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IN SITU POLARIZATION MODULATION–FOURIER TRANSFORM INFRARED SPECTROELECTROCHEMISTRY OF PHENAZINE AND PHENOTHIAZINE DYE FILMS AT POLYCRYSTALLINE GOLD ELECTRODES

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Abstract—Polarization modulation–Fourier transform infrared (PM-FT*ir*) spectra were obtained *in situ* for polymer films of neutral red and thionine, and for a film of leucomethylene blue generated on a gold electrode as a function of potential. The spectra of the polymer films revealed that the aromatic rings lie mostly parallel to the electrode surface in both the reduced and oxidized forms. In contrast, the spectrum of the adsorbed leuco methylene blue film indicated that most of the molecules within the film are oriented perpendicular to the gold surface.

Key words: neutral red, thionine, methylene blue, spectroelectrochemistry, PM-FT*ir*.

INTRODUCTION

In the last decade, chemically modified electrodes that employ thin films of photoactive dyes on metal and semiconductor surfaces have been used in the formation of a variety of photogalvanic cells, electrochromic devices, photo-electrocatalytic surfaces and chemical sensors[1–13]. In particular, electrodeposited films of dyes belonging to the phenothiazine, phenoxazine and phenazine families are particularly easy to form, and have been utilized extensively[1]. The solution electrochemistry of the phenazine and phenothiazine dyes neutral red, thionine and methylene blue is reviewed in Fig. 1. Neutral red and thionine solutions can form polymer films on metal and semiconductor substrates if the electrode is held at potentials very positive of the dye's oxidation potential. At this point, radical cations are formed and polymerization takes place through the formation of secondary amine bridges[1, 2, 6]. Methylene blue does not exhibit the same polymerization behavior at positive potentials as the other two species because the molecule lacks the terminal primary amino groups[1]. The reduced form of the molecule, leucomethylene blue, does form an electroactive film on the electrode surface; however this film is unstable and redissolves when the electrode is removed from the potentiostatic control. This paper examines the molecular structure of these

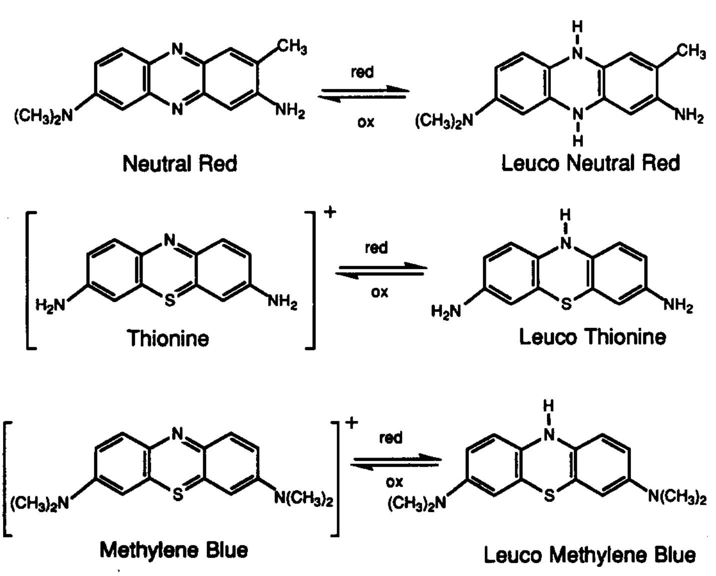

Fig. 1. Oxidation–reduction chemistry of neutral red, thionine and methylene blue in aqueous solution.

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three different dye films adsorbed onto polycrystalline gold electrodes as a function of potential *in situ* by the technique of polarization modulation-Fourier transform infrared (PM-FT*ir*) spectroscopy[14–30].

The technique of PM-FT*ir* spectroscopy has been previously applied to thin films and adsorbed monolayers at metal surfaces in both *ex situ*[17–21] and in *in situ*[22–30] experiments. To date, the majority of FT*ir* spectroelectrochemical measurements have employed a variety of potential modulation techniques to obtain the *ir* spectra of adsorbed species at metal electrode surfaces[31–35]. For *in situ* PM-FT*ir* measurements, a thin layer electrochemical cell identical to those employed in the potential difference FT*ir* measurements is employed[22]. The surface sensitivity of the PM-FT*ir* experiment arises from the strong polarization dependence of the electric fields at the electrode surface[36]. Only *p*-polarized light (light that is linearly polarized with its electric field vector in the plane of incidence) is present at the electrode surface in the *ir* region. This polarization dependence of the *ir* light at the interface results in the "surface selection rule" that vibrational modes with a transition dipole moment parallel to the surface will not be observed in the FT*ir* spectrum[37, 38]. Therefore, in addition to structural information the PM-FT*ir* measurements can yield information about the orientation of the film species with respect to the electrode surface.

2. EXPERIMENTAL SECTION

The working electrode used in these studies consisted of a polycrystalline gold plug, (99.99%, Englehard Corporation) that was 1.6 cm in diameter and 0.5 cm thick. A brass rod was silver-soldered to the back face of the plug; this assembly was then pressure-mounted into a virgin Teflon rod. Prior to each experiment, the gold surface was polished with progressively finer slurries of alumina (Buehler), down to 0.05 μm in order to obtain a mirror-like surface. After thorough rinsing and sonication to remove all alumina residues, the surface was briefly treated with a hydrogen peroxide–sulfuric acid mixture. The electrode was then further cleaned by cycling at 50 mV s^{-1} in a nitrogen-purged 0.25 M sulfuric acid solution until the characteristic voltammogram for a clean polycrystalline gold surface was obtained[39].

The thin layer spectroelectrochemical cell used in the PM-FT*ir* experiments was designed and constructed in this laboratory[40]. It is made of high-density polyethylene and provides for the placement of a saturated calomel electrode (*sce*) reference isolated from the solution compartment and of a platinum wire (99.9%, DF Goldsmith) which acted as the counter electrode. The cell was connected in a three-electrode configuration to a Princeton Applied Research Model 173 potentiostat/galvanostat controlled by a Model 175 universal programmer. All cell potentials are reported vs. *sce*.

The *ir* radiation reached the electrode through a 250 × 4 mm circular calcium fluoride window (Harrick Scientific). The cell design provides for flushing and for varying the distance of the electrode surface with respect to the calcium fluoride window. During the collection of the spectra, the electrode was placed at an average distance of 5 μm from the inner face of the window. The optical setup consisted of a Mattson Instruments Cygnus 100 FTIR spectrometer modified as described previously[15]. The angle of incidence of the beam with respect to the normal of the outer face of the calcium fluoride window was 60°. All spectra were taken at a resolution of 2 cm^{-1}. The differential reflectance spectra were obtained from the ratio of a sample (difference) and a background (sum) file; each file contained between 800 and 1000 interferometer scans that were collected in alternate blocks of 64[40]. Because the PM-FT*ir* technique was employed, no background spectrum of a reference sample was needed in these measurements. The differential reflectance spectra (%$\Delta R/R$) have been converted to absorbance units for comparison with other FT*ir* measurements.

Methylene blue obtained from Kodak was used after recrystallization from ethanol/water solutions. Thionine acetate and neutral red were of puriss grade (Fluka) and were used without further purification. The mid-*ir* transmittance spectra from 1250 to 1700 cm^{-1} of neutral red, thionine and methylene blue in KBr pellets are shown in Fig. 2a, b and c, respectively. The assignments of the most intense bands are summarized in Table 1. The water employed for all solutions was Millipore-filtered and then doubly distilled in glass from a $KMnO_4$/NaOH solution and then from sulfuric acid (Fluka). The sulfuric acid used in the electrochemical experiments was obtained from GFS and was of reagent (ACS) grade. All other chemicals were of Fluka puriss

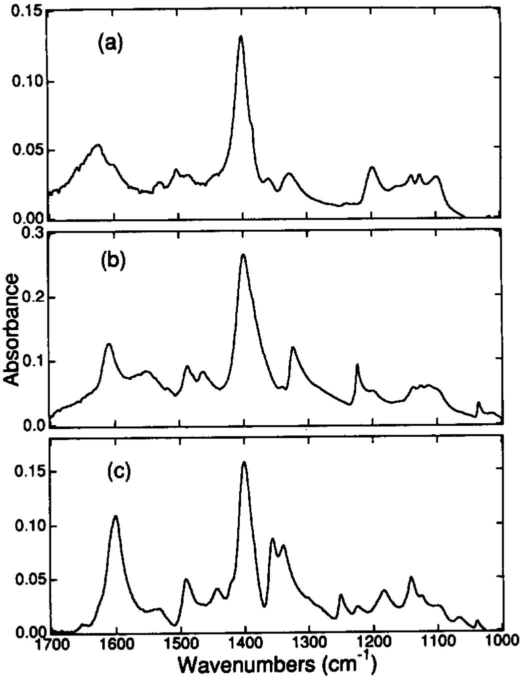

Fig. 2. FT*ir* transmission spectra of dyes in potassium bromide pellets: (b) neutral red; (b) thionine acetate and (c) methylene blue chloride.

