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Inhibition of Charge Transport by Ethidium Bromide and DNA Gating of Ion Motion at TCNQ Conducting Salt Electrodes

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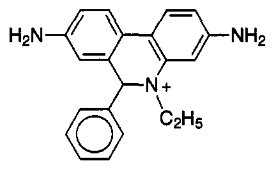
Abstract: Treatment of TCNQ thin film electrodes derived either from a 9-aminoacridinium$(\mathrm{TCNQ})_2$ or from TTF−TCNQ with ethidium bromide solution produced hydrophobic surface layers that inhibited ion motion. The passivation process was shown by electrochemical quartz crystal microgravimetry (EQCM) to involve an ion exchange step and a subsequent anodic oxidation coupled to the unidirectional ejection of countercations from the films. The quartz crystal microgravimetry (QCM) frequency of the passivated films exhibited a slow increase which was attributed to loss of water and/or disruption of the hydrogen bonding network at the ethidium-modified interface. The aqueous solution electroactivity of the ethidium-modified films could be restored by exposure of the surfaces to dilute solutions of herring testes DNA, which turned on (or "gated") the square wave EQCM ion motion at these electrodes.

While the nature of charge transport at conducting organic salt electrodes in the TTF−TCNQ family has attracted attention in recent years,[1−5] there have been few reports of purposeful surface modification of conducting salt electrodes. Thin films of these materials are attractive as substrates for chemically modified interfaces because (i) the molecular nature of the conducting salts is amenable to synthetic manipulation, (ii) the high charge densities and rapid charging characteristic of these films portend applications with excellent sensitivity, and (iii) the materials have a degree of biocompatibility due to their organic nature. Consistent with the latter point, there have been numerous reports of enzyme electrodes that employ organic conducting salt mediators.[6] In the present work, ion exchange chemistry was used to modify the surface of TCNQ conducting salt electrodes and thereby control the ion and electron motion at the electrode/aqueous electrolyte solution interface.

The well-known structure of the ethidium cation, which is widely used to visualize bands of DNA in electrophoretic separations, is as follows: This species binds to polynucleotides via an intercalation mechanism in which the cation fits into a hydrophobic pocket between base pairs in a major groove of the double helix. The formation constant for the complex is approximately 10^4-10^6, and the kinetics are fast under typical aqueous electrolyte conditions at room temperature.[7] It was these properties that prompted the present study of modified conducting salt electrodes designed to be sensitive to the presence of DNA.


ethidium

The polycrystalline TCNQ films examined in this study were derived in most experiments from thin films of either 9-aminoacridinium$(\mathrm{TCNQ})_2$ (**1**)[8] or TTF−TCNQ (**2**).[9] In both cases, the TCNQ(0/1−) redox couple was activated by lattice oxidation of either the acridinium cation or the TTF donor molecule following literature procedures.[1,8,10] The activation processes differ slightly for the two conducting salt electrodes. For **1**, the oxidation involves loss of a proton and formation of a TCNQ−acridine charge-transfer complex.[8,10] For **2**, the TTF lattice sites undergo oxidation. The resulting cyclic voltammograms reveal persistent surface waves, separated by 0.24 ± 0.01 V(in 1 M KOAc), which integrate to a coulometric charge corresponding to a maximum of approximately 100 equivalent monolayers of acceptor sites. The voltammetric patterns were similar for the TCNQ(0/1−) couples generated from **1** and **2**. Similar behavior was found when the films were prepared from pure TCNQ or LiTCNQ, but the films were less adherent and/or more soluble and the CV behavior was less well behaved. The visible spectra indicated that the dimer dianion was the predominant TCNQ species in the reduced films derived from the 9-aminoacridinium salt.[8] Nonetheless, in the discussion and scheme below, the reduced surface state is depicted as A^-M^+ where M^+ is a counterion originating in the electrolyte solution.

Treatment of the activated TCNQ thin film electrodes with ethidium bromide (EB) following the protocol described below significantly decreased the electroactivity of the TCNQ(0/1−) couple. The aqueous solution electroactivity of films passivated in this manner could be restored by exposure of the surface to

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[®] Abstract published in *Advance ACS Abstracts*, November 1, 1994.

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dilute solutions of DNA. Electrochemical quartz crystal microgravimetry (EQCM),[11] which was employed to follow the passivation and reactivation phenomena, gave apparent equivalent mass values derived from the charge and frequency transients at the DNA-treated electrodes that indicated permselective-like behavior with respect to motion of unhydrated counterions.

Experimental Section

Experimental details are similar to a previous study.[10]

Materials. The 9-aminoacridinium–TCNQ salt (**1**), (9-AA$^+$)-(TCNQ)$_2$, was synthesized as described previously;[8] TTF–TCNQ (**2**) was a gift from Prof. R. N. Compton of our department. Ethidium bromide (EB) was obtained from Aldrich, and herring testes DNA, type XIV, was obtained from Sigma Chem. Co.

