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Spectroscopic and Electrochemical Characterization of Polyaniline and a Ruthenium Complex, *mer*-[RuCl₃(dppb)(py)], in the Form of Langmuir–Blodgett Films

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Received August 20, 2001

Langmuir monolayers and Langmuir–Blodgett (LB) films have been produced from polyaniline and a biphosphinic ruthenium complex, referred to as Rupy. Strong, repulsive interaction between the two components led to a nonlinear change in area per molecule and surface potential with the concentration of Rupy in the mixed film. Molecular interaction was also denoted in the spectroscopic and electrochemical properties of the Y-type LB transferred films. The Raman spectra of mixed PANI–Rupy films indicated that the degree of oxidation of PANI increased linearly with the concentration of Rupy. With PANI being increasingly oxidized by presence of Rupy, the electroactivity of the mixed films decreased with the amount of Rupy, to become undetectable when the mixed LB film is 50% mol in Rupy. The presence of Rupy caused the electrical properties of the mixed LB films to be less sensitive to environmental changes. The electrical capacitance of a mixed film changed only by 15% when the sample was taken from vacuum to air, whereas the change was 215% for a pure PANI LB film.

Introduction

The production of new materials with tailored properties has been a challenge facing chemists, physicists, and materials scientists in general. The synthesis of macromolecules containing inorganic moieties is particularly interesting because one can combine the distinct properties of the two types of materials in a convenient way. The usefulness of conducting polymers, from the organic side, and of metallic complexes, on the inorganic side, has been largely demonstrated in separate endeavors, but a number of reports have appeared recently of supramolecular systems comprising polymers and metallic complexes. This has been done to investigate electroluminescent properties,^{1–6} as well as for electro-oxidation of alcohols for which modified electrodes have been fabricated from polypyrrole films incorporating monophosphinic ruthenium complexes.^{7–9}

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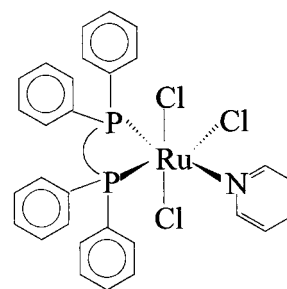
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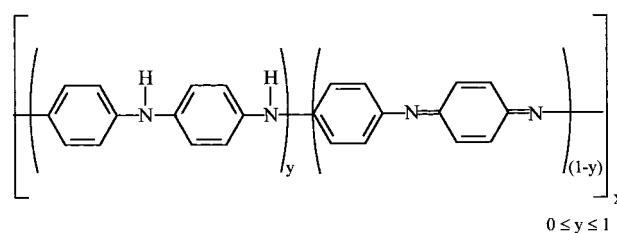
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(a)



(b)

Figure 1. Structure of Rupy complex (a) and PANI (b).

In this work, we investigate the film-forming characteristics and the electrochemical properties of a neutral biphosphinic ruthenium complex, viz. *mer*-[RuCl₃(dppb)(py)] (dppb = 1,4-bis(diphenylphosphino)butane, py = pyridine), Rupy for short, added into polyaniline (PANI) films. Figure 1 shows the structure of Rupy (a) and PANI (b). Films were prepared using the Langmuir–Blodgett (LB) technique, which allows a precise control over film thickness and molecular architecture. The aim of com-

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binning PANI with the ruthenium complexes is to enhance the properties of the polymer films for possible applications in electronic devices and sensors. We show that the presence of the Ru complex brings the transfer ratio close to one for the fabrication of LB films, similarly to the effect widely reported for fatty acids. In addition, we show that the electrical properties of the mixed PANI–Rupy LB films are much less sensitive to environmental changes than films from pure PANI. This has important implications for the use of PANI films in sensors of gases and taste. The distinct features of the mixed films arise from strong interaction between PANI and Rupy at the molecular level. We investigate this interaction for the Langmuir monolayers as well as for the transferred LB films. Various techniques are employed in this task: surface pressure and surface potential measurements for the monolayers, whereas the deposited LB films were characterized with FTIR and Raman spectroscopies, spectroelectrochemical and cyclic voltammetry measurements.

Experimental Details

Rupy was synthesized according to the procedures described in ref 10. PANI, in its emeraldine base form, was synthesized chemically using the now standard method.¹¹ PANI (1 mg) was dissolved in 1.3 mg of camphor sulfonic acid (CSA), 1 mL of *m*-cresol and 10 mL of chloroform, with the mixture being kept under sonication for ca. 2 h. This mixture was then filtrated to remove undissolved PANI, probably the higher molecular weight fractions. This solution could be stored for weeks without precipitation.¹² Rupy was dissolved in chloroform.