Table 1. Infrared absorption frequencies (in cm^{-1}) and vibrational assignments for KBr pellet spectra of neutral red, thionine and methylene blue

Neutral red	Thionine	Methylene blue	Assignment	Reference
$1600 \pm 2 cm^{-1}$	1607	1599	Aromatic $\nu_{(C=C)}$	[42–43], [46–49]
1401	1398	1399	Conj. Rings $\nu_{(C-C)}$	[46–49]
1359	*	1356	Asym. $\nu_{(Ar-N)}$	[42–43]
1327	1321	1339	Sym. $\nu_{(Ar-N)}$	[42–43]

* Absorption was not observed.

quality. All solutions used in electrochemical reactions were purged with nitrogen.

3. RESULTS AND DISCUSSION

3.1. *Neutral red*

A neutral red film was formed by cycling the clean gold electrode in a bulk cell at $100 mV s^{-1}$ in a 147 μM dye solution that was also 1 M in Na_2SO_4; the solution pH was adjusted to 2.5 with H_2SO_4. Figure 3a shows the resulting cyclic voltammogram. The formation of the radical cation can be observed around 1.00 V. No reverse peak is seen for this wave, indicating that the radical cation has undergone a rapid chemical reaction[1]. The solution was continuously purged with nitrogen and stirred with a Teflon-covered magnetic stir bar. The limits of the electrochemical scan were −0.590 to 1.160 V. After approximately 300 cycles, the electrode was removed and rinsed with water. At this point the electrode surface presented an amber color upon inspection. The electrode was transferred to the spectroelectrochemical cell, which was flushed with a purged solution of 1 M HCl. Sodium sulfate was not used here as the supporting electrolyte because the $HO-SO_3^-$ stretch at $1190 cm^{-1}$ interfered with the observation of the bands of interest. Integration of the voltammogram in HCl for this film yielded a surface charge density of $1197 \mu C cm^{-2}$. This charge density can be associated with an approximate surface covering of 37 monolayers if a monomer area of $1 nm^2$ (the

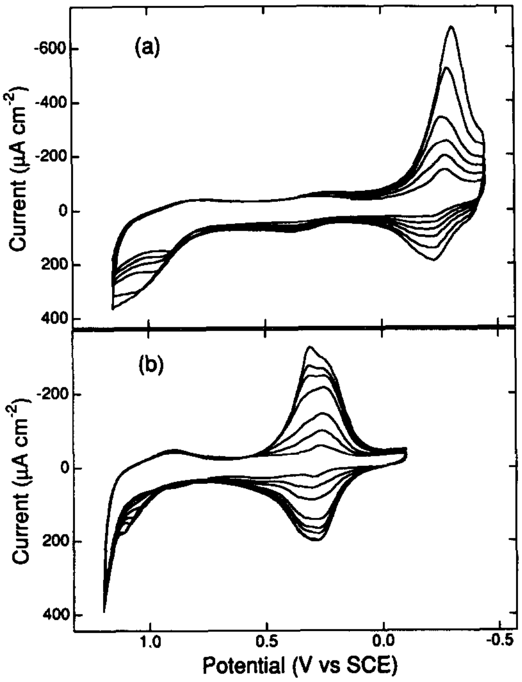

Fig. 3. Electrochemical polymerization of dyes on a gold surface. Convection was provided by mechanical stirring and a nitrogen purge. Scan rate, $100 mV s^{-1}$: (a) 147 μM neutral red, 1 m Na_2SO_4, pH adjusted to 2.5 with H_2SO_4; (b) 89 μM thionine acetate, 1 M H_2SO_4.

Table 2. Infrared absorption frequencies (in cm^{-1}) and vibrational assignments for the *in situ* PM-FT*ir* spectra of leuco neutral red, thionine, leuco thionine and leuco methylene blue films on a polycrystalline gold electrode

Leuco neutral red	Leuco thionine	Thionine	Leuco methylene blue	Assignment	Reference
*	*	*	1607	Arom. $\nu_{(C=C)}$	[50]
*	1507	1507	N/A	Bridge $\gamma_{(N-H)}$	[41–43]
$1490 \pm 2 cm^{-1}$	1483	N/A	1504	Ring $\gamma_{(N-H)}$	[41–43]
N/A	N/A	N/A	1442	Sym. $\delta'_{(methyl)}$	[42]
*	*	1396	*	Conj. Rings $\nu_{(C-C)}$	[46–49]
*	1321	1321	1307	$\nu_{(Ar-NR)}$	[42]
*	*	*	1260	$\nu_{(Ph-N-PH)}$	[27]

* Absorption was not observed.

N/A Absorption does not apply to this molecule.

approximate size of a monomer unit lying flat on the electrode surface) is assumed.

PM-FT*ir* differential reflectance spectra of the chemically modified electrode were collected at electrode potentials of 0.160 and −0.340 V. The spectrum obtained at −0.340 V (Fig. 4a) shows only one absorption at 1490 cm^{-1}; no bands were observed for the film at 0.160 V. The absorption observed for the reduced polymer film is assigned to the N–H bending vibration of the ring heteroatoms (Table 2)[41–43]. The fact that no bands are observed for the oxidized film is attributed to the *ir* surface selection rules, and suggests that the neutral red monomer units are lying flat on the electrode surface. In the reduced form, the three-ring unit of the neutral red assumes a "puckered" configuration when the double bonds on the ring heteroatoms are reduced. This puckering apparently leads to a change in film structure that results in the observation of the N–H bending vibrations.

Even though this experiment is carried out at a very low pH, the frequency of the NH bands imply that the ring amino groups are not protonated[42–43]. This can be explained by the fact that amino groups bridging aromatic rings have a markedly decreased basicity with respect to other secondary amines. For example, the K_b of diphenylamine is 6.16×10^{-14}, whereas for diethylamine the corresponding value is 3.01×10^{-4}[44]. This argument is further supported by the observation that nitrogen heteroatoms in these heterocyclic molecules are not very reactive to electrophilic attack[45].

3.2. *Thionine*

The thionine film was prepared in a manner similar to the neutral red film from a 89 μM dye solution in 1 M H_2SO_4. Figure 3b depicts the voltammogram corresponding to the polymerization. After rinsing, a dark purple film was visible on the gold surface. The electrode assembly was transferred to the spectroelectrochemical cell, where 1 M HCl acted as the supporting electrolyte. A surface coverage of 69 monolayers was estimated from integration of the voltammogram in HCl (again assuming a monomer area of 1 nm^2) from an integrated current of 2215 μC cm^{-2}.

PM-FT*ir* differential reflectance spectra were obtained at 0.400, 0.250 and −0.100 V (Fig. 4b). The assignments for the absorption bands are summarized in Table 2. The spectrum of the oxidized form of the film has bands at 1507, 1396 and 1321 cm^{-1}. These have been identified, respectively, as the N–H bend of the bridging amino groups, a ring vibration mode and the Ar–N stretch. Both the 1396 and the 1321 cm^{-1} absorptions in this film are observed in the pellet spectrum (Fig. 2b).

The 1321 cm^{-1} peak is also present in the reduced film, but the absorption at 1396 cm^{-1}, which corresponds to a ring stretching mode, disappears upon reduction as the conjugation (and planarity) of the ring system is lost. This band was assigned by correlation with the vibrational spectrum of phenazine [46] and of anthracene (the same three-ring system without heteroatoms)[47–49], both for which this band is the most intense absorption.

