is trapped by the 2-AQ bound in the film. It should be noted that uptake of Fe(CN)₆^{3-/4-} into the polymer film adversely affects the electrochemical response of the viologen at 10 mV/s.³ The retarded rate of charge transport through the film is likely a consequence of electrostatic cross-linking.

A similar release of trapped charge occurs in the (BV-Q-BV⁶⁺)_n polymer when a small amount of I⁻ is placed in the electrolyte. In the absence of electrostatically bound quinone, I⁻ effectively mediates the release of trapped charge from (BV-QH₂-BV⁶⁺)_n via the I⁻/I₃⁻ redox couple. However, in the (BV-QH₂-BV⁶⁺)_n/(2-AQH₂)_m system, where most cation sites are compensated with 2-AQ, there appears to be no (or slow) uptake of I⁻ into the film and therefore no mediated release of trapped charge, Figure 5. Over longer periods of time or at higher I⁻ concentrations (~ 1 mM or greater), enough I⁻ can enter the film to allow a slow release of trapped charge.

Using the polymer derived from anodic polymerization of TV²⁺, we have designed a charge-trapping system with a built-in mediator for release of trapped charge. The (TV²⁺)_n system utilizes the pendant viologen redox group as mediator for charge trapping, while the polythiophene conducting polymer backbone is used to mediate charge release. In the absence of electrostatically bound quinone, the (TV²⁺)_n polymer has three distinct redox processes in CH₃CN. At +0.7 V vs a Ag reference, the

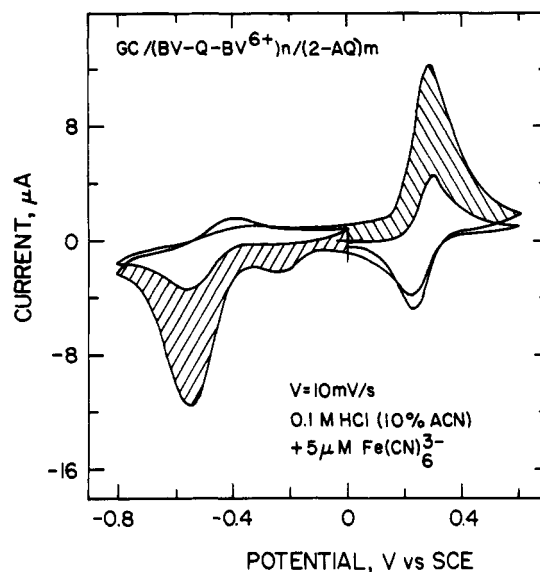


Figure 4. Cyclic voltammety showing mediated charge release by Fe(CN)₆³⁻. The coverage of BV-Q-BV⁶⁺ was $\sim 1 \times 10^{-8}$ mol/cm². A GC/(BV-Q-BV⁶⁺)_n/(2-AQ)_m-modified electrode was cycled in 5 μM Fe(CN)₆³⁻ solution from 0 to +0.6 V until the desired amount of Fe(CN)₆³⁻ was incorporated into the film. This film contains ~ 1 Fe(CN)₆³⁻ per BV-Q-BV⁶⁺ repeat unit. The charge trapping (shaded area between 0 and -0.8 V) is mediated by the viologen at ~ 0.5 V, and charge release (shaded area between 0 and +0.6 V) is mediated by Fe(CN)₆³⁻ at +0.3 V.

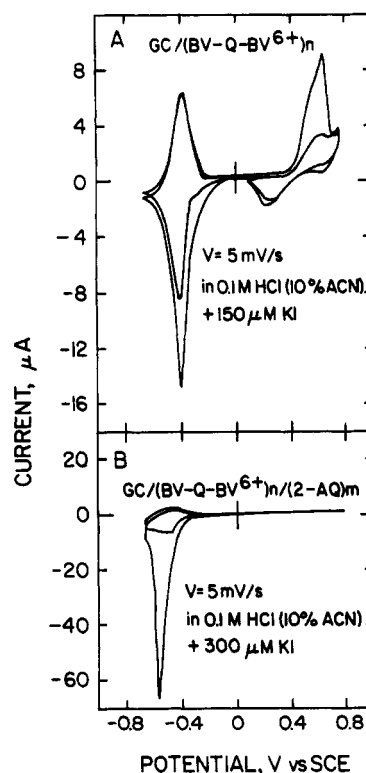


Figure 5. (A) Mediated release of trapped charge from a GC/(BV-Q-BV⁶⁺)_n-modified electrode with I⁻. The coverage of BV-Q-BV⁶⁺ was $\sim 1.6 \times 10^{-8}$ mol/cm². (B) The release of trapped charge by I⁻ is inhibited after complete compensation of cationic charge on the polymer with 2-AQ. The scan rate is 5 mV/s, and the electrolyte is 0.1 M HCl (10% ACN) with the indicated amount of KI added.

onset for oxidation of the thiophene polymer backbone is observed, while at -0.35 and -0.81 V, the reduction of the pendant viologen to the +1 and 0 charge states occurs. At pH 1 in aqueous solution, the first viologen reduction and the onset of oxidation of the thiophene polymer remain separated by about 1 V with the redox potential of the 2,6-AQ/2,6-AQH₂ redox couple lying in the

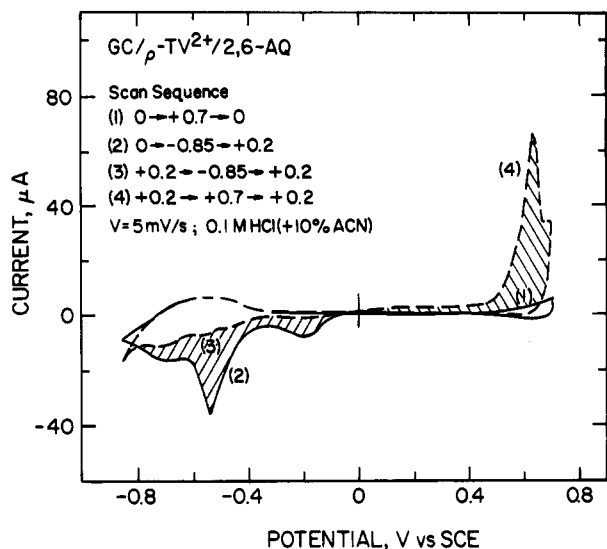


Figure 6. Electrochemistry of a glassy carbon electrode modified with $(TV^{2+})_n$ and 2,6-AQ. The coverage of $(TV^{2+})_n$ was $\sim 7 \times 10^{-8}$ mol/cm², and the charge on the viologen is 100% compensated by the exchange of 2,6-AQ into the film.

middle of this potential window. The potential region between polythiophene oxidation and viologen reduction provides a window where charge in the form of 2,6-AQH₂ can be trapped in the polymer assembly.

The behavior of the $(TV^{2+})_n(2,6-AQ)_m$ is shown in Figure 6. First, the potential is scanned to +0.85 V, which is just positive of the onset of polythiophene oxidation. Then the electrode is scanned to -0.85 V, where the one-electron reduction of the viologen as well as the viologen-mediated two-electron reduction of the quinone occur. When the electrode is then scanned positive to +0.2 V, only reoxidation of the viologen occurs, leaving the quinone trapped in the reduced form as 2,6-AQH₂. It is significant that at +0.2 V the potential is sufficient to oxidize 2,6-AQH₂; however, only a very small amount of oxidation occurs. The small amount of oxidation of 2,6-AQH₂ that does occur can be assigned to the small amount of quinone that is in contact with, or can diffuse to, the electrode surface. Subsequent scans to negative potentials result only in reduction and reoxidation of the viologen. However, when the electrode potential is scanned to +0.7 V, reoxidation of 2,6-AQH₂ occurs, as illustrated by the large wave at +0.8 V. The release of charge occurs 0.5 V positive of the thermodynamic potential for oxidation of 2,6-AQH₂. We interpret this behavior as an indication that the electronically conductive $(TV^{2+})_n$ backbone acts as a mediator of charge release, and in the case of $(TV^{2+})_n$, both the thiophene backbone and the viologen redox couple act as extensions of the electrode surface. We have obtained similar results by electrostatically binding 2,6-AQ to a polypyrrole with a viologen pendant to the pyrrole nitrogen.¹⁹ However, the more positive oxidation of the thiophene polymer in relation to the pyrrole polymer provides a wider potential window where charge can remain trapped in the electrode-confined film.

Summary

We have demonstrated that electrostatic binding is a suitable approach to the design and assembly of polymer systems which trap a high density of charge. We have shown that at low pH binding of sulfonated quinones to the highly charged BV-Q-BV⁶⁺ polymer is fairly persistent and shows charge trapping similar to that found for other viologen-quinone assemblies.¹⁻⁴ The $(BV-Q-BV^{6+})_n(2-AQ)_m$ system allows a large ratio of charge-trapping to charge-mediating components to be used. In addition, we have demonstrated several methods whereby the trapped charge can be released in this system by changing the pH as well as by mediation with redox couples such as $Fe(CN)_6^{4-/3-}$ or by a conducting polymer backbone.

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