

Spectroelectrochemical Studies on Metallophthalocyanines Adsorbed on Electrode Surfaces

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ABSTRACT

Co(II)- and Fe(II)-phthalocyanines adsorbed on platinum and various carbon electrode surfaces have been studied by spectroelectrochemical techniques. The metallophthalocyanine (MPc) films were prepared on substrate electrodes by a drop-dry method after dissolving them in pyridine. While not much change in spectroscopic properties is observed for MPc's adsorbed at the platinum electrode, both the Soret and Q bands were significantly broadened when adsorbed on the carbon electrodes. Also, the metal-ligand charge transfer (MLCT) bands are observed from CoPc films adsorbed on carbon substrates even if they are not reduced. These observations lead to a conclusion that the MPc molecules not only undergo oligomerization but also interact strongly with carbon surfaces by perhaps sharing π -electrons of carbon.

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INTRODUCTION

Metallophthalocyanines (MPc's) have been the subjects of various studies due to their catalytic activities for many reduction/oxidation reactions. Their spectroscopic and electrochemical studies have been reviewed recently in books and review articles.^{1,2}

Numerous studies on MPc's were conducted in various solvents using spectroscopic,^{3,4} electrochemical,⁵⁻⁷ and spectroelectrochemical⁸⁻¹⁰ techniques. These studies in solution phases have led to establishing the energy levels of these molecules (Fig. 1).¹¹ The metal phthalocyanines show two distinctive electronic transitions in the UV-VIS spectral region, i.e., the Soret band in the UV region and the Q-band in about 600 ~ 750 nm region. The Soret bands are not very sensitive to the valence state of the MPc's, whereas the Q-bands are sensitive to the central metal ions, their valence states, and the solvent. When the first row transition metal-Pc's are reduced, central metal ions are reduced during the first electron transfer, while the the second electron transfer takes place to the phthalocyanine rings. As a result of increased charge on the central metal atoms, metal-ligand charge transfer (MLCT) bands are observed from the reduced MPc's in a spectral region between the Soret and Q bands, if an MPc has a reducible central metal ion.¹²⁻¹⁴

Only a limited number of spectroscopic studies on MPC's in their adsorbed states has been reported due to the experimental difficulties encountered.¹⁵⁻¹⁹ Appleby *et al.* were the first to attempt at correlating spectroscopic properties of adsorbed iron phthalocyanines with their catalytic activities.¹⁵ Yeager *et al.*¹⁶ reported the reflectance spectra of monolayers of tetrasulfonated transition metal phthalocyanines adsorbed on electrode surfaces. These authors concluded from this study that adsorbed phthalocyanine molecules are lined up with their ring plane

perpendicular to the electrode surface. Van der Ham *et al.*¹⁷ obtained reflectance spectra in acidic media for Fe- and Co-Pc's films on glassy carbon and gold electrodes by modulating electrode potentials. The modulation amplitude of 50 mV (rms) was used at a modulation frequency of 15 Hz. These spectra should thus be interpreted as those obtained from the electrochemical changes in spectral features brought in by the potential modulation of 50 mV near the dc bias potentials. Most recently, Kim *et al.*^{18,19} reported spectra from cobalt tetrasulfonated phthalocyanine irreversibly adsorbed on the basal plane of highly oriented pyrolytic graphite.

MPC's have been used as effective catalysts for oxygen reduction, which is used as a cathode reaction in fuel cells and metal-air batteries.^{1,2} Most of the studies conducted on catalytic activities of these MPC's addressed the reaction mechanism of the MPC-catalyzed oxygen reduction rather than the catalytic mechanism involved.² Kobayasi and Nishiyama²⁰ concluded that the reaction could be explained by the conventional electrochemical catalytic regeneration (EC') mechanism.

Despite many studies reported on MPC's in solution phases, their solution behavior is not easily delineated with the catalytic activities taking place in the adsorbed states on electrode surfaces. Thus, the catalytic mechanism for oxygen reduction is not very well understood. In this report, we describe our findings from the spectroelectrochemical studies on the Co(II)- and Fe(II)-phthalocyanine films on the surfaces of various electrodes. We used the MPC films adsorbed at platinum as well as various carbon substrates.

EXPERIMENTAL

EM Science's Omnisolve, glass distilled pyridine (Py) was used after appropriate

distillations. Co(II)Pc and Fe(II)Pc were obtained from Eastman Organic and used without further purification. Doubly distilled, deionized water was used to prepare 1 M KOH solutions. Union Carbide's highly oriented pyrolytic graphite (HOPG) was used by slicing and attaching the slice on a graphite rod by silver epoxy.

The adsorbed Fe(II)Pc and Co(II)Pc films were prepared by a drop dry method in which a few drops of saturated phthalocyanine solutions in pyridine were placed on the reflective electrode surfaces and dried in the air. Electrodes used for these purposes include platinum, glassy carbon, HOPG and partially transparent carbon electrodes. The partially transparent carbon electrode was prepared by spin coating quartz glass slides with glassy carbon powder suspended in acetone and dried.

A Hewlett-Packard model 8452A photodiode array spectrophotometer was used for transmittance type spectral measurements for MPC's adsorbed on partially transparent carbon electrodes (PTCEs). For spectroelectrochemical measurements on nontransmitting substrates, reflectance spectral measurements had to be made on the reflective surfaces. For these substrates, a reflective disk working, an Ag/AgCl, saturated KCl reference, and a platinum spiral wire counter electrodes were used. The working electrode was a platinum (area = 0.331 cm²), glassy carbon, or HOPG disk. A near normal incidence reflectance mode assembled with a bifurcated quartz fiber optical probe was used for the spectroelectrochemical measurements. Details of the instrumental setup have been described elsewhere.²¹⁻²³

A Princeton Applied Research (PAR) model 173 potentiostat-galvanostat along with a PAR 175 universal programmer was used for electrochemical and derivative cyclic voltabsorptometric (DCVA) experiments. A one compartment electrochemical cell housing a

reflective platinum disk electrode (diameter 2.0 mm), Ag/AgCl-saturated KCl reference electrode, and a platinum wire spiral counter electrode was used for potential measurements.

RESULTS AND DISCUSSION

Linear Sweep Voltammograms at Catalyst Modified Electrodes

In order to see the relative catalytic effects of adsorbed Co(II)Pc and Fe(II)Pc on various electrodes, we first ran linear sweep voltammograms (LSVs) at the phthalocyanine modified electrodes. Fig. 2 shows the LSVs recorded at (a) platinum and (b) highly oriented pyrolytic graphite (HOPG) electrodes with and without phthalocyanine molecules. While both Co(II)Pc and Fe(II)Pc films show significant catalytic effects on oxygen reduction on carbon electrodes (Fig. 2(b)), they show negative catalytic effects at platinum electrodes. The Co(II)Pc coated electrode shows a larger negative catalytic effect on the oxygen reduction than its Fe(II)Pc-coated counterpart. The presence of Co(II)Pc films makes the oxygen reduction kinetics significantly slower than that at the bare platinum electrode.

The MPc films on carbon electrodes show large catalytic effects compared to bare carbon electrodes (Fig. 2(b)). The catalytic effects at a variety of other carbons are similar to those shown in Fig. 2(b). In general, the catalytic effects appear to be larger on better defined carbon electrodes such as HOPG than most other carbon electrodes. This is perhaps because the oxygen reduction kinetics is poorer at the basal plane of the HOPG than that at the edge plane. In general, Co(II)Pc films show a better oxygen reduction kinetics than Fe(II)Pc except at the Pt electrode. However, the half wave potentials of the oxygen reduction at the catalyst modified carbon electrodes are more negative than those at the phthalocyanine modified Pt electrodes.