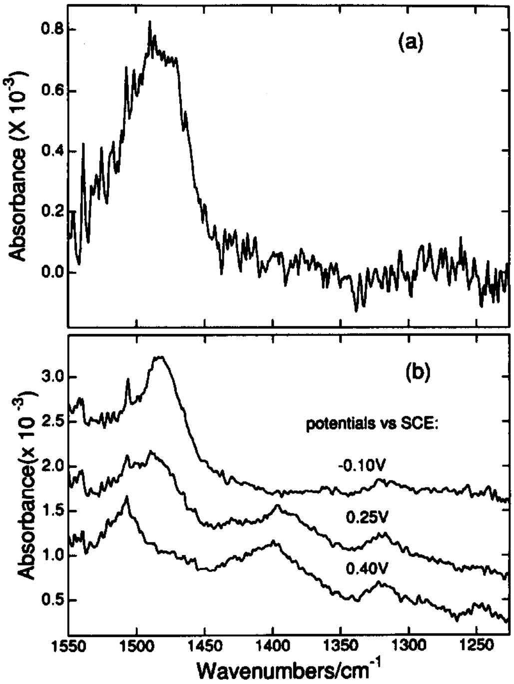

Fig. 4. *In situ* PM-FT*ir* spectra of films of polymerized dyes at a gold electrode. The electrode was coated by cycling in a dye solution (see text). After rinsing with water, the electrode was transferred to the electrochemical cell. Supporting electrolyte: 1 M HCl: (a) leuconeutral red film in, $E = -0.340$ V; (b) thionine/leucothionine film at −0.100 V (reduced film), 0.250 V (intermediate), 0.400 V vs. *sce* (oxidized).

The film in the reduced form has the same 1507 cm^{-1} signal as the oxidized form, with a second band growing on the side as the potential goes negative. This second absorption has a maximum at approximately 1483 cm^{-1}, and is attributed to the N–H bending of the ring heteroatom (analogous to the 1490 cm^{-1} peak for the leuconeutral red film). Similar to the neutral red film, the bridging secondary amino groups of the thionine polymer do not appear to be protonated either in the oxidized or reduced form.

3.3. *Methylene blue*

The electrochemical properties of leucomethylene blue film formation were first studied in a bulk electrochemical cell. A typical voltammogram is shown in Fig. 5a for a 103 μM methylene blue solution with 1 M NaF supporting electrolyte and a 0.05 M phosphoric acid buffer that was adjusted to a pH of 7.9 with NaOH. The leucomethylene blue films were formed by holding the electrode potential for a specified length of time at −0.500 V. The dissolution of the films was observed by scanning in the anodic direction. The resultant oxidation waves as a function of adsorption time are shown in Fig. 5b.

After 30 s of film formation, a dissolution wave was observed at −0.189 V. For longer generation times, this wave decreased at the expense of another that grew at a more positive potentials. After 5 min of film formation, no vestige of the original dissolution wave was detected, and the wave correspond-

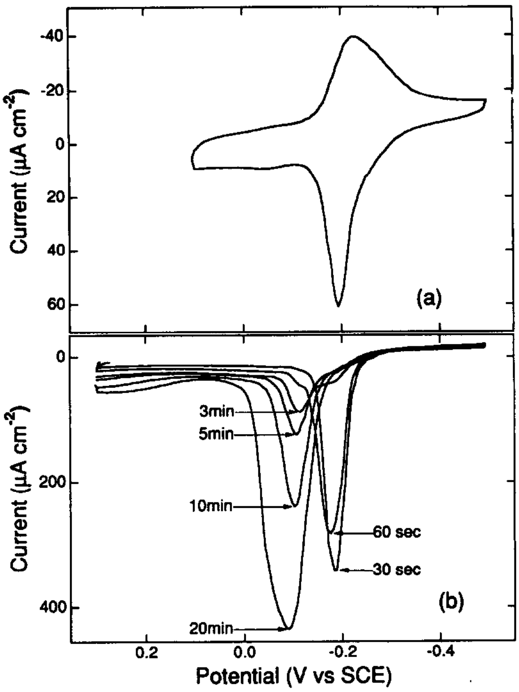

Fig. 5. Methylene blue electrochemistry at a polycrystalline gold electrode. 103 μM methylene blue, 1 M NaF, 0.05 M PO$_4^{-3}$, pH 7.9, 50 mV s^{-1}: (a) typical cyclic voltammogram; (b) stripping profile (scan rate = 50 mV s^{-1}) for leucomethylene blue films generated by holding the electrode potential at −0.500 V vs *sce* for 0.5–20 min.

ing to the new film continued to grow. The dissolution of this second surface species was observed at −0.091 V after 20 min of film generation. This behavior was also observed for this surface at a generation potential of −0.275 V. Since the first surface species was not stable for more than 30 s, only the more stable form of the film could be studied with the PM-FT*ir* measurements.

Leucomethylene blue films were prepared at an electrode potential of −0.500 V in the thin layer spectroelectrochemical cell by continued flushing of the methylene blue dye solution. A 91 µM dye solution was introduced into the thin layer cell with the electrode removed from the window by approximately 1 mm. This dye solution was replenished periodically by flushing. Growth of the films was terminated by replacing the dye solution with background electrolyte while maintaining potentiostatic control. The gold electrode was then brought up to the window to collect the PM-FT*ir* spectra. Dissolution of the leucomethylene blue films was studied by pulling back the electrode and scanning anodically at 15 mV s^{-1}.

Spectra of leucomethylene blue films were collected following generation times of 7.5, 15, 25 and 35 min, and are shown in Fig. 6. These spectra agree with our previous *ex situ* measurements of leucomethylene blue films[12], and indicate that this film consists solely of leucomethylene blue. The frequencies of the observed absorption maxima and the band assignments are listed in Table 2. The bands at 1607 and 1484 cm^{-1} have been assigned to stretching modes of the conjugated C=C bonds[50]. The strong band at 1504 cm^{-1} is analogous to the band observed at approximately 1490 cm^{-1} in the leuco forms of neutral red and of thionine, and is assigned to the N–H bending vibration of the ring heteroatom. The peak at 1442 cm^{-1} corresponds to the asymmetric deformation of the terminal methyl groups, and the absorption band below 1100 cm^{-1} as assigned to the phosphate ion from the buffer that appears to have been incorporated into the film.

The strong spectra of the leucomethylene blue films suggest that, unlike the neutral red and thionine films, the ring moieties in the leucomethylene blue multilayer are oriented perpendicular to the

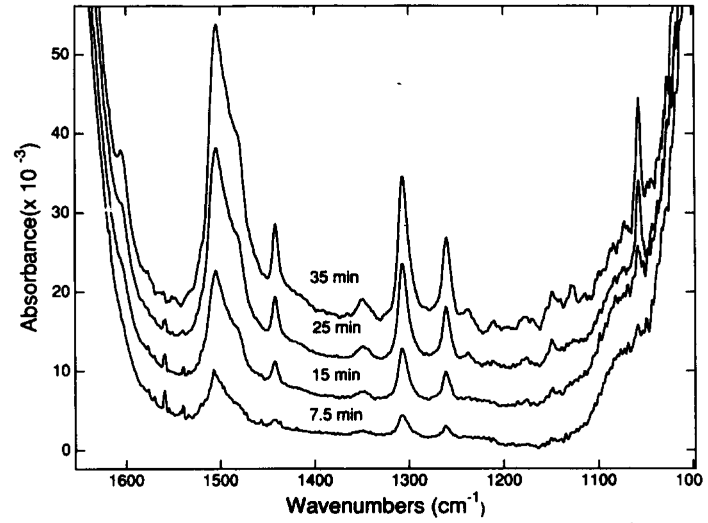

Fig. 6. *In situ* PM-FT*ir* spectra of leucomethylene blue films generated on a polyscrystalline gold electrode by holding the electrode potential at −0.500 V vs. *sce* for 7.5–35 min. The films were generated in the thin layer spectroelectrochemical cell from a 91 µM solution of methylene blue in 1 M NaF, 0.05 M H$_3$PO$_4$, pH 7.9. Film growth was halted by replacing the dye solution with purged background electrolyte while under potentiostatic control. See text for more details.

electrode surface. This molecular orientation is in agreement with the findings of previous electrochemical studies on leucomethylene blue at gold surfaces[8–12]. The thickest film in Fig. 6 corresponds to an observed surface charge density of $640\,\mathrm{mC\,cm^{-2}}$. Based on this assumption, a surface coverage of 13 monolayers can be calculated for the thickest film using a molecular area of $1\,\mathrm{nm}^2$[10].

4. CONCLUSIONS

In summary, PM-FT*ir* spectra were obtained *in situ* for polymer films of neutral red and thionine as a function of electrode potential, and for a film of leucomethylene blue generated on a gold electrode. Even though the polymer films were relatively thick, the observed spectral features were weak, implying that the monomers are oriented almost parallel to the electrode surface. The absorption bands for the N–H bending vibration suggest that the amino groups of these polymers are not protonated in spite of the acidic environment of the supporting electrolyte. Furthermore, the existence of secondary amino bridges between monomers in the thionine films has been confirmed with the N–H absorption band at $1507\,\mathrm{cm}^{-1}$. The spectral features of the leucomethylene blue film were more intense than those of the polymer films, even though the surface charge density was three to four times lower, due to the fact that the planes of the molecules are lying perpendicular to the electrode surface.

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