The Langmuir monolayers and LB films were produced with a KSV5000 Langmuir trough, housed in a class 10 000 clean room. Monolayers were spread onto acidic subphases, pH = 2, obtained from Millipore ultrapure water (resistivity 18.2 MΩcm) and HCl. All experiments were conducted at room temperature, approximately 22 °C. The PANI–Rupy mixed solutions with 10%, 30%, and 50% in mol of Rupy were prepared immediately prior to being spread. Monolayer compression was carried out at a barrier speed of 10 mm min⁻¹. Surface pressure and surface potential measurements were conducted with a Wilhelmy plate and a Kelvin probe, respectively, both provided by KSV. Stability tests were performed for the mixed PANI–Rupy and pure PANI films. The surface pressure was kept at 17 mN m⁻¹ while the time evolution of the area per molecule was recorded. For a period of 7 h, the area per molecule decreased only ca. 10%, which indicates good stability. Successive cycles of compression–decompression of the films were carried out. After only 2 cycles the films reached stability, with the pressure–area isotherms being the same in consecutive runs.

LB films were produced by transferring pure PANI and mixed PANI–Rupy monolayers onto ITO (indium–tin-oxide)-coated glass (Asahi Glass Co., Japan), quartz or silicon wafers (Aldrich). The typical dipping speed was 3 mm min⁻¹, with 30 min elapsing between the first and the second layer and 5 min for the subsequent layers when the substrate was out of the aqueous subphase. Y-type LB films were produced keeping the surface pressure at 17 mN m⁻¹ (PANI and mixed films) and 15 mN m⁻¹ (Rupy). All the films analyzed here contained 61 layers, with the exception of the films used in the atomic force microscopy (AFM) experiments, which had 41 layers. The transfer ratio (TR) for the mixed PANI–Rupy LB films was ca. 0.9 in the upstrokes and 0.8 in the downstrokes, whereas it was 0.8 and 0.6 for pure PANI LB film in the upstrokes and downstrokes, respectively. These values are averages calculated from all TR values found for each one of the 61 layers. For mixed, as well as pure PANI films, TR

tends to decrease slightly after 40 layers have been deposited. The thickness and roughness of the LB films were measured using AFM, with a Nanoscope IIIa from Digital Instruments. AFM images were obtained in the intermittent contact mode (i.e., tapping mode), employing a rectangular, oscillating silicon cantilever.

The LB films on silicon wafers were characterized by FTIR spectroscopy using a BOMEM MICHELSON FT, MB 102, in the 4000 to 300 cm⁻¹ range and 4 cm⁻¹ resolution (20 scans min⁻¹). UV–vis absorption measurements were carried out in a HITACHI U-2001 spectrophotometer in the range between 350 and 800 nm, for the LB films deposited onto ITO. These films were subjected to various electric potentials with a potentiostat–galvanostat FAC 2001. For LB films deposited onto quartz substrates, the absorption spectra were obtained in the range from 350 to 1600 nm. Cyclic voltammograms were obtained on LB films deposited onto ITO, using a potentiostat FAC2000 and a three-electrode electrochemical cell with 30-mL volume. The reference electrode was Hg/Hg₂SO₄/K₂SO₄(sat.), a 1.0 cm² platinum foil was used as auxiliary electrode and the working electrode was the LB film onto ITO. The experiments were conducted with a HCl 1 mol L⁻¹ solution. The Raman scattering spectra (Stokes) of LB films on ITO were recorded using a Renishaw Research Raman Microscope System RM2000 equipped with a Leica microscope (DMLM series). The 50×-microscope objective was used to focus the laser beam onto a spot of ca. 1.0 μm². The Raman spectrum was recorded using a Peltier cooled (–70 °C) CCD array detector and a spectrograph equipped with a 1200 g/mm grating, which allows collecting the spectra with ca. 4 cm⁻¹ resolution. The high throughput of the instrument permits the use of very low power lasers at the sample: 2 μW for the 780 nm, 450 μW for the 633 nm and 125 μW for the 514.5 nm laser lines. Raman data acquisition and analysis were carried out using the WiRE software for Windows and Galactic Industries GRAMS/32™ C software including the 3D package. The electrical capacitance was measured with a HP4263A LCR Meter at 1 kHz on LB films deposited onto interdigitated gold electrodes.

Results and Discussion

Langmuir Monolayers and LB Films from PANI–Rupy. For a systematic investigation of the mixed films, we also produced pure PANI and Rupy monolayers, where the latter are reported for the first time but the former have already been extensively characterized.^{13–24} Figure 2 shows the surface pressure isotherms of pure and mixed monolayers. In Figure 2a, the area per molecule at the condensed phase, extrapolated to zero pressure from the high-pressure part of the curve, is ca. 32 Å² for the Rupy monolayer. This is much smaller than expected for the molecule because the cross section for Rupy according to the CPK model using Hyperchem program is ~140 Å², indicating the formation of nonmonomolecular structures.