We believe that the opposite effects shown by Co(II)- and Fe(II)-Pc's on carbon and platinum electrodes result from their electronic configurations. The Fe(II) in FePc is a d^6 low spin, which is free of unpaired electrons, whereas Co(II) ion in Co(II)Pc has a d^7 low spin with magnetic moment with a range of 2.1 ~ 2.9 BM at room temperature, confirming the presence of an unpaired electron. This unpaired electron may interact with the atomic orbital on platinum. Hoare²⁴ argues that the Pt-O alloy shows a larger catalytic effect on oxygen reduction because the formation of the oxide raises the Fermi level of platinum due to the filling of the platinum d orbital and thus requires less overpotential for oxygen reduction compared to the reduced platinum. Platinum has a $5d^96s^1$ configuration and the unpaired electron on Co(II) in CoPc may be used to fill the last hole on the 5d-orbital. Thus, the unpaired electron on the 3d-orbital of Co(II) may be shared between Co(II) and Pt atomic orbitals by forming a stable complex between Co(II) and Pt. In other words, the Co(II)Pc adsorption may be described as "chemisorption," whereas Fe(II)Pc appears to be physisorbed. This may lead to two important consequences: the inhibition of oxygen adsorption on the platinum surface, resulting in an inhibition of alloy formation in its oxidized state. This would lead to the loss of catalytic effects on platinum due to the lack of PtO. This explains the observation shown in Fig. 2(a) where the catalytic effect on the platinum electrode is poisoned more by the presence of Co(II)Pc than Fe(II)Pc. The extra unpaired electron on Co(II) also explains its larger catalytic effect than that shown by Fe(II)Pc on carbon substrates as will be discussed below.

Spectroelectrochemistry of Adsorbed MPc's

The electronic absorption spectra of Co(II)Pc and Fe(II)Pc adsorbed on the reflective

platinum electrode have been recorded at various potentials under the nitrogen atmosphere and the results are shown in Fig. 3. These difference spectra were recorded with the films at the open circuit used as a reference. Therefore, the spectra shown here represent differences in spectral features caused by applying potentials specified in the figure to the phthalocyanine coated electrodes.

The Co(II)Pc film (Fig. 3(a)) on platinum shows a significant blue shift for the Soret band to about 280 nm when compared to that in the pyridine solution, where Co(II)Pc has an absorption maximum at about 320 nm.²⁵ On the other hand, the Q band shows a slight red shift. The Q band undergoes a series of changes as the applied potential becomes more negative. These observations indicate that the ground state energy levels ($a_{1u}\pi$ and $a_{2u}\pi$; Fig. 1) are affected in the opposite direction, since the excited states of both the Soret and Q transitions ($e_g\pi^*$) must be identical. Also evident is that a broad metal-ligand charge transfer (MLCT2; Fig. 1) band with its maximum absorbance at about 450 nm is present at all potentials. The MLCT2 bands are observed in solution phases¹¹⁻¹³ as well as from thin films²⁶ when Fe(II)Pc and Co(II)Pc are reduced. The MLCT2 band is observed at all potentials at the platinum electrode surface because Co(II) in CoPc is isoelectronic with Fe(I) in reduced FePc. There may be some contributions to this charge transfer from the Pt d-orbital as well. When Fe(II)Pc is reduced, it shows the well defined MLCT2 band (Fig. 3(b)). In other words, the electronic configuration of Co(II) in the unreduced Co(II)Pc is identical to that of the reduced Fe(II)Pc, which allows the MLCT2 band to be observed for Co(II)Pc even in the solution phase although it is not well defined. This situation makes the reduction potential of the Co(II)Pc-oxygen adduct reasonably positive and thus Co(II)Pc is expected to act as a better catalyst than Fe(II)Pc on electrodes other than

platinum. Finally, the rather strong interaction of Co(II)Pc with platinum by sharing their d-electrons might have affected the energy levels of π -electrons, i.e., $a_{1u}\pi$ and $a_{2u}\pi$. This must have caused the change in the ground state energy levels of phthalocyanines in opposite directions so that both blue and red shifts may be observed in the electronic spectra. Again, the interaction of platinum must be stronger for Co(II)Pc as it displays a larger blue shift.

The situation is different when Fe(II)Pc is coated on the platinum electrode surface (Fig. 3(b)). Both the Soret and Q bands are affected similarly but to the less extent than in the case of Co(II)Pc. Note, however, that the bands corresponding to the MLCT2 appears only at potentials less negative than -0.6 V. At this potential, the Fe(I) in reduced FePc isoelectronic with Co(II) in unreduced CoPc. The Fe(II)Pc film has a more negative reduction potential than oxygen. This is substantiated by the derivative cyclic voltabsorptometric (DCVA) curves shown in Fig. 4(a) and (b), which also show cyclic voltammograms for oxygen reduction recorded concurrently with the DCVA curves. In the DCVA experiments, the derivative absorption signal with respect to time is recorded as a function of potential at a selected wavelength at which a reactant or product of an electrochemical reaction absorbs photons. Thus, the DCVA signal is selective to a species absorbing light at the selected wavelength. As can be seen in Fig. 4, DCVA signals monitor the fate of the Fe(II)Pc film at 380 nm and 732 nm selectively without being interfered by the reduction wave for oxygen. These wavelengths were chosen based on the spectral responses of these bands in Fig. 4(b). The DCVA curves shown in Fig. 4 indicate that the small bump in the CV starting at about -0.5 V in the CVs is due to the reduction of Fe(II)Pc.

We conclude from these observations that the catalytic activity of oxygen reduction at Pt electrodes is less inhibited at the Fe(II)Pc-modified electrode than at the Co(II)Pc-modified

one. This is because Co(II)Pc seems to be chemisorbed onto the platinum surface by sharing an unpaired electron on their d-orbitals, whereas the adsorption of Fe(II)Pc on the platinum surface may be described as physisorption. Both electrochemical and spectroelectrochemical observations support this postulate.

Films on the other substrates show larger effects on the absorption spectra of Co(II)Pc and Fe(II)Pc as shown in Figs. 5 - 7. It is clearly seen in these figures that spectra of both Co(II)Pc and Fe(II)Pc are strongly affected on all substrates studied, although the spectra of Co(II)Pc appear to be affected more. Generally, the spectra of adsorbed Co(II)Pc have broader absorption peaks with significant red shifts than those of Fe(II)Pc, although the transition energies and oscillator strengths vary depending on the substrates. Weak MLCT absorption bands appear to overlap with both Soret and Q bands for Co(II)Pc films, which are already broadened. Note that a very well defined MLCT band is observed for Co(II)Pc on the partially transparent carbon electrode (Fig. 7(a)), whereas no C-T band is observed for Fe(II)Pc.

The spectra of adsorbed Fe(II)Pc on carbon substrates are much better resolved than those of Co(II)Pc, although it is not the case on the HOPG surface. In general, the bands are broader and red shifted, compared to those observed in solution. The bands are particularly broader on the HOPG electrode, which might have resulted from the lifted baseline. When we measured the reflectance of the HOPG surface in 1 M KOH solutions without adsorbed phthalocyanines (not shown), we found that the apparent reflectance went up more or less uniformly throughout the whole wavelength region, resulting in the baseline lift. We believe the reduction in reflectance intensities took place due to the etched surface of HPOG by the strong alkaline solution. The reduction in reflectance, i.e., increase in absorbance, should have been more notable at a very

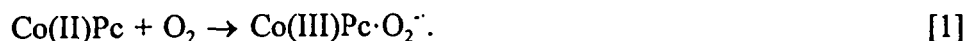
well defined HPOG surface compared to other surfaces, because HOPG has much fewer defect sites compared to other types of carbons.

The band broadening of Co(II)Pc and Fe(II)Pc spectra on carbon substrates might have resulted from the aggregate formation (see below) and the extensive interaction of the π -electron orbitals of phthalocyanines with π -electrons clouds on carbon. The interaction might be at its maximum at the basal plane of HOPG because of the ideal situation for such an overlap. Two observations support this postulate: the absorption spectra recorded at the basal plane of HOPG (Fig. 6) and spectra recorded on oxidized and reduced glassy carbon surfaces (not shown). The spectra on HOPG show almost no vibrational features due perhaps to the vibrational relaxation of the excited states through the overlapped π -electron clouds on carbon. Also, the spectra recorded from phthalocyanines adsorbed on oxidized and reduced glassy carbon surfaces are basically identical except that generally lower absorbance is observed from the oxidized surface. This indicates that phthalocyanines interact more with carbon surfaces *via* π -electron clouds rather than with functional groups such as carbonyl and/or hydroxyl groups. If the metal ions phthalocyanines interact with carbon substrates through metal ion's coordination with functional groups, we should see stronger adsorption on oxidized carbon surfaces. A similar observation has been made for dicobalt cofacial porphyrin.²⁷ However, phthalocyanine molecules with sulfonate substituents are known to interact with solid surfaces through the sulfonate group.¹⁶ These observations suggest that phthalocyanine ring interacts with carbon in different ways depending on whether a functional group is present or not on the ring. Also, we believe that the mode of interaction of phthalocyanines is different on platinum and carbon surfaces.

The band broadening and red shift may best be interpreted as due to oligomerization or

polymerization of these compounds on carbon surfaces. Spectral shapes are in qualitative agreement with those of dimeric forms reported in the literature.^{7,9} Phthalocyanines have also been known to undergo a dimerization reaction even at reasonably low concentrations, as low as about $5 \times 10^{-5} M$ in dimethyl sulfoxide (DMSO).⁷ The dimerization/oligomerization is not significant at the platinum surface as can be seen in Fig. 2 if it occurs at all. However, the MLCT band is observed for Co(II)Pc on carbon substrates as well as on platinum. In the case of Co(II)Pc, bands might have become even broader than they actually are due to the overlap of both Soret and Q bands with the charge transfer band.

The observations described thus far explain the differences shown by Co(II)Pc and Fe(II)Pc on platinum and carbon electrodes. Firstly, the extra unpaired electron on Co(II)Pc causes the metal-ligand charge transfer to be observed in its spectra in both the solution and solid phases. The MLCT band is less prominent in the solution phase probably because the central metal ion is strongly complexed with solvent molecules above and below the phthalocyanine plane. This is shown by the fact that the MLCT band was stronger in DMSO than in pyridine because DMSO is a better electron donor than pyridine.²⁵ The extra unpaired electron allows the Co(II)Pc molecule to form an adduct with oxygen in the same way as a Co(II)-Schiff base complex would according to



Thus, the reduction of the adduct should result in the release of the superoxide, which undergoes a rapid disproportionation reaction to produce a peroxide ion, and Co(II)Pc. The ability of forming the charge-transfer complex of Co(II)Pc should make it a better catalyst than Fe(II)Pc on carbon electrodes. On the other hand, the same ability poisons the catalytic ability of the

platinum electrode more than Fe(II)Pc does. Secondly, effective oligomerization or polymerization of phthalocyanines on carbon electrodes may make the catalytic activities larger. The polymeric forms of the first row transition metal phthalocyanines are known to be better catalysts than their monomeric counterparts.^{15,28} Thus oligomers formed at carbon surfaces may lower the excited energy levels, resulting in red shifts and band broadening. This would also lower the reduction potential. The aggregate formation appears to be more effective for Co(II)Pc than Fe(II)Pc. This may have to do with respective electronic configuration of these ions.

The dependence of applied potentials on the spectrum of Co(II)Pc films on the partially transparent carbon electrode is shown in Fig. 8. A series of negative absorption bands are recorded as the potential applied becomes more negative in the nitrogen atmosphere. Negative bands are observed because the absorption spectrum recorded at the open circuit potential was taken as a reference for the calculation of the absorbance. The series of negative absorption bands indicate that Co(II)Pc is progressively "more" reduced, although the MLCT2 band is observed at a potential as positive as -0.1 V. The spectra also indicate that the original state of Co(II)Pc had an intense, well defined charge transfer band with its maximum at 506 nm, which is consistent with the result shown in Fig. 7(a).

When the experiments are run in the oxygen atmosphere (Fig. 8(b)), a few differences in spectral features are noted. Firstly, the negative absorption bands are generally lower than those recorded in the nitrogen atmosphere, albeit the difference may not be large. This suggests that a regenerative reaction, *i.e.*,



produces Co(II)Pc back and, thus, not as much Co(I)Pc is present on the surface. This is

consistent with the mechanisms forwarded from the results of our solution phase studies.²⁵ Secondly, the MLCT2 band is lower in the presence of oxygen in comparison to the Q band. This suggests that the charge-transfer character has been reduced in the presence of oxygen due to the formation of adducts as described by reaction [1]. In other words, partial charge transfer might have occurred to oxygen molecules as well. Also, the half widths of the CT band increased compared to those in Fig. 8(a), suggesting that the Co(II)Pc and molecular dioxygen must be interacting. Thirdly, the decrease in absorbance of the Soret band at 356 nm is much smaller here than that shown in Fig. 8(a); we believe this is due to the superoxide and/or peroxide band observed below about 320 nm with its maximum located about 300 nm.²⁹ The offsetting effect of the positive absorption due to the generation of superoxide/peroxide made the negative Soret band less pronounced. Finally, the relatively high absorbance of the Q band in relation to other bands may be interpreted as due to the interaction of oxygen with the phthalocyanine molecule; Yeager *et al.* attributed the enhancement of this band in the presence of oxygen to its complexation with oxygen.¹⁶

CONCLUSION

Our results show that Fe(II)Pc and Co(II)Pc films on the electrode surface display different spectroscopic properties from those in solution phases. The spectral shifts, band broadening, and changes in absorbance values indicate that these molecules interact with the different substrate surfaces to different extents. The spectral features are strongly affected the adsorption on carbon surfaces. The band broadening appears to depend on the crystal faces of carbon substrates as the behavior is different for different carbons used. From this observation,

we conclude that Co(II)Pc and Fe(II)Pc interact most strongly with the plane perpendicular to the benzene rings on the graphite structure. This type of interaction would provide the maximum overlap between the π -electron systems of phthalocyanine molecules and carbon. Also, metal-ligand charge transfer bands, which are very weak or not present in solution phases for both phthalocyanines, are observed for Co(II)Pc on carbon substrates even without being reduced. This indicates that Co(II)Pc is in a better position to transfer its electron to dioxygen molecules when adsorbed on carbon surfaces. The relative intensities of charge transfer bands depend on the type of carbon, suggesting that they may be crystal face specific. The charge transfer band is not observed for Fe(II)Pc films.

We conclude from these observations that Co(II)Pc forms oligomers more effectively and forms the adduct with oxygen more easily according to reaction [1] at the carbon surfaces. This explains why Co(II)Pc acts as a more effective catalyst than Fe(II)Pc *via* regenerative reduction of oxygen by Co(II)Pc.

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Figure Captions:

1. Simplified molecular orbital energy level diagram. After Lever *et al.* (Ref. 11).
2. Single sweep voltammograms recorded at: (a) platinum and (b) basal plane of highly oriented pyrolytic graphite (HOPG) electrodes. The voltammograms were recorded at bare, Co(II)Pc coated, and Fe(II)Pc electrodes. The voltammograms were recorded in 1.0 M KOH saturated with oxygen at a scan rate of 50 mV/s.
3. Absorbance spectra recorded at Co(II)Pc (a) and Fe(II)Pc (b) coated platinum electrodes at applied potentials indicated on the figure.
4. Derivative cyclic voltabsorptometric curves at 380 and 732 nm at an Fe(II)Pc coated platinum electrode, which are concurrently recorded with cyclic voltammograms for oxygen reduction. The scan rate was 50 mV/s.
5. Absorption spectra recorded for Co(II)Pc (a) and Fe(II)Pc(b) adsorbed on glassy carbon electrodes.
6. Absorption spectra recorded for Co(II)Pc (a) and Fe(II)Pc (b) adsorbed on HOPG electrodes.
7. Absorption spectra recorded for Co(II)Pc (a) and Fe(II)Pc (b) adsorbed on partially transparent carbon electrodes.
8. (a) Absorbance spectra for the Co(II)Pc film on a partially transparent carbon electrode recorded in 1.0 M KOH saturated with nitrogen as a function of applied potential and (b) spectra recorded from the same electrode as in (a) with oxygen saturated.

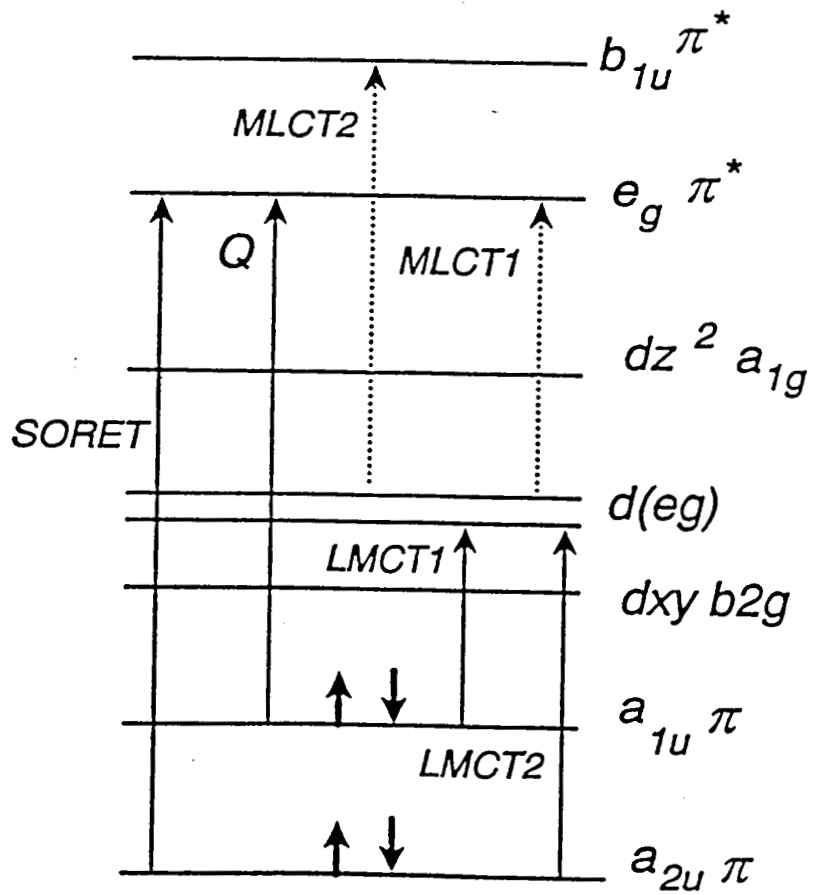


Fig. 1

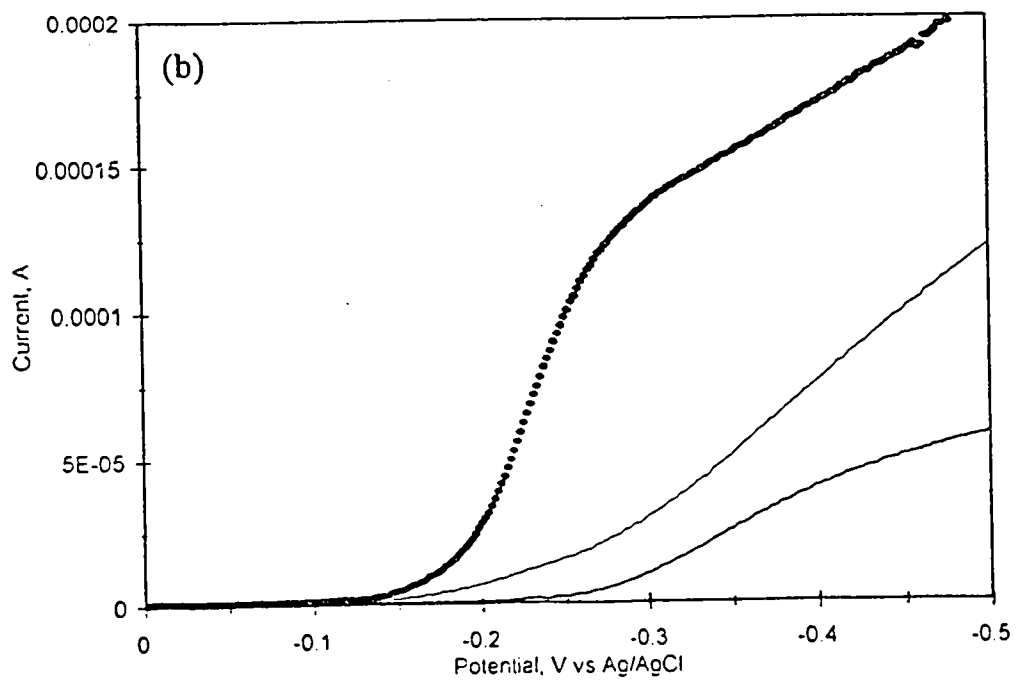
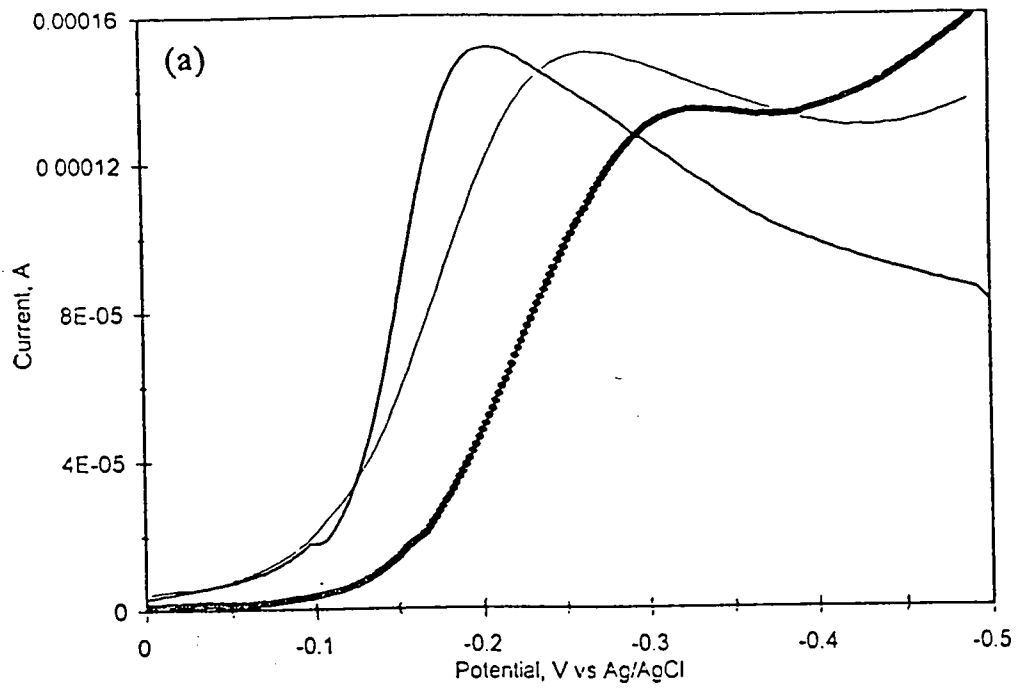
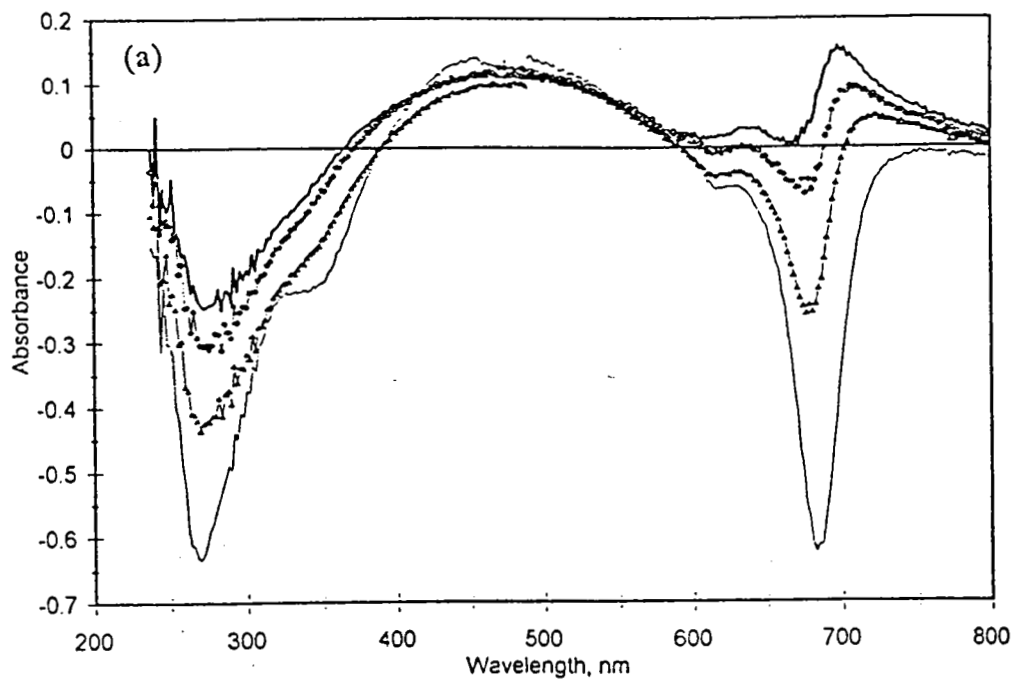
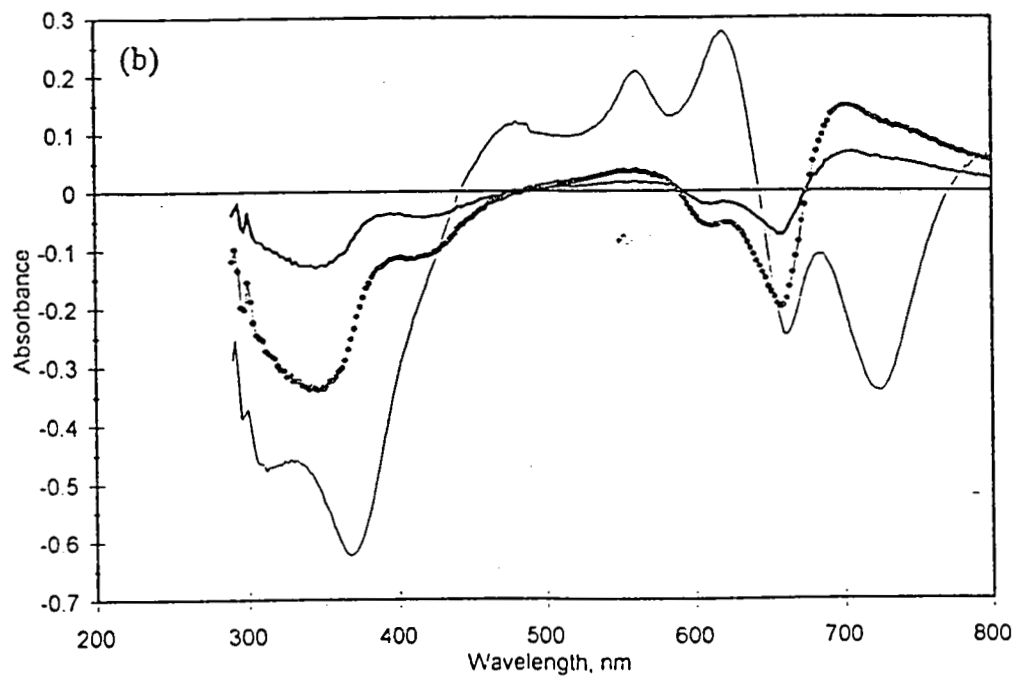


Fig. 2



— +0.2V — 0.0V — -0.2V — -0.5V



— 0.0V — -0.3V — -0.6V

Fig. 3

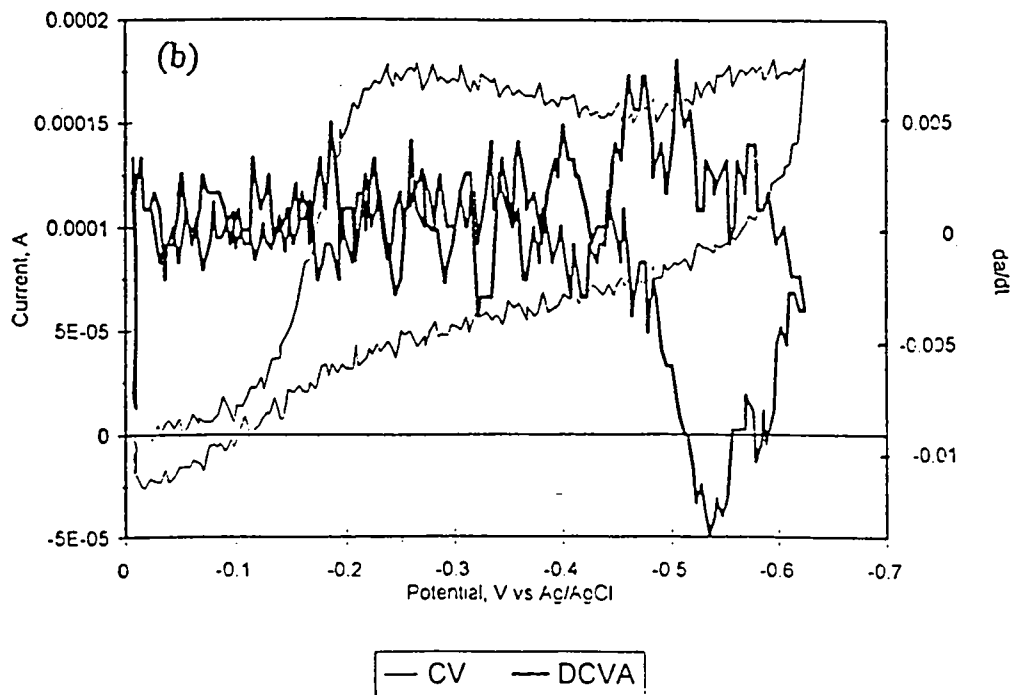
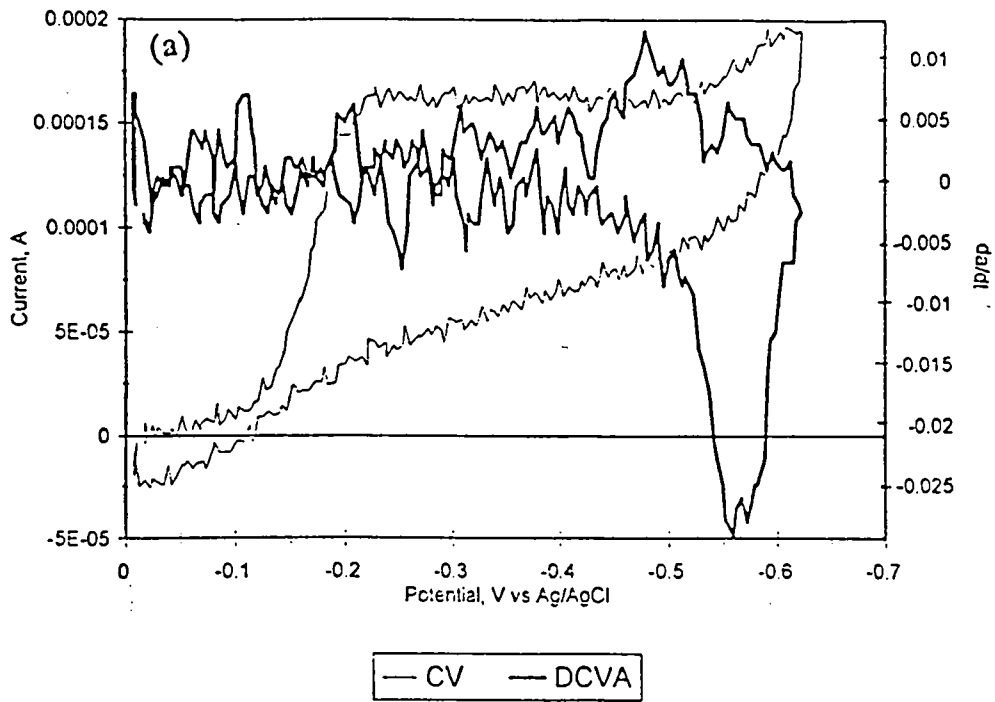


Fig. 4

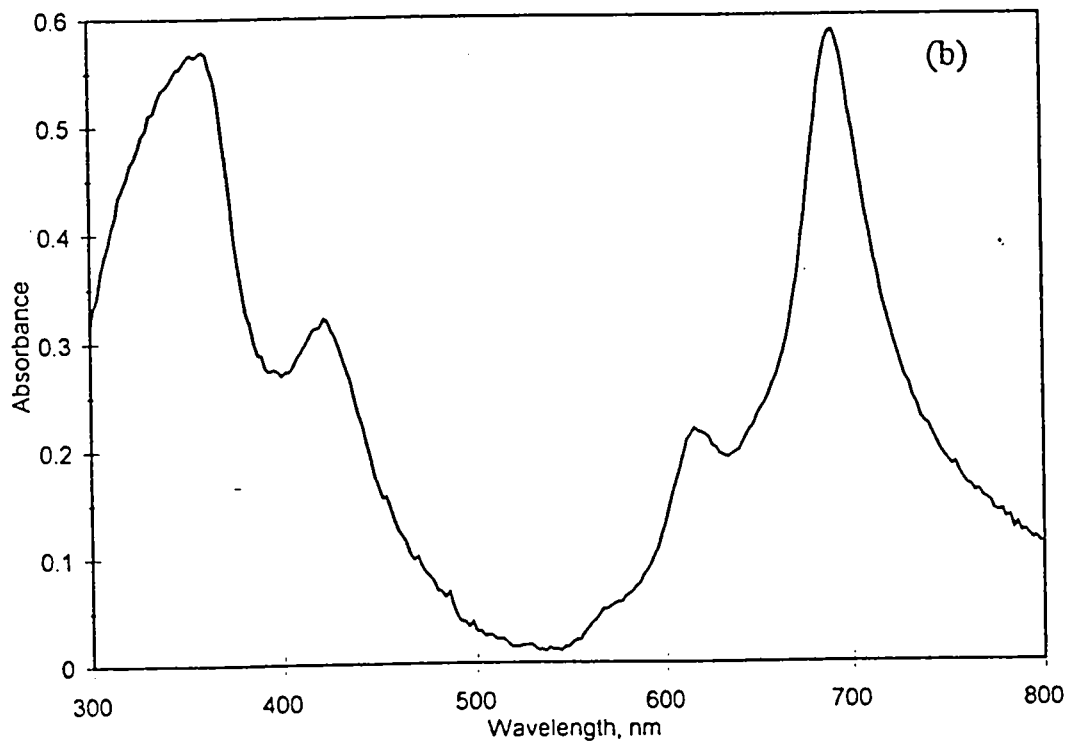
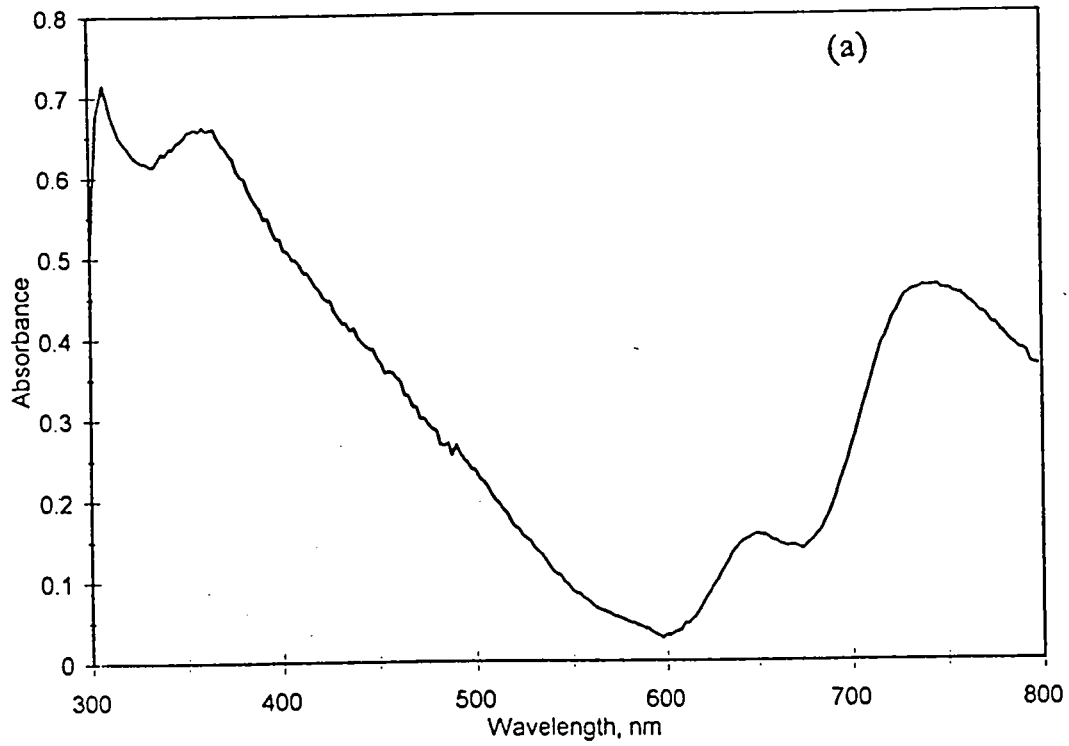


Fig. 5

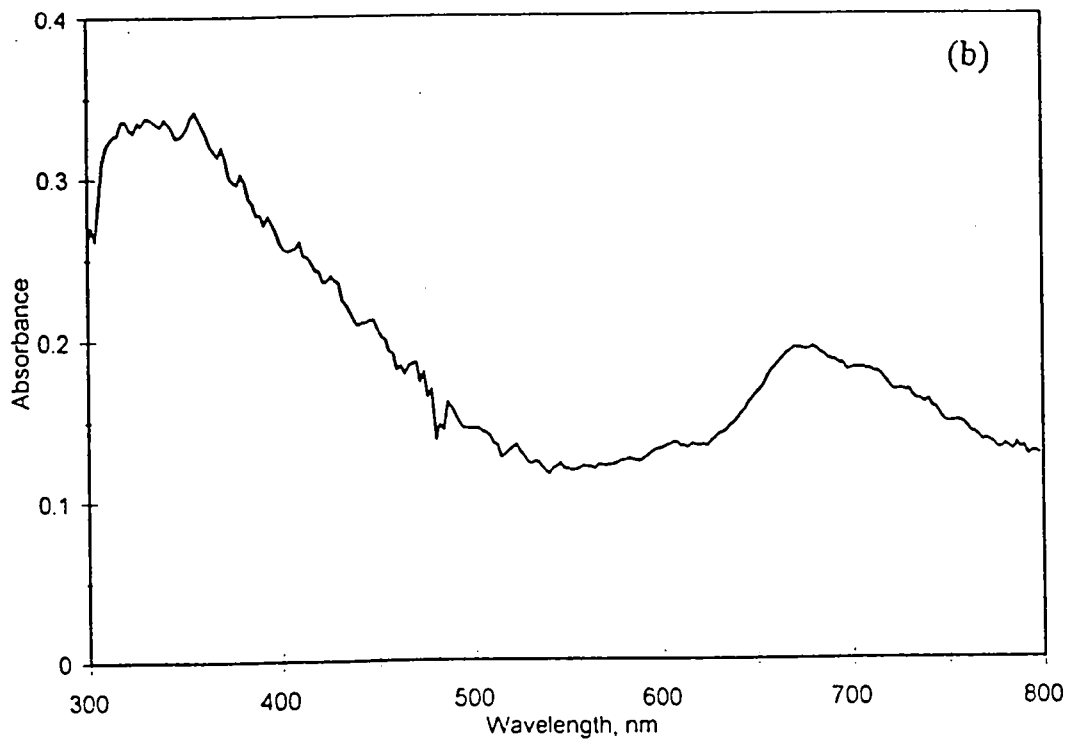
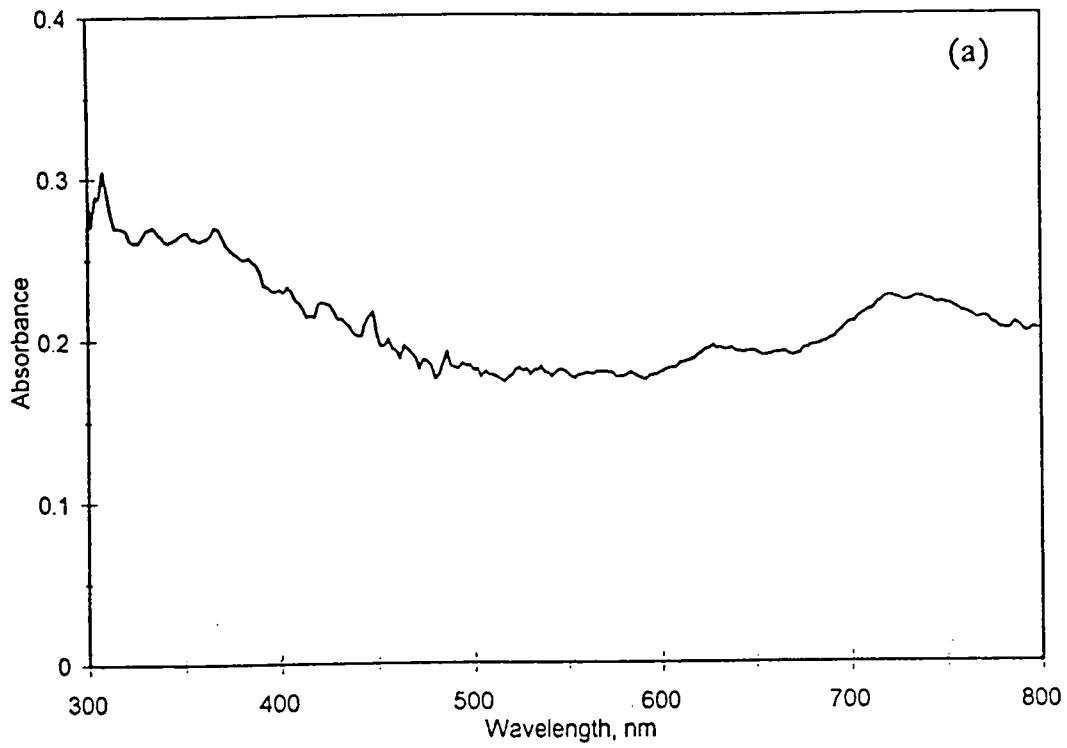


Fig. 6

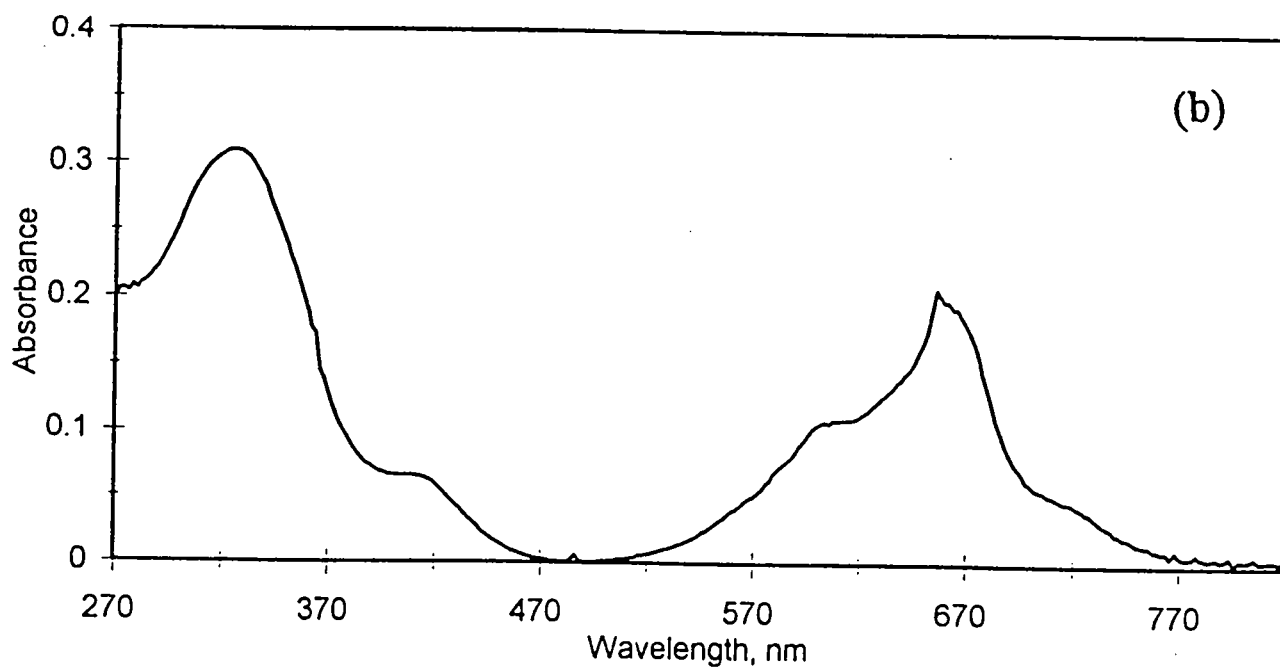
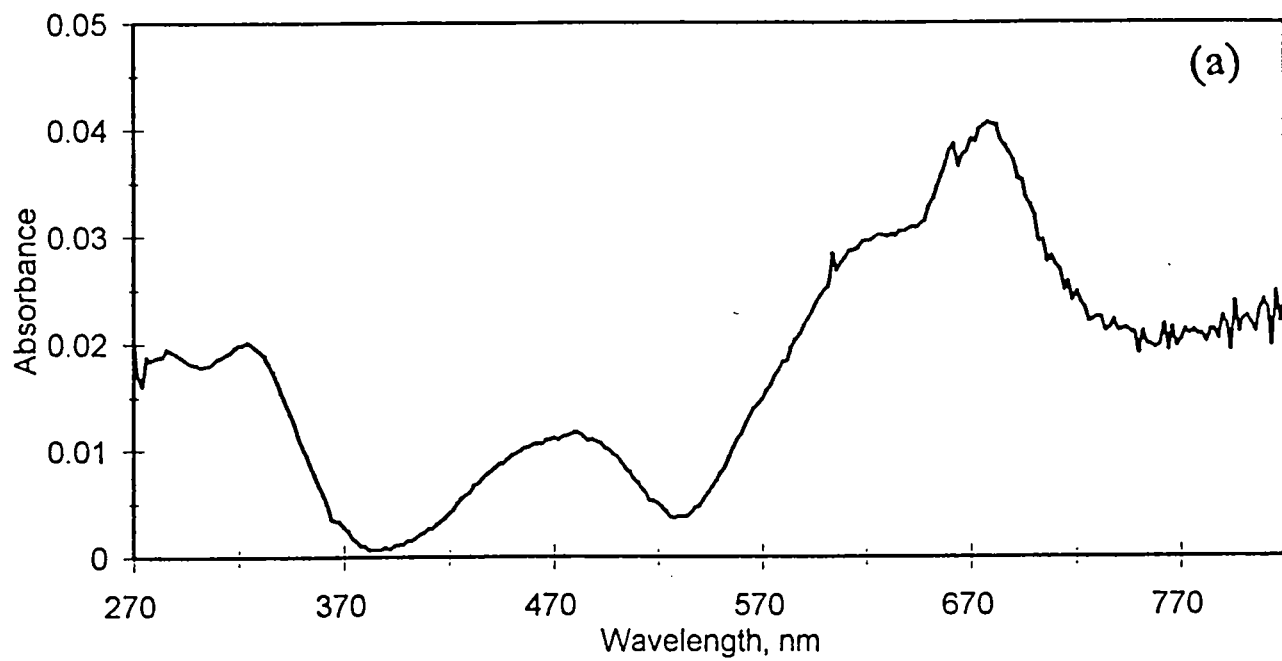
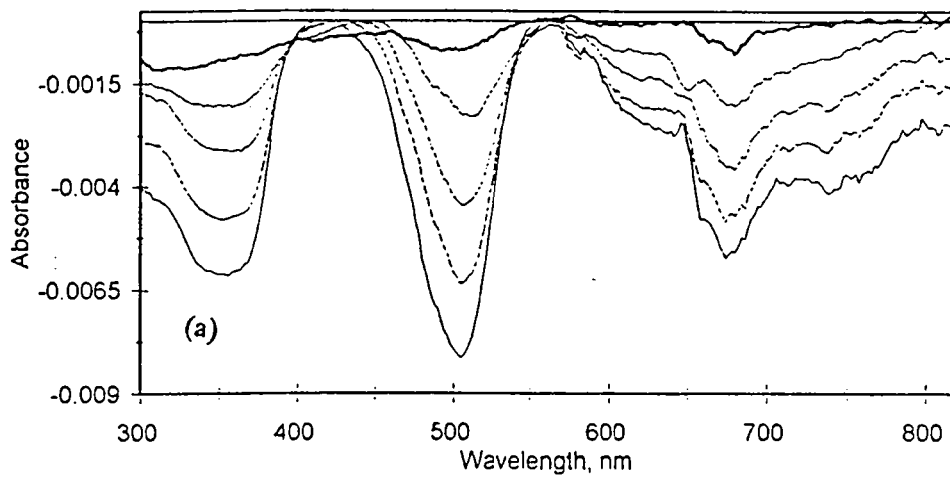
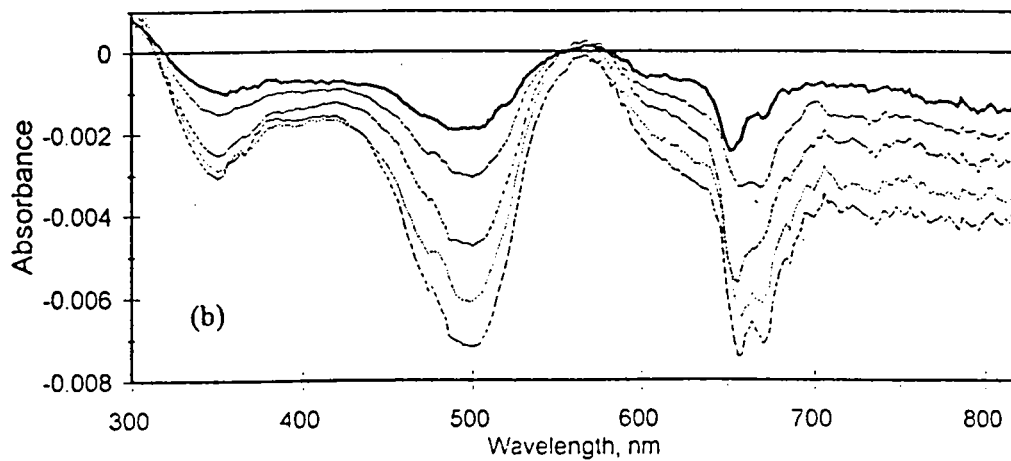


Fig. 7



— -0.1V — -0.2V ··· -0.3V - - -0.4V — · -0.5V



— -0.1V — -0.2V ··· -0.3V - - -0.4V — · -0.5V

Fig. 8