Procedures. Reported thicknesses of the conducting salt films were estimated from the frequency change, Δf, observed when a dry film was applied to the 5 MHz, AT-cut, planoconvex quartz crystals (ICM Corp.) using the relation $d_f = d_Q(\Delta f/f_o)$, where d_Q is the thickness of the crystal. The QCM was calibrated by constant current deposition of silver from a 0.5 M HNO$_3$/0.5 M AgNO$_3$ solution. A calibration factor, C_f, of 300 ± 49 Hz/μg was obtained. The difficulty of using the Sauerbrey equation to estimate the surface mass of organic films on QCM crystals immersed in solution is well-known.[11] Film nonuniformity and the radial dependence of the mass sensitivity[12] are two of the experimental artifacts that impacted the present measurements. While care was taken to apply the conducting salt films as uniformly as possible to the entire active electrode surface (vapor-deposited gold, area = 0.348 cm^2) in contact with the QCM crystal, these artifacts and the physical differences between electrodeposited silver and organic salts mean that the equivalent mass values reported below should be viewed as "apparent equivalent masses."

The passivation and reactivation experiments were performed by treatment of the conducting salt electrodes with successive portions of 5 mL solutions. The solution transfers were made with a Pasteur pipet. In a typical procedure, the electrode was activated in 1 M KOAc and held in a reduced state at a negative potential (-100 or −150 mV for films derived from **1** or **2**, respectively). Then the KOAc solution was replaced with a 0.01 M EB solution for approximately 10 min. In these "dosing" experiments, the 0.01 M EB solution was first layered on top of a thin layer (0.2–0.3 cm) of 1.0 M KOAc. Then the solution was mixed by rapid addition of more 0.01 M EB solution from a pipet. This resulted in an even exposure of the electrode surface to the ethidium-containing solution. During the mixing step, either frequency–time/potential–time or frequency–time/current–time EQCM data pairs were continuously acquired. The EB solution was then replaced with a fresh 1 M KOAc solution, and the EQCM experiments were performed as described below. Reactivation was performed by replacement of the solution with dilute solutions of herring testes DNA, in either pH 7.4 HEPES buffer, 0.1 M NaCl, or 0.1 M KCl at DNA concentrations between 2 and 200 ppm. The reactivation phenomenon described below does not seem to have a simple concentration dependence. This dependence is under investigation; the results reported here were obtained at DNA concentrations of approximately 100 ppm.

Results and Discussion

Passivation of the TCNQ electrodes prepared from either **1** or **2** was performed in the same manner: treatment of the reduced film with a dilute solution of EB followed by an anodic oxidation step. However there were distinct differences in the EQCM response for these electrodes indicating a non-innocent role for the 9-aminoacridine or TTF donor species.

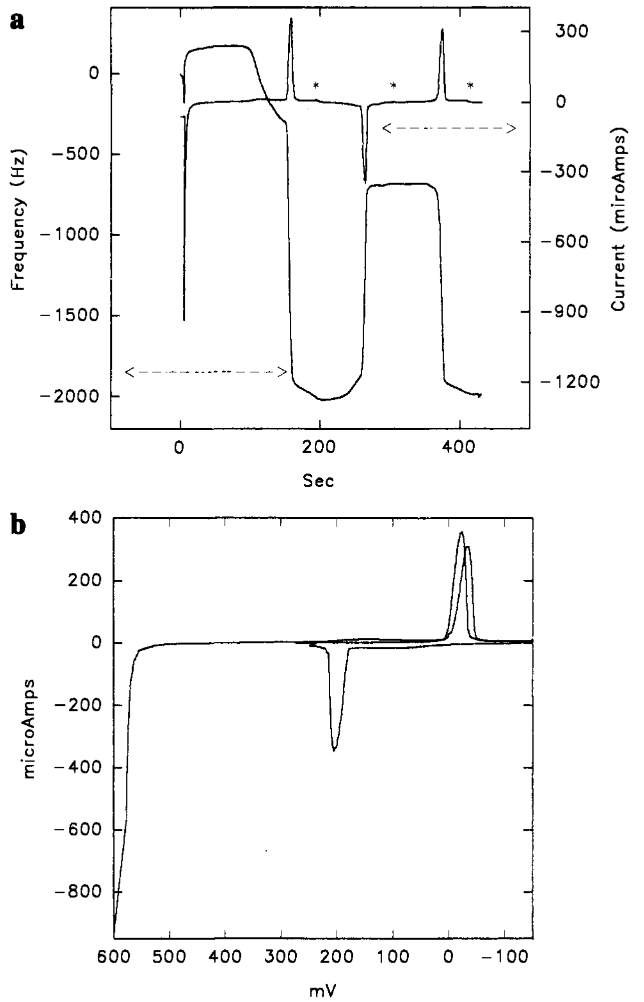

Figure 1. (a) Cyclic voltammogram and frequency response for the break-in of a 9-AA–TCNQ$_2$ film in pH 7.4 HEPES buffer containing 0.1 M NaCl. Sweep rate = 5 mV/s. Sweep range: 600 → −150 ↔ 350 mV. E_{sw} is marked by *. (b) i-time data in conventional CV format.

Films Prepared from 9-Aminoacridinium(TCNQ)$_2$. Figure 1 shows the EQCM response for activation and subsequent redox cycling of an electrode coated with a 0.20 μm film of **1** in contact with pH 7.4 HEPES buffer. The behavior is entirely analogous to that reported previously for generation of TCNQ films from this compound in a simple unbuffered electrolyte solution of Ca(OAc)$_2$ or KOAc at moderate concentration. The cathodic peaks (positive current) are assigned to reduction of TCNQ and insertion of counterions, and the anodic peaks are due to oxidation of the lattice anions coupled to the ejection of counterions. The large frequency transient coincident with the initial *reduction* of the activated lattice (at t ≈160 s in Figure 1) is attributed to hydration and/or surface structural changes that increase the viscous drag at the interface. After activation and cycling between the TCNQ(0/1−) oxidation states, the apparent equivalent mass calculated from the charge and frequency transients was large, 184 ± 7, consistent with transfer of solvent and counterions (presumably Na(H$_2$O)$_n$$^+$) during the redox process.

After treatment of the reduced electrode with 0.01 M EB (see the Experimental Section), the EQCM response in fresh pH 7.4 buffer solution was dramatically attenuated. As seen in Figure 2, after a single cycle, both the peak currents and the corresponding frequency transients were less than 10% of the initial values, indicating that the electrode surface was passivated by the EB treatment. A quantitative measure of the extent of passivation is given by the coulometric charge for either the cathodic or anodic process after the EB treatment, which was ca. 9% of the initial value. In Table 1 these values are denoted as Q_{pass}. The surfaces remained passivated under continuous

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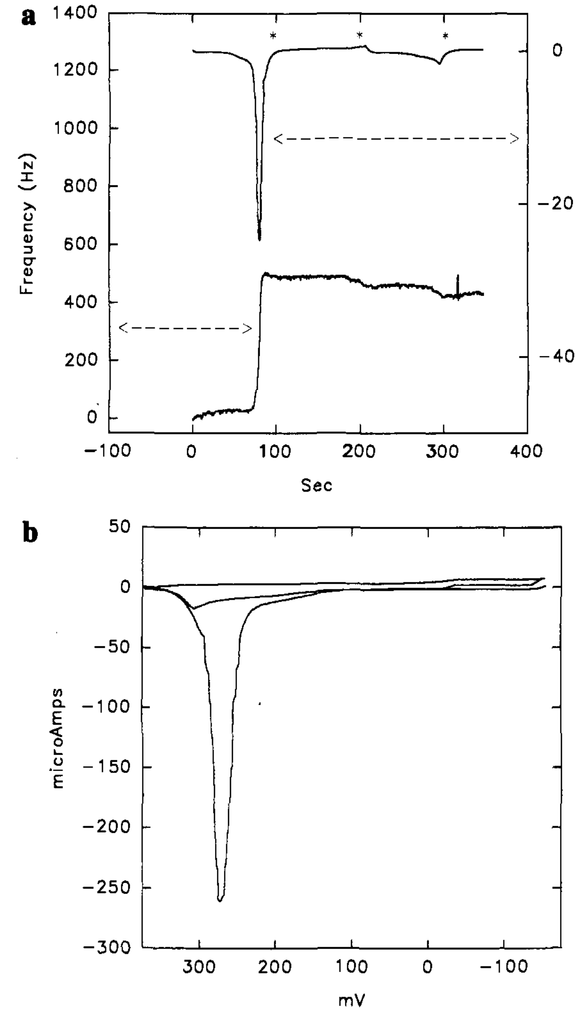

Figure 2. (a) CV and frequency response for the film in Figure 1 in pH 7.4 HEPES buffer after exposure to 0.01 M ethidium bromide. Sweep rate = 5 mV/s. Sweep range: −150 ↔ 400 mV. (b) *i*-time data in conventional CV format.

Table 1. Coulometric Measurements for the TCNQ(0/1−) Redox Process at Modified Conducting Salt Electrodes

film no.[a]	Q_{init}, mC[b]	Q_{ej}, mC[c]	Q_{pass}, mC[d]	Q_{react}, mC[e]
1 (from **1**)	0.55	0.39 (71%)	0.03 (5%)	
2 (from **1**)	0.670	0.57 (85%)	0.02 (3%)	0.50 (75%)
3 (from **1**)	1.24	1.00 (79%)	0.09 (7%)	0.53 (42%)
4 (from **1**)	1.63	1.53 (94%)	0.19 (12%)	0.98 (60%)
5 (from **1**)	2.24	2.13 (95%)	0.31 (14%)	0.65 (29%)
AVE (compd **1**)		85 ± 10%	8.2 ± 4.7%	52 ± 20%
1 (from **2**)	0.88	1.02 (105%)	0.17 (19%)	0.34 (39%)
2 (from **2**)	1.09	0.95 (87%)	0.036 (3.3%)	0.78 (71%)
3 (from **2**)	1.27	1.36 (107%)	0.158 (12%)	0.42 (33%)
4 (from **2**)	2.23	2.42 (108%)	0.044 (2%)	1.04 (47%)
5 (from **2**	3.60	4.89 (136%)	0.33 (9.2%)	1.32 (36%)
AVE (compd **2**)		109 ± 18%	9 ± 7%	45 ± 15%

[a] Electrode area = 0.348 cm^2. [b] Charge for the anodic process after activation and two or three redox cycles. [c] Total anodic charge after treatment with 0.01 M EB. [d] Anodic charge after passivation was complete. [e] Maximum anodic charge after treatment with DNA solution and subsequent redox cycling.

cycling in the absence of EB in the HEPES buffer solution. Furthermore, after 24 h in fresh buffer solution containing no EB, the EQCM response of the passivated electrodes did not change.

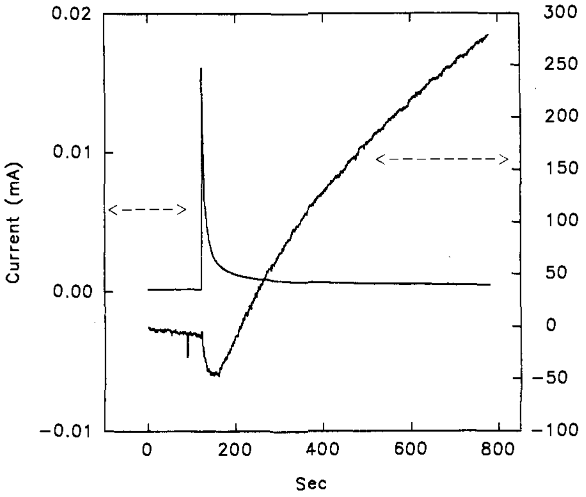

Figure 3. Current and frequency response of a reduced 9-AA−TCNQ$_2$ film dosed with 0.01 M ethidium bromide at a potential of −150 mV.

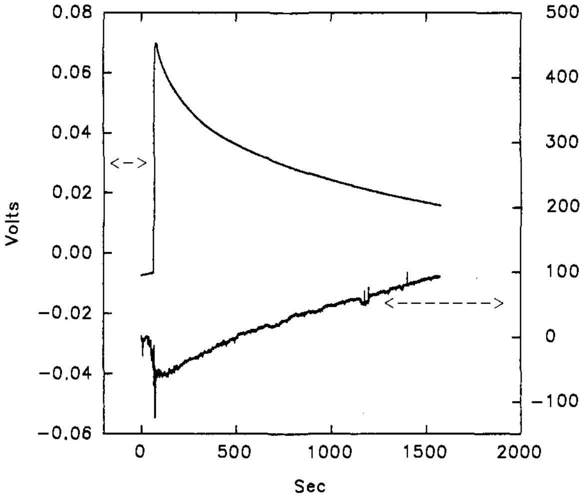

Figure 4. Potential and frequency response of a reduced 9-AA−TCNQ$_2$ film dosed with 0.01 M ethidium bromide at an open circuit.

Details of the passivation mechanism were revealed by a combination of voltammetry and EQCM experiments. Treatment of the reduced film with 0.01 M EB solution, at either an open or closed circuit, produced a complex response. See Figures 3 and 4. In both cases, the initial QCM frequency decrease, which was coincident with the dosing of the electrode surface, was followed by a slow frequency increase. (Control experiments with blank solutions containing no EB showed spikes in the frequency transients with a duration of less than 1−2 s that were associated with the mixing process. The spikes evident in the frequency responses in Figures 3 and 4 are attributed to this phenomenon.) The initial frequency decrease in Figs 3 and 4 is attributed to an ion exchange of surface counterions (Na$^+$ in this case) for ethidium cations.

$$A^-M^+_{\text{surf}} + Et^+ \rightleftarrows A^-Et^+_{\text{surf}} + M^+ \qquad (1)$$

After the initial ion exchange, there was an apparent slow solvent loss and/or surface restructuring associated with the long-time frequency transients seen in Figures 3 and 4. This process can be understood in view of the relative hydrophobic character of the ethidium and sodium cations.[13−16] It is also likely that the hydrophobic nature of the ethidium-modified surface significantly disrupted the hydrogen bonding structure at the surface. (An alternative interpretation that the frequency

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[13] Ethidium is well-known to occupy a hydrophobic pocket in an intercalation complex with DNA.[7b,14−16]

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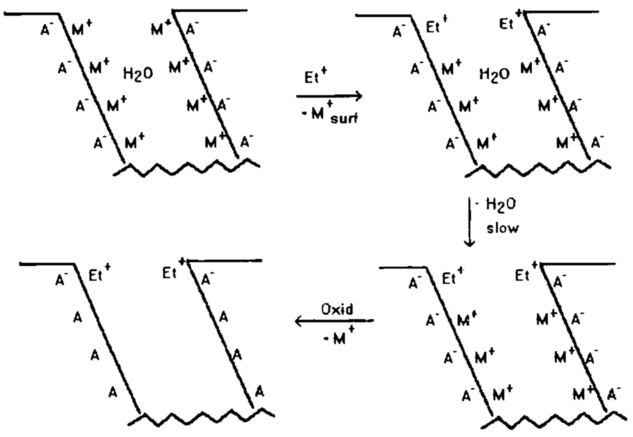
Scheme 1



increases were due to loss of TCNQ species is unlikely in view of the insolubility of the ethidium−TCNQ salt.[17]) The positive, open-circuit potential transients seen upon dosing the reduced films with 0.01 M EB are consistent with a charge-transfer interaction between the ethidium cation and the anionic surface sites. The current (or charge) transients seen in these experiments, which are small relative to the initial peak currents or charge under the peaks in the CVs of the activated films, were probably due to oxidation of neutral surface sites produced by air oxidation of the $TCNQ^-$ in the dosing procedure.

After treatment of the reduced films with 0.01 M EB, the EB solution was removed and replaced with fresh buffer solution. The initial positive potential sweep at these electrodes produced an anodic wave at $E_{pk} = 0.29$ V vs SCE (vs 0.22 V for the untreated electrode) that was coupled to a frequency increase indicating loss of cations and/or solvent molecules (see Figure 2). Often the electrodes were almost completely passivated in the −200 to 600 mV vs SCE range after one pass through the oxidation wave. In some cases, subsequent cycles showed further mass loss coupled to frequency increases in the region of the oxidation wave. The total charge under these waves (denoted Q_{ej} in Table 1, where the subscript ej implies ejection of counterions) was 85% (average of six trials), and the apparent equivalent mass estimated from the frequency transient was 70 ± 14 g $equiv^{-1}$.

The above EQCM response of the ethidium-modified electrodes indicates that unidirectional ion motion is operative at these surfaces. Prior to treatment with EB, migration of the cation in and out of the film balances the electron flow; after modification, cations are free to exit the film during the anodic step but are blocked from entering the film in the reduction step. This behavior is rationalized by Scheme 1, in which ethidium cations exchange for surface sites to form an hydrophobic barrier to ion motion. Upon oxidation, the counterions that are located in subsurface sites or channels between crystallite particles are driven out of the film in the oxidation step.

Films Prepared from TTF−TCNQ. EQCM of the oxidative lattice activation of films prepared from **1** was performed according to the activation protocol of Jaeger and Bard.[1] The initial frequency transient (see Figure 5), which indicated extensive hydration of the lattice coincident with uptake of anions from the solution, was followed by an EQCM square wave pattern indicating facile ion motion in and out of the surface film when the electrodes were cycled between the A(0/1−) oxidation states. At slow sweep rates, a square wave EQCM pattern was seen, indicative of a global equilibrium in the context of the Hillman and Bruckenstein theory.[18] The magnitude of the charge under the surface voltammetric waves was directly related to the amount of oxidative charge consumed in the activation step: $Q_{init} = 0.30Q_{latt} + 0.02$, where Q_{latt} is the charge in millicoulombs consumed in the activation process ($r = 0.91$). The apparent equivalent mass for the activation step was 73 ± 22. It is tempting to assign this process to lattice oxidation and incorporation of acetate counterions; however, in the view of Jaeger and Bard,[2] activation of TTF−TCNQ surfaces in 1 M KOAc took place via formation of soluble donor cations.

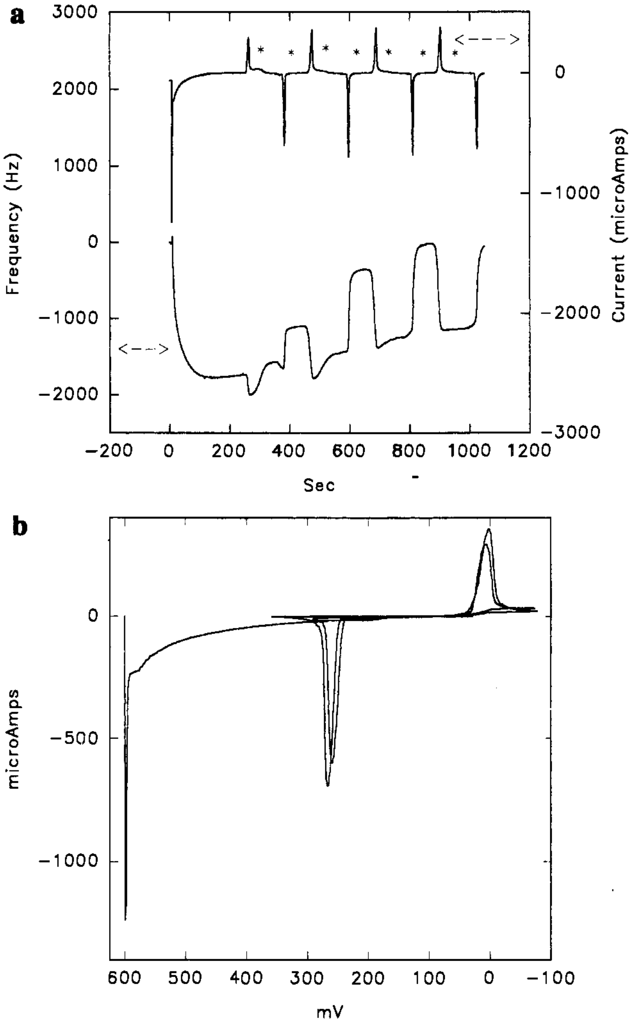


Figure 5. (a) Cyclic voltammogram and frequency response for the break-in of a TTF−TCNQ film in 1 M KOAc. Sweep rate = 5 mV/s. Sweep range: 600 → −50 ↔ 350 mV. E_{sw} is marked by *. (b) *i*-time data in conventional CV format.

In Table 2, the EQCM parameters for the TCNQ(0/1−) couples generated from the two conducting salts are compared. In general, the behaviors are quite similar, although the voltammetric waves generated from the TTF−TCNQ salt are somewhat narrower than those generated from the 9-aminoacridinium salt.[19,20]

Exposure of a reduced TTF−TCNQ film to the 0.01 M EB solution as for the films derived from **2** produced a complex result; see Figures 6 and 7. For these films, however, the frequencies and potential transients were opposite in sign to

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Table 2. EQCM Voltammetry of TCNQ(0/1−) Films Generated from Conducting Salt Electrodes[a]

	reduction		oxidation		
electrode	E_{pk} (mV)	FWHM (mV)	E_{pk} (mV)	FWHM (mV)	equiv mass (D)
1(init)[b]	−48 ± 9	27 ± 3	223 ± 3	31 ± 4	184 ± 7
1(ej)[b]			292 ± 15	46 ± 10	70 ± 14
1(react)[b]	−55 ± 20	30 ± 5	240 ± 30	35 ± 6	25 ± 3
1(init)[c]	3 ± 3	23 ± 4	226 ± 5	27 ± 4	101 ± 13
2(init)[d]	25 ± 6	21 ± 3	277 ± 6	18 ± 3	142 ± 26
2(ej)[d]			331 ± 16	55 ± 9	18 ± 8
2(react)[d]	10 ± 11	22 ± 4	240 ± 16	30 ± 5	24 ± 11

[a] Sweep rate = 5 mV/s. init: after activation and redox cycling. ej: after treatment with 0.01 M EB. react: after exposure to DNA solution. [b] TCNQ film prepared from **1** in pH 7.4 HEPES buffer and 0.1 M NaCl. [c] TCNQ film prepared from **1** in 1 M KOAc. [d] TCNQ film prepared from **2** in 1 M KOAc.

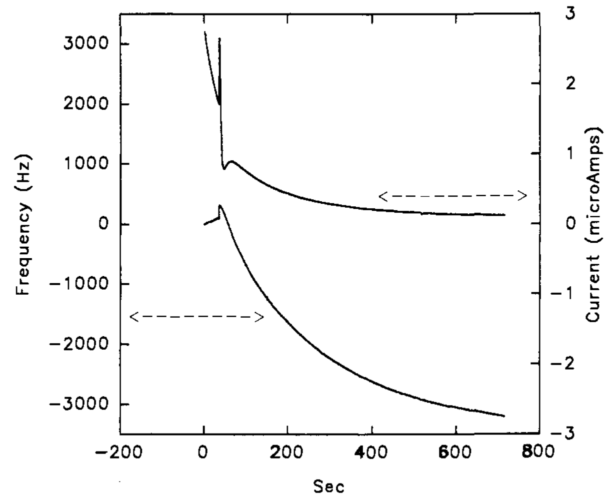

Figure 6. Current and frequency response of a reduced TTF−TCNQ film dosed with 0.01 M ethidium bromide at a potential of −52 mV.

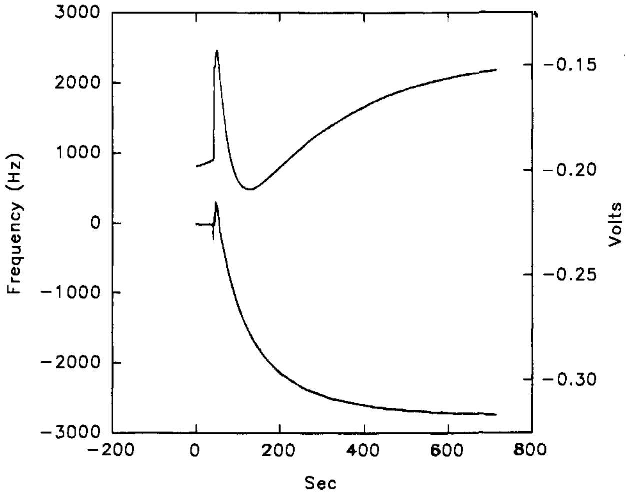

Figure 7. Potential and frequency response of a reduced TTF−TCNQ film dosed with 0.01 M ethidium bromide at an open circuit.

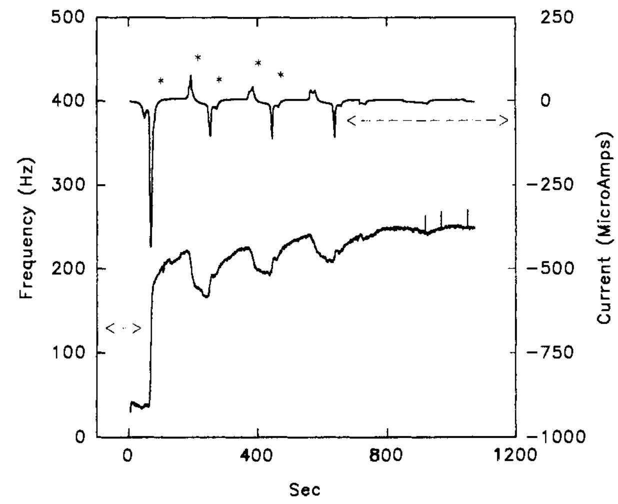

Figure 8. CV and frequency response for the film in Figure 5 in 1 M KOAc after exposure to 0.01 M ethidium bromide. Sweep rate = 5 mV/s. Sweep range: −100 ↔ 400 mV.

those of Figures 3 and 4 for films derived from **1**. The frequency initially increased sharply and then decreased significantly over a period of several hundred seconds to eventually reach a level several thousand hertz lower than prior to the EB treatment. The current transient shown in Figure 6, which is superimposed on a drifting background current, is much smaller than the voltammetric peak currents obtained on these electrodes before treatment with EB. The charge associated with this transient was much smaller than the value of Q_{init}. The open-circuit potential initially increased, as for films derived from **1**, but then displayed a complex behavior that featured a potential minimum at $t = 180$ s.

These frequency transients are understandable in terms of nucleation and growth of ethidium bromide crystals on the electrode surface. The frequency change of approximately 3000 Hz seen in Figures 6 and 7 would correspond to an ethidium bromide film of approximately 0.1 μm thickness in the absence of changes in the hydrodynamic properties of the interface.

The voltammetric response of these EB-treated TTF−TCNQ electrodes paralleled that of the films derived from **1**. Figure 8 shows the EQCM response of the electrode of Figure 5 after treatment with EB and reimmersion in the 1 M KOAc background electrolyte solution. On the first positive potential sweep, the anodic surface wave (which exhibited a small prewave in this case) was coupled to a 180 Hz frequency increase followed by progressively smaller waves on subsequent cycles until an almost completely passivated state was attained. This behavior can again be understood by postulating unidirectional ion motion, in this case through an ethidium bromide layer.

Values for the surface charges of these electrodes are collected in Table 1. The behaviors are similar for the films prepared from either of the two precursor salts. Both are passivated by the EB treatment to approximately 10% of the initial coulometric charge under the voltammetric waves. Furthermore, as discussed below, both films are reactivated to approximately 50% of the initial value by exposure to the DNA solution. Full restoration of the electroactivity would not be expected since the electrodes are probably coated with adsorbed species, including ethidium−DNA complexes, from the polynucleotide solution.

Furthermore an almost quantitative accounting of the charge in the passivation process is evident in the data. For the films derived from **1**, the value of Q_{ej} is 85% of the initial value. This observation is accounted for in Scheme 1 by the formation of an electroinactive ethidium−TCNQ complex on the electrode

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(19) It can be noted that the origin of the 0.26 V peak splitting seen in these voltammograms is not fully understood. For the related $TTFBr_{0.7}$ system, Henning et al. have proposed a square scheme involving solid state transformations to explain similar patterns.[20] The peak widths, which are considerably more narrow than expected for simple reversible surface waves, can be simulated with positive interaction parameters.

(20) (a) Henning, T. P.; White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 3937. (b) Henning, T. P.; White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1984**, *104*, 5862.

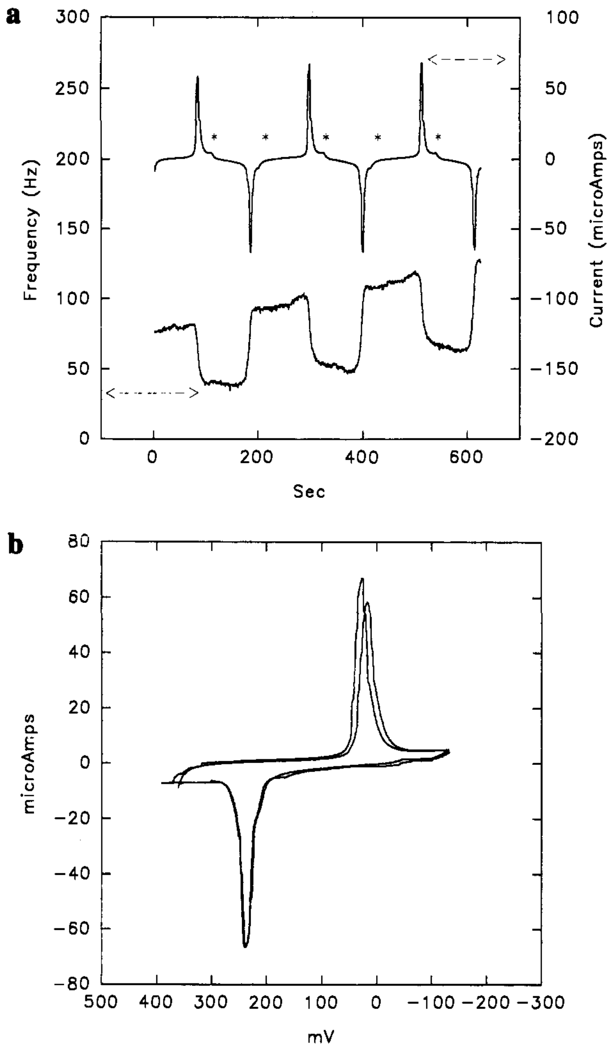

Figure 9. (a) CV and frequency response for the film in Figure 2 in a solution of 110 ppm DNA in pH 7.4 HEPES buffer. Sweep rate = 5 mV/s. Sweep range: 350 ↔ −150 mV. E_{sw} is marked by *. (b) *i*-time data in conventional CV format.

surface. This interpretation is further supported by the frequency decrease seen immediately after exposure of the electrodes to the EB solution. The decrease is consistent with ion exchange of surface cations for ethidium, i.e. eq 1. For films derived from **2**, the value of Q_{ej} is equal to Q_{init} within experimental error. This is consistent with nucleation and growth of an EB layer on the electrode surface and the transients of Figures 6 and 7.

Film Reactivation. Exposure of the passivated electrodes to dilute solutions of DNA dramatically restored the electroactivity of the TCNQ(0/1−) surface waves. This phenomenon is illustrated for a film derived from **1** in Figure 9, which shows the effect of a 110 ppm solution of herring testes DNA on the EQCM response. Upon replacement of the buffer solution with a DNA-containing solution, there was an immediate reactivation of both the voltammetric surface waves and the associated ion motion indicated by the square wave patterns in Figures 9 and 10. Control experiments without DNA in solution gave no indication of reactivation. In fact, as noted above, the EB-treated surfaces remained inactive for periods up to 24 h in the absence of DNA.

For the electrodes derived from **2**, which are presumably coated with a layer of EB, the reactivation generally required several potential cycles through the TCNQ(0/1−) waves; see Figure 10. These EQCM transients were obtained on the same electrode that produced the data of Figures 5 and 8. After approximately 12 cycles in this case, a maximum level of reactivation was achieved. (These values are given as Q_{react} in Table 1.) Approximately equal levels of reactivation were realized for the electrodes prepared from the two precursor salts.

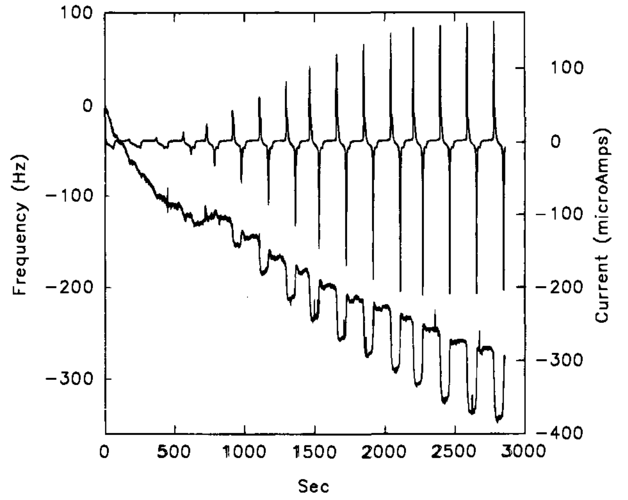

Figure 10. CV and frequency response for the film in Figure 8 in a solution of 100 ppm DNA and 250 mM KCl. Sweep rate = 5 mV/s. Sweep range: 350 ↔ −100 mV.

For the experiment of Figure 10, the square wave frequency pattern was superimposed on a frequency decrease of approximately 300−400 Hz. This behavior is possibly due to the rehydration of the film as it is cycled between redox states or to increased viscous drag or mass of adsorbed DNA−ethidium complexes. Analysis of the coupling of ion and electron motion at these ethidium-modified surfaces derived from **1** in the presence of DNA in pH 7.4 HEPES buffer using the Bruckenstein and Hillman description indicated that the interfaces were permselective to a cation with an apparent equivalent mass of 25 ± 3. This is much smaller than the value of 184 ± 7 calculated from the pattern obtained on the electrode before treatment with ethidium. Likewise, for the electrodes prepared from **2**, the apparent equivalent mass calculated from the frequency and charge transients in the presence of DNA was 24 ± 11, also much less than the initial value of 142 ± 26. These values suggest that there is very little solvent movement (either coordinated or free) in and out of the electrodes after exposure to the DNA solutions.

The exact role of the DNA in the activation (or "gating") mechanism is not fully understood. Presumably DNA complexes surface ethidium cations and possibly forms an adsorbed polyelectrolyte interfacial layer. While the EQCM response suggests that the coupled ion motion involved the transfer of a sodium ion (equivalent mass = 23) between the TCNQ electrode/hydrated DNA interface, further speculation is unwarranted in view of the complex viscoelastic properties of these interfaces.

Summary

Ethidium bromide modification of the surfaces of TCNQ conducting salt electrodes significantly decreased the electroactivity of the TCNQ(0/1−) redox process in aqueous electrolyte solutions. For films derived from 9-aminoacridinium(TCNQ)$_2$, the coulometric *Q*-values were consistent with a modification procedure involving surface ion exchange reactions. For activated surfaces derived from TTF−TCNQ, which presumably contained positive TTF$^+$ sites, growth of a surface film of EB was indicated. In both cases, unidirectional ion motion was observed upon subsequent EQCM voltammetry at the modified surface. The results can be understood by postulating that the ethidium surface layers provide a hydrophobic barrier to the transfer of cations in and out of the electrode surface. The ion motion at both passivated surfaces was sensitive to the presence of DNA in solution, which turned on (or "gated") the square wave EQCM pattern. The apparent equivalent masses calculated from the charge and frequency transients at the DNA-treated electrodes were significantly less than the values obtained at the unmodified surfaces.

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