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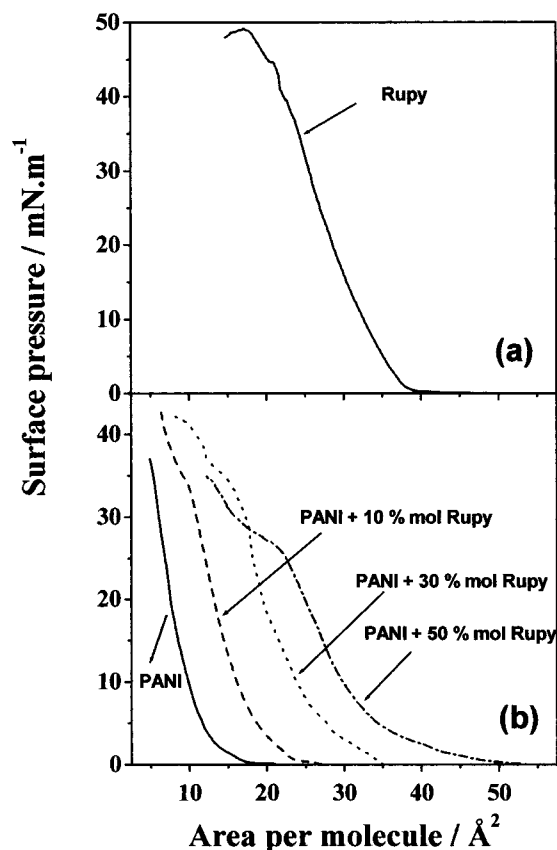


Figure 2. Surface pressure–area isotherms for pure Rupy on water subphase containing HCl (pH = 2) (a). Isotherms for the mixtures of PANI–Rupy and pure PANI spread on HCl (pH = 2) subphases, with the area per molecule being calculated per PANI monomer (b).

A similar behavior was observed for a related ruthenium complex.²⁵ For the mixtures, Figure 2b, we note that Rupy is added in the PANI monolayers, as the extrapolated area per molecule at the condensed phase increases from 12 Å² for pure PANI up to 38 Å² for the monolayer containing 50% mol of Rupy, whereas it is 20 Å² for 10% mol and 30 Å² for 30% mol of Rupy in PANI. Figure 3 indicates that there is a repulsive interaction between PANI and Rupy in the mixed Langmuir, which is denoted by the superlinear dependence of the extrapolated area on the Rupy concentration. Ideal additivity of the components should lead to a linear increase in the area per molecule.²⁶ The low area value (12 Å²) for pure PANI also suggests the formation of nonmolecular structures in the Langmuir films, similarly to what was observed for pure Rupy. Analogously to the surface pressure–area isotherms, the surface potential–area isotherms shown in Figure 4b were shifted to higher areas per molecule when the Rupy concentration increased. The surface potential is not zero for large areas per molecule due to the formation of aggregates. This occurred when higher volumes were spread in order to record both surface pressure and surface potential isotherms simultaneously. It is a known property of the majority of polymer monolayers.^{12–14} Surface potential isotherms are reproducible for small areas per molecule, but show dispersion at large areas per molecule when aggregates are present. As shown in Figure 4b, the maximum surface potential, observed for condensed monolayers, increased from about 400 mV for pure PANI

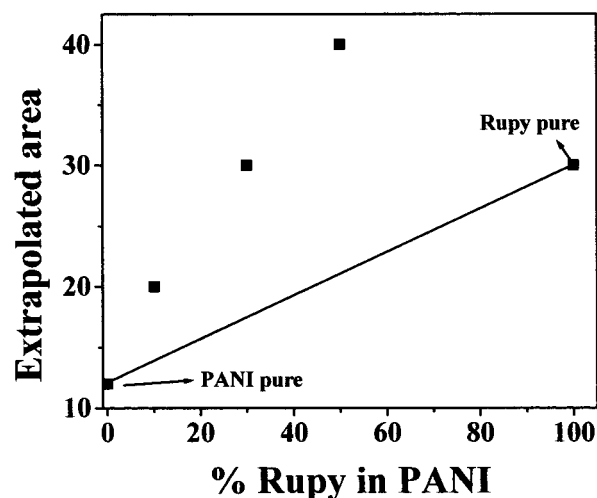


Figure 3. Extrapolated area for the various Langmuir films versus %mol of Rupy in the film. The values 0 and 100%mol represent pure PANI and pure Rupy, respectively. The linear plot corresponds to the expected behavior for immiscible components.

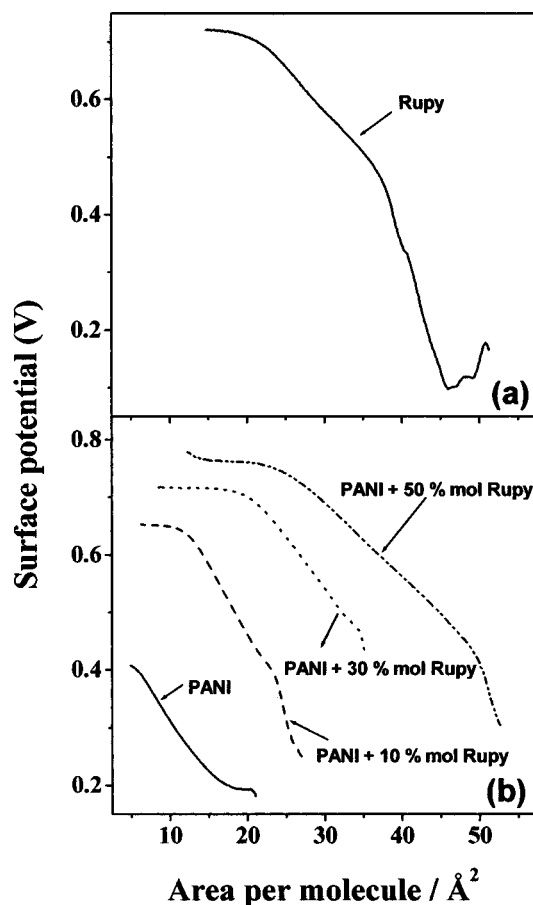


Figure 4. Surface potential–area isotherms for pure Rupy on water subphase containing HCl (pH = 2) (a). Isotherms for PANI–Rupy mixtures and pure PANI spread on water subphase containing HCl (pH = 2), with the area per molecule being calculated per PANI monomer (b).

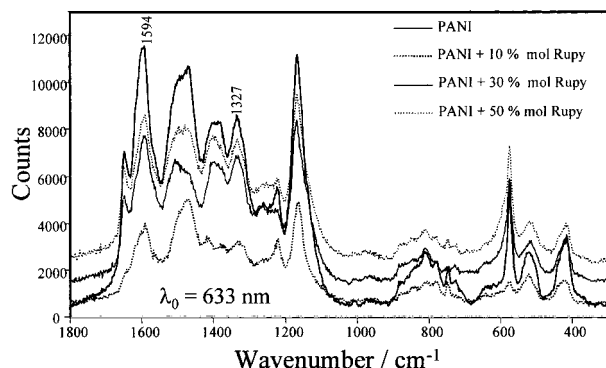
to 650, 715, and 770 mV for the mixtures containing 10%, 30%, and 50% in mol of Rupy, respectively. As shown in Figure 4a the maximum surface potential for pure Rupy monolayer was 720 mV (Figure 4a), and these values again point to interaction between PANI and Rupy. In this case, the interaction leads to a positive contribution in the dipole moment as the surface potential for the mixed films are

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Table 1. Thickness and Relative Roughness of 41 Layer Films of Pure and Mixed Compounds

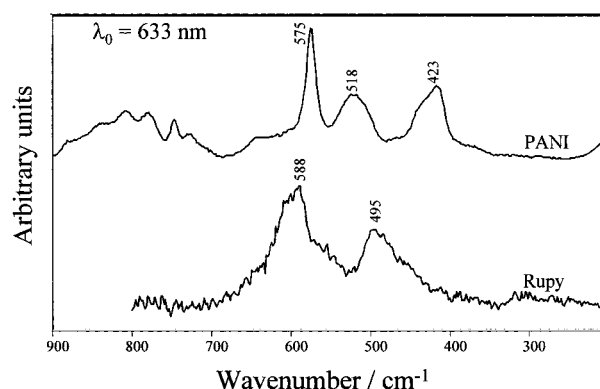
	PANI	Rupy	PANI-Rupy 10% in mol	PANI-Rupy 30% in mol	PANI-Rupy 50% in mol
thickness (nm)	60	40	38	42	71
roughness (% of thickness)	11	5	12	12	13

**Figure 5.** Resonance Raman spectra ($\lambda_0 = 633$ nm) of PANI, PANI + 10% mol Rupy, PANI + 30% mol Rupy and PANI + 50% mol Rupy.

higher than expected from a linear increase with the amount of Rupy. It must be stressed that a quantitative treatment of surface potential data cannot be made because it is not possible to estimate the dipole moment contributions from individual groups in macromolecular materials.

Characterization of PANI-Rupy LB Films. The transfer of LB films from PANI is known to require special precautions,¹² and the resulting films are normally Z-type LB films. The incorporation of Rupy improves transferability of PANI films considerably. Indeed, as indicated in the Experimental section upon introducing Rupy, the transfer ratio was increased and Y-type LB films could be produced. We compared the thickness and root-mean-square roughness of a series of 41-layer LB films, as obtained by AFM. Table 1 shows the results, which indicate that the interaction between PANI and Rupy caused the thickness to be much higher for the 50:50% mixture. The relative roughness of the mixed films was practically independent of the Rupy contents.

FTIR results (not shown) for LB films deposited onto silicon wafers showed the presence of both PANI and Rupy in the mixed LB films. However, the low relative intensity of the characteristic vibrational bands of Rupy, and band overlapping of PANI and Rupy components, did not allow us to extract relevant structural information. Infrared and Raman are complementary techniques for materials characterization. Raman scattering (RS) and resonant Raman scattering (RRS) spectra were measured with $\lambda_0 = 514.5, 633,$ and 780 nm laser lines, to further investigate the interaction between PANI and Rupy. Figure 5 shows the results obtained with the $\lambda_0 = 633$ nm laser line for LB films of pure PANI and of mixed PANI-Rupy with three distinct relative concentrations. Figure 5 shows the results obtained with the 633 nm laser line for LB films of pure PANI and of mixed PANI-Rupy with three distinct relative concentrations. Rupy presented a very weak Raman signal and its spectrum shown in Figure 6 was only recorded using the 633 nm laser line (RRS) and much more accumulations than that required for PANI. The Raman spectra show that the presence of Rupy only decreases the intensity of the Raman bands of PANI as

**Figure 6.** Resonance Raman spectra ($\lambda_0 = 633$ nm) of PANI and Rupy.**Table 2. Center (cm^{-1}), Full Width at Half Maximum (fwhm) (cm^{-1}) in Parenthesis and Relative Intensities (in *italic*) Obtained by Fitting with the Gaussian Function the Raman Scattering Spectra Recorded Using $\lambda_0 = 780, 633,$ and 514.5 nm Laser Lines for LB Film of PANI on ITO**

780 nm	633 nm	514.5 nm	assignments
1645 (17) <i>17</i>	1646 (23) <i>52</i>	1645 (14) <i>22</i>	stretching vibration of the benzene ring
1620 (16) <i>36</i>			
1592 (38) <i>79</i>	1594 (47) <i>98</i>	1605 (58) <i>100</i>	C-C benzenoid ring stretching
1508 (31) <i>46</i>			C=N and CH=CH stretching vibrations
1472 (39) <i>26</i>	1486 (62) <i>52</i>	1487 (56) <i>58</i>	
1382 (31) <i>59</i>	1392 (36) <i>23</i>	1406 (27) <i>14</i>	C-N-C and C=N stretch cation radical (C-N ⁺ stretching)
1325 (25) <i>33</i>	1327 (38) <i>36</i>	1328 (43) <i>29</i>	
1265 (11) <i>5</i>	1250 (37) <i>10</i>	1246 (38) <i>11</i>	C-N stretching
1226 (19) <i>22</i>	1222 (16) <i>21</i>	1220 (17) <i>14</i>	
1162 (45) <i>100</i>	1161 (41) <i>100</i>	1165 (40) <i>57</i>	C-N benzene-diamine
970 (24) <i>6</i>		961 (22) <i>3</i>	
857 (46) <i>20</i>			C-H out-of-plane
806 (46) <i>30</i>	820 (96) <i>19</i>	803 (123) <i>17</i>	
732 (32) <i>14</i>	726 (38) <i>7</i>		ring in plane deformation benzene radical
641 (33) <i>5</i>	621 (82) <i>6</i>		
575 (14) <i>39</i>	575 (15) <i>49</i>	571 (16) <i>11</i>	

can be seen in Figure 5. There is no significant shift of the Raman bands and no new bands are observed, which is the norm for weak "physical" intermolecular interactions. Such an effect is observed when the polarity around the Raman scatterer increases. For instance, the Raman scattering decreases when the ionic concentration increases in an electrolyte.

The assignment of the main peaks for PANI is provided in Table 2. The Raman assignment of polyemeraldine salts has been done by many authors; in this work we adopted the assignments of Furukawa et al.²⁷ and Lourn et al.²⁸ From Figure 7, one may note that the ratio between the intensities of the bands at 1327 cm^{-1} , a measure of the extent of oxidation of PANI, and at 1594 cm^{-1} , which is proportional to the amount of reduced PANI, increases with the concentration of Rupy. This is also confirmed by cyclic voltammetry as illustrated in Figure 8a. The increase in Rupy contents causes oxidation of PANI with the film containing 50% in mol of Rupy being more oxidized than the film of pure PANI. Such changes in the Raman spectra were also observed upon applying a potential on a PANI film.²⁹ The interference of Rupy in the oxidation state of PANI is also manifest in the cyclic voltammograms shown

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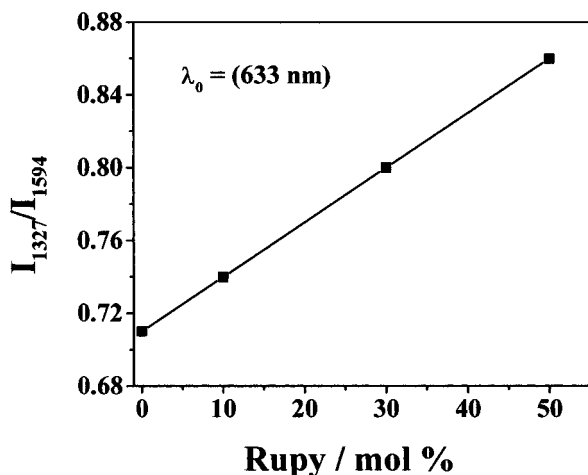


Figure 7. Change in the intensity ratio between the bands at 1327 and 1594 cm^{-1} , which denotes the degree of oxidation of PANI, as a function of the concentration of Rupy.

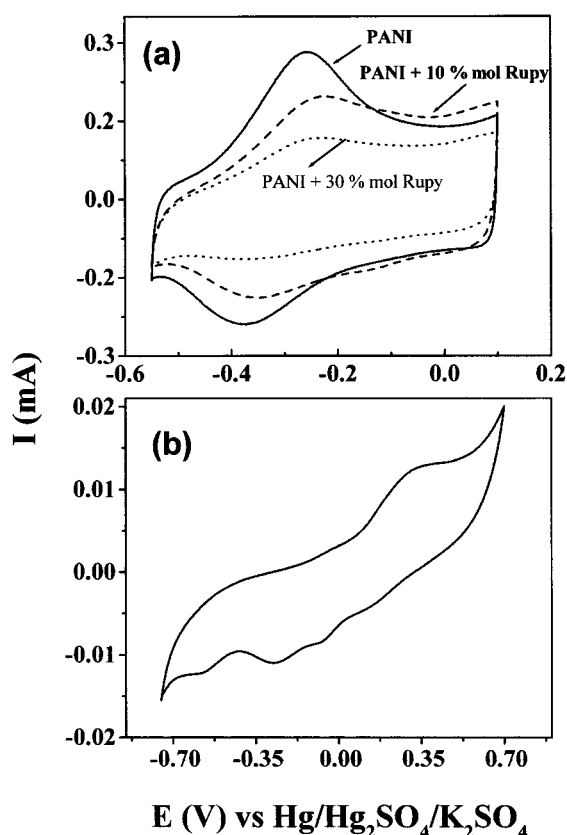


Figure 8. Cyclic voltammograms for LB films from PANI with a sweeping rate of 50 mVs^{-1} and mixed PANI–Rupy films (a) and Rupy with a sweeping rate of 100 mVs^{-1} (b). All measurements were carried with a HCl 1M electrolyte.

in Figure 8a, to be discussed below. The use of different laser lines was important because the resonance condition is achieved differently for the two components of the films. For instance, in the pure Rupy LB film detectable Raman scattering was only observed with the $\lambda_0 = 633 \text{ nm}$ laser line, as shown in Figure 6. The electronic absorption band of Rupy is showed in Figure 9. This laser line is in resonance with the electronic absorption band of Rupy, which gives the shoulder in 650 nm, in Figure 9, indicating that the UV–vis absorption band of Rupy (around 650 nm) is associated with the chemical groups responsible for the Raman bands at 588 and 495 cm^{-1} in Figure 6,

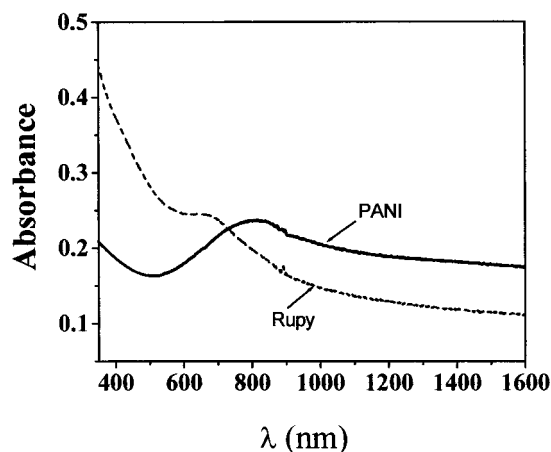


Figure 9. Electronic absorption spectra recorded for the pure LB films of PANI and Rupy on quartz substrates and no applied potentials.

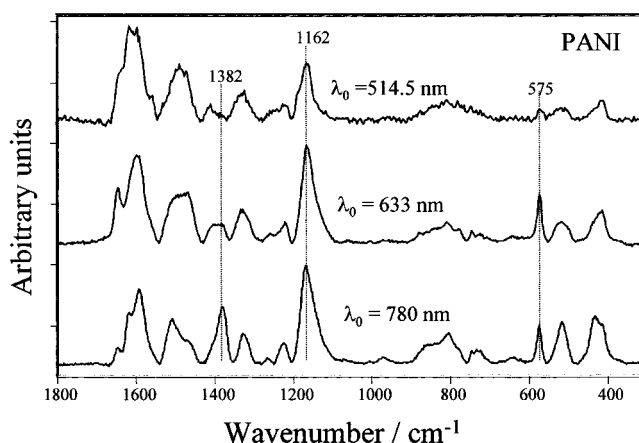


Figure 10. Resonance Raman spectra ($\lambda_0 = 514.5$, 633, and 780 nm) of PANI, with baseline correction.

probably due to Phosphor–Ru stretching.³⁰ Similar results were found for pure LB films of *mer*-[RuCl₃(dppb)(4-Mepy)] (dppb = 1,4-bis(diphenylphosphine)butane, 4-Mepy = 4-methyl-pyridine).³⁰ A similar analysis can be made for the LB film of pure PANI, whose Raman scattering spectra are shown in Figure 10. They were recorded using the $\lambda_0 = 514.5$, 633, and 780 nm laser lines, which are out of resonance, in preresonance and in full resonance with the absorption band at 800 nm showed in Figure 9, respectively. A change in intensity for the band at 1382 cm^{-1} , attributed to the $-\text{C}=\text{N}-$ stretching, is noted. It is stronger for the 780 nm laser line and vanished for the 514.5 nm laser line, thus confirming that the absorption band at 800 nm must be assigned to the quinoid species.²⁷ By the same token, the bands at 1162 and 575 cm^{-1} are assigned to the benzene ring, whose intensities decrease using the 514.5 nm laser line (out of resonance with the absorption band at 800 nm).

The addition of the ruthenium complex alters the electroactivity of the PANI LB film substantially. Figure 8a shows the voltammograms for LB films deposited onto ITO from pure PANI and mixed PANI–Rupy with 10% and 30% mol of Rupy. The film with 50% mol of Rupy did not display any electroactivity. The voltammograms were obtained with a sweeping rate of 50 mVs^{-1} in HCl 1 mol

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L⁻¹. For the pure PANI LB film, the redox pair corresponds to the interconversion between the oxidation states leucoemeraldine (insulating, transparent yellow) and emeraldine (conducting, green).³¹ As the amount of Rupy is increased, these peaks become less defined and the current drops. These results are consistent with those from Raman scattering discussed above, in that incorporation of Rupy causes PANI to become increasingly oxidized. As a result, for 50% mol of Rupy PANI is completely oxidized and displays no electroactivity. The electrochemical response of a pure LB film of Rupy is illustrated in Figure 8b, where an anodic peak is seen at 0.35 V while two less defined cathodic peaks appear at 0.28 and 0.58 V. The appearance of two reduction peaks, attributed to the redox Ru^{III}/Ru^{II} process, is explained by the strong interaction between the Rupy molecules in the LB film.²⁵ It should be stressed that the oxidation peak for ruthenium is at a higher potential than observed in the mixed films (Figure 8a), because in the latter films such a high potential cannot be reached, as the PANI-containing films possess a second irreversible oxidation peak at 300 mV.

The UV-vis absorption spectra of 61-layer LB films from pure PANI and pure Rupy on quartz substrates and no applied potentials are shown in Figure 9. For PANI, a broad band appears centered at 810 nm, which indicates that the partially oxidized PANI (emeraldine form) is doped, as one should expect because the monolayers were transferred from an acidic subphase. The pure Rupy LB film displays a band centered at approximately 660 nm. The spectral characteristics were investigated for LB films under applied electric potentials varying from -0.3 to 0.1 V, in the range between 350 and 850 nm on ITO. Figure 11a shows the results for pure PANI, with a shoulder at 425 and a tail reaching the maximum at ca. 800 nm. The spectra are taken up to 900 nm only due to the limitation of the ITO substrate, which is required for electrochemistry measurements. It should be stressed that ITO does not contribute to the absorption. The strong tail at 800 nm means that PANI is protonated, which was expected because the LB film was transferred from an acidic subphase (pH = 2). The band at 425 nm is altered due to the consumption of polarons and formation of bipolarons.³²⁻³⁵ The wide band centered at 800 nm is associated with quinoid species, i.e., with the oxidation of PANI, and therefore it increases with increasing applied potentials. In the mixed films illustrated in Figure 11b and 11c, the tail at 800 nm does not display so much change as in the pure PANI, since the incorporation of Rupy had already increased the degree of oxidation of PANI. Hence, when a potential is applied, only a small change is seen.

One of the possible uses of LB films from conducting polymers is in sensors for gases or tastants. Sensing may be performed by monitoring changes in electrical capacitance or conductivity of the film. For thick spun or evaporated PANI films, one must be aware of the strong dependence of the electrical properties on the environmental changes.³⁶ We have found that incorporation of Rupy caused the mixed LB films to be much less sensitive to environmental changes. For instance, the capacitance at 1 kHz varied by only ca. 15% when the sample was changed from vacuum to ambient air. In contrast, for a

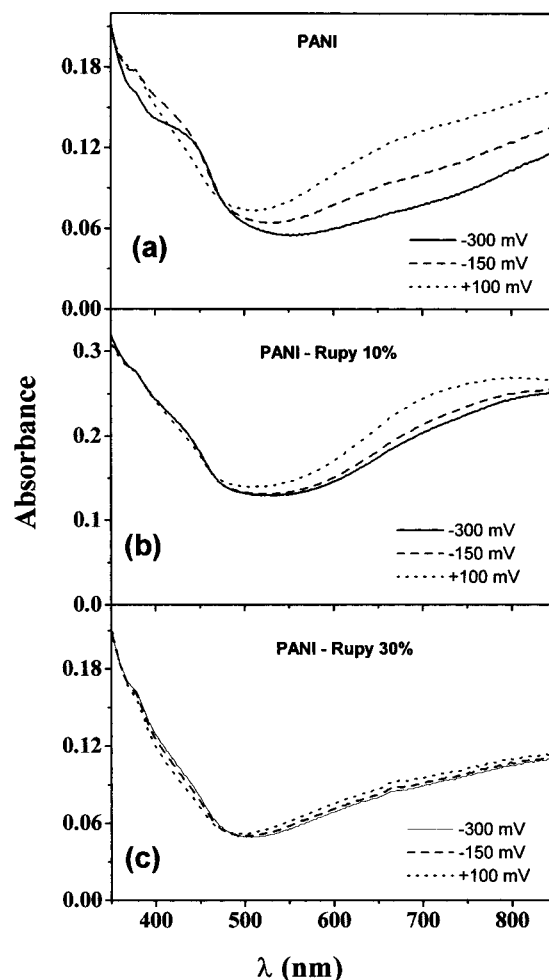


Figure 11. Electronic absorption spectra of LB films on ITO substrate from PANI (a), PANI-Rupy 10% mol (b) and PANI/Rupy 30% mol (c), in HCl 1 M under distinct applied potentials (vs Hg/Hg₂SO₄/K₂SO₄).

pure PANI LB film the change was ca. 215% under the same conditions. The improvement in stability also made it possible to measure the capacitance of mixed PANI-Rupy films at low frequencies (100 Hz), which was not possible for pure PANI films due to the large variation in the signals. The improved stability against environmental changes may have important implications for the applications of thin films in sensors. A detailed study of mixed LB films for gas sensing is under way.

Conclusions

The metallic complex Rupy forms nonmonomolecular structures when spread on an aqueous subphase, and can be mixed in polyaniline (PANI) monolayers, as demonstrated in surface pressure and surface potential isotherms. Interaction between the two components is very strong, as incorporation of small amounts of Rupy substantially affected both the area per molecule and the surface potential of the Langmuir films. The mixed monolayers are amenable to transfer as Y-type LB films, and FTIR and Raman spectroscopy of the deposited LB films confirmed the transfer of both PANI and Rupy. The absence of shifts in the Raman bands of the mixed LB film, in comparison with the pure LB film of PANI, appears to suggest only a physical interaction between PANI and Rupy. However, the incorporation of Rupy in LB films induces oxidation of PANI with its consequent loss of electroactivity. For instance, mixed films containing

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50%mol of Rupy displayed no electroactivity. Such changes in the electrochemical properties suggest charge transfer between the two components, which is consistent with the Raman scattering data. The addition of Rupy caused the mixed LB films to exhibit a capacitance that was not strongly affected by environmental changes, which makes the films potential candidates for gas sensors.

Acknowledgment. This work was supported by FAPESP and CNPq (Brazil) and NSERC (Canada). We are also indebted to Dr. Luiz H.C. Mattoso for allowing us to use the system of electrical capacitance measurements.

LA011330F