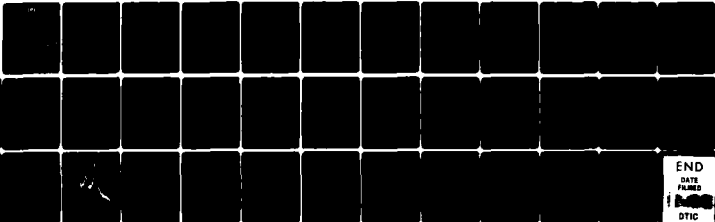AD-A090 476 NORTH CAROLINA UNIV AT CHAPEL HILL WILLIAM R KENAN JR--ETC F/G 7/4
ELECTRONIC AND PHOTOELECTRON SPECTRAL STUDIES OF ELECTROACTIVE --ETC(U)
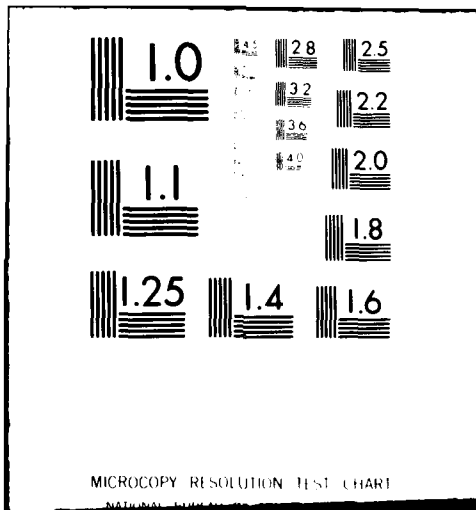SEP 80 K W WILLMAN, R D ROCKLIN, R NOWAK   N00014-76-C-0817
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TECHNICAL REPORT NO. 14

AD A090476

ELECTRONIC AND PHOTOELECTRON SPECTRAL STUDIES
OF ELECTROACTIVE SPECIES ATTACHED TO SILANIZED C AND Pt ELECTRODES

by

K. W. Willman, R. D. Rocklin, R. Nowak, K.-N. Kuo,

F. A. Schultz and Royce W. Murray

Prepared for Publication in

Journal of the Electrochemical Society

Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

September 1980

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
fourteen	AD-A090476	

4. TITLE (and Subtitle)
Electronic and Photoelectron Spectral Studies of Electroactive Species Attached to Silanized C and Pt Electrodes

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
K. W. Willman R. D. Rocklin R. Nowak K.-N. Kuo F. A. Schultz and R. W. Murray

8. CONTRACT OR GRANT NUMBER(s)
N00014-76-0817

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

12. REPORT DATE
11 September 1980

13. NUMBER OF PAGES
thirty

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

modified electrode, porphyrin, fluorescence, reflectance spectroscopy, spectroelectrochemistry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Block No. 20: ABSTRACT, continued:

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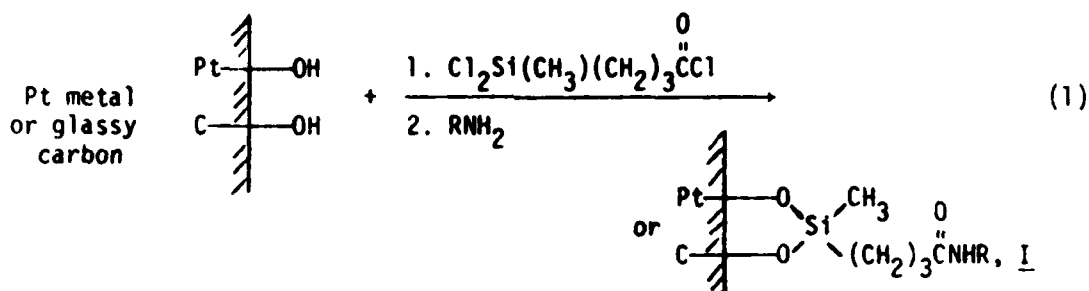
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ABSTRACT

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silent Co(III/II) porphyrin reaction). Electroactive films 500 monolayers thick
can be prepared from the ferrocene by spin coating reactive silane; in aqueous
sulfuric acid voltammetry of these films indicates a phase-like property.

This is a study of surface chemistry, electrochemistry and spectroscopy of amine-substituted electron transfer couples (RNH_2), attached to superficially oxidized glassy carbon and platinum electrodes, using 4-(methyldichlorosilyl)butyryl chloride (designated __BCl__ silane)

$$\text{Pt metal or glassy carbon} \quad \begin{array}{c} Pt \text{---} OH \\ C \text{---} OH \end{array} \quad + \quad \frac{1. \ Cl_2Si(CH_3)(CH_2)_3\overset{O}{\overset{\|}{C}}Cl}{2. \ RNH_2} \longrightarrow \qquad (1)$$

$$or \quad \begin{array}{c} Pt \text{---} O \\ C \text{---} O \end{array} \underset{Si}{\overset{CH_3}{\diagdown}} (CH_2)_3\overset{O}{\overset{\|}{C}}NHR, \ \underline{I}$$

When RNH_2 is tetrakis(__p__-aminophenyl)porphyrin, __I__ is designated $Pt,C/\!\!\sim\!\!(NH_2)_4TPP$; when RNH_2 is __p__-aminophenylferrocene, __I__ is $Pt,C/\!\!\sim\!\!NH_2PhCpFeCp$. Amine derivatives constitute an important pathway to attaching redox molecules to electrode surfaces, and have been used to immobilize chiral[2] and redox[3-7] reagents on thionyl chloride activated carbon, and in chemisorption on Pt oxide and carbon[9] surfaces. The acid chloride __BCl__ silane is a general surface linking reagent for monolayers of amines on both metal oxides[10] and carbon, and as shown here can also be used in a spin coated polymerized (siloxane) form to attach multilayers of amines to electrodes. Earlier reactions of organosilane reagents with glassy carbon surfaces[11] ultimately proved ineffectual for immobilizing redox materials[12]. Reaction 1 is the first example of immobilizing redox substances on glassy carbon with organosilane chemistry.

Spectroscopic data to further our understanding of electron transfer reagents attached to electrodes is at present limited, especially with respect to correlations with electrochemical behavior and with solution spectra. We apply here spectroscopic measurements, to $Pt/\!\!\sim\!\!(NH_2)_4TPP$ surfaces, not previously employed on electrochemically active modified electrodes. We report the first example of reflectance spectroscopy of a covalently assembled modified electrode, including spectroelectrochemical experiments in which the electrode is under

active potential control so changes in surface oxidation state can be spectrally as well as electrochemically followed. Secondly, we have used a fluorescence technique to compare quantitatively the amount of $(NH_2)_4TPP$ actually bound to Pt with that which is electrochemically active. Thirdly, we have applied an X-ray photoelectron spectroscopy (XPS) technique[12] to determine the average number of surface amide bonds formed by $(NH_2)_4TPP$ in Reaction 1. Besides yielding useful surface structural insights, the spectroscopic experiments reveal some interactions between the attached molecules and the electrode.

EXPERIMENTAL

Preparation of Modified Glassy Carbon Electrodes. Polished glassy carbon (Atomergic Grade V-10, 2.6 mm diameter) cylinders were oxidized in a low wattage 380 mtorr O_2 radiofrequency plasma for 30 minutes, reacted with a 5% solution of BCl silane in toluene at room temperature for one hour, rinsed briefly with toluene, then reacted with ca. 4 mM aminophenylferrocene at 25°C or $(NH_2)_4TPP$ in refluxing toluene for ca. 2 hours, thoroughly washed with toluene and methanol, and stored under CH_3CN. $C/\sim(NH_2)_4TPP$ surfaces were metallated by reaction with $CoCl_2$ or $CuCl_2$ solutions[3].

Preparation of Modified Pt/PtO Electrodes. For reflectance spectroscopy and cyclic voltammetry, the surface of a superficially oxidized 0.29 cm² Pt disk, mirror polished (1 μm diamond compound) and Teflon shrouded, was covered with a drop of neat BCl silane and allowed to stand in laboratory air for ca. 1.5 minutes. Excess silane was rinsed off with a stream of toluene and a drop of solution of 1 mg. $(NH_2)_4TPP$ in 5 ml. toluene was allowed to stand on the Pt surface for ca. 5 minutes. If the porphyrin became protonated (green), a fresh drop was added. The amidized surface was thoroughly washed with DMF which is effective at removal of adsorbed porphyrin. The surfaces were metallated by warming (40-50°C) in a 0.5 M solution of $CoCl_2$ or $CuCl_2$ for 2 days and several hours, respectively, followed by washing in DMF.

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XPS of dangling amine groups on Pt/↜(NH$_2$)$_4$TPP was conducted by reacting the surface with 0.1 M 3,5-dinitrobenzoyl chloride in toluene for 1 hour, washing with toluene, and observing the N ls spectra with a DuPont Model 650B Electron Spectrometer.

Preparation of Pt/↜(NH$_2$)$_4$TPP surfaces for fluorescence experiments was as above except Pt flag electrodes were immersed in neat BCl silane and then (NH$_2$)$_4$TPP-toluene solution.

Spin Coating of BCl Silane on Pt. A polished, Teflon shrouded, 0.16 cm^2 disk, pre-oxidized with HNO$_3$, was spun at 28,000 rpm in a 6N HCl-saturated N$_2$ atmosphere. A specific number of droplets of 10% BCl silane in benzene was slowly delivered to the center of the horizontally spinning electrode. This surface was exposed to a refluxing benzene solution of aminophenylferrocene for 30 minutes and washed with benzene and CH$_3$CN. Depending on the number of BCl silane droplets applied, the still highly reflecting Pt surface is either metallic or shiny golden in color.

Chemicals. Tetrakis(p-aminophenyl)porphyrin, (NH$_2$)$_4$TPP was synthesized[13] and purified as before[3b]. Aminophenylferrocene was a gift of Professor W. F. Little, University of North Carolina, Chapel Hill. The BCl silane, 4-(methyldichloro-silyl)butyryl chloride (Silar), used as received, was stored under N$_2$. Toluene and benzene were Na°-dried; CH$_3$CN, DMF and DMSO were stored over molecular sieves.

Reflectance Spectroscopy. The unpolarized beam of a computer-interfaced Harrick rapid scanning spectrometer[14] was reflected at near-normal incidence from a Pt/↜(NH$_2$)$_4$TPP or Pt/↜(M)(NH$_2$)$_4$TPP modified surface mounted in the cell of Figure 1. This cell has connections for auxiliary and reference (NaCl-SCE; SSCE) electrodes so the potential of the modified electrode surface can be controlled while acquiring reflectance spectra. About 500 spectra can be acquired, averaged, and stored in 15 seconds. A background spectrum was similarly acquired for subtraction from the modified electrode spectrum by removing,

polishing, and carefully replacing the Pt disk in the cell. Comparison spectra of $(NH_2)_4TPP$ and $Co(NH_2)_4TPP$ solution in the desired oxidation states were obtained in an optically transparent thin layer (5×10^{-3} cm) electrode cell[15].

Fluorescence spectroscopy. Modified $Pt/\sim(NH_2)_4TPP$ flags were first scanned with cyclic voltammetry in 0.1 $\underline{M}$ Et_4NClO_4/DMSO, to determine the coverage of electrochemically reactive porphyrin, Γ_{elec}, and then hydrolytically stripped in a small, measured volume of refluxing HCl (conc.) for 1 hour. Exhaustive removal of the porphyrin was confirmed by reflectance and electrochemical inspection. The hydrolysate fluorescence spectrum was taken with a Hitachi MPF-2A spectrofluorimeter (λ_{exc} = 439 nm), calibrating the intensity axis with standard $(NH_2)_4TPP$ solutions.

RESULTS AND DISCUSSION

Cyclic Voltammetry of Modified Electrodes. The electrochemical behaviors of aminophenylferrocene and of $(NH_2)_4TPP$ immobilized as in Reaction 1 are well behaved and similar to observations by other established attach-ment chemistries [3,5,7-10]. Exemplary cyclic voltammetry of the attached mole-cules is shown in Figure 2 and data are given in Table 1, Entries 1,3-9. Surface formal potentials $E^{o\prime}_{surf}$ are similar to solution analog values[16] and the small ΔE_p values reflect fast electron transfer rates. Coverage values from anhy-drous silanization reactions (Entries 1, 4-9) are within monomolecular expecta-tions. The carbon-immobilized $(NH_2)_4TPP$ is easily metallated which is useful in "tuning" the porphyrin potential as an electrocatalytic electron transfer mediator[17] The electrochemistry of $Pt/\sim(NH_2)_4TPP$ and $C/\sim(NH_2)_4TPP$ surfaces is virtually identical (Figure 2, Curves B,C), except that Γ on the former are larger due to the non-anhydrous silanization procedure (Experimental). The broadening of surface waves of BCl-attached species can usually be accounted for by surface activity effects as illustrated by the fit[10] of theory of Brown and

Anson[18] to experiment in Figure 2, Curve B. The derived activity parameters are the same on C and Pt so this broadening is not specific to the electrode material.

That the BCl silane actually promotes aminophenylferrocene attachment to carbon is confirmed by omitting the silanization step, whereupon the ferrocene wave is much smaller or entirely absent[19] (Figure 2A).   The C/~NH$_2$PhCpFeCp electrode is very stable in the ferrocene state and has a t$_{1/2}$ ~ 3 hours when electrochemically maintained in the ferricenium state[20] in CH$_3$CN. XPS of C/~NH$_2$PhCpFeCp surfaces shows a Si 2p peak at 102.4 e.v. and   Fe 2p$_{3/2}$ peak at 708.0 e.v. characteristic of the silane and of ferrocene, respectively. Conversion of the 2.18 I$_{Fe}$/I$_{Si}$ intensity (area) ratio to an atom ratio[21] indicates that about 50% of the attached silane undergoes amide-coupling with the aminophenylferrocene. The rest of the BCl silane is hydrolyzed to carboxylic acid; XPS typically shows no residual chloride.

That BCl silane becomes attached to superficially oxidized Pt surfaces by Pt-O-Si bonds as represented in Reaction 1 seems fairly well established[8,10,20,22]. How BCl bonds stably to glassy carbon surfaces is less certain. Carbon oxide surface functionalities are important since the RF plasma pre-oxidation of the glassy carbon increases the intensity of the Si 2p silane band by about 3-fold over polished but not preoxidized carbon. We previously represented[11] carbon silanization as a surface silyl ether bond, but these surfaces are surprisingly stable if they are silyl ethers.   Perhaps formation of two surface bonds as assumed in Rxn. 1 provokes this stability. Although it is possible that some siloxane polymer formation   enhances   stability,   our experience with organosilanes suggests that polymers are unlikely under the anhydrous reaction conditions used for glassy carbon in this study. However the BCl silane bonds to glassy carbon, this acid chloride silane provides a

bridge by which the same amine redox reagent can be attached to either carbon or a metal oxide in a similar chemical environment.

XPS Analysis of $(NH_2)_4TPP$ Bonding to BCl Silanized Pt. $(NH_2)_4TPP$ is a tetrafunctional amine but all of the amine sites do not necessarily couple to BCl silane sites. This problem can be analyzed by derivatizing any dangling amine with 3,5-dinitrobenzoyl chloride followed by N 1s XPS of the nitro (406.6 e.v.) vs. amide plus porphyrin nitrogen bands (ca. 400 e.v.) (Figure 3). The relative N 1s band areas indicate that the nitro tag reagent reacts on the average with 1.9 dangling amine groups per porphyrin, which leads us to surmise an average of 2 amide bonds between each porphyrin and BCl silane sites. We obtained[7] the same result for $(NH_2)_4TPP$ attached to thionyl chloride activated carboxylic acid groups on glassy carbon. Given the added steric flexibility afforded by the carbon chain on the BCl silanized Pt as compared to acid chloride sites presumably affixed directly to a glassy carbon lattice, observation of the same average amide bond number to these surfaces with $(NH_2)_4TPP$ is surprising. Perhaps the formation of multiple surface bonds is more constrained by steric interactions between adjacently bonded $(NH_2)_4TPP$ molecules than by simple steric register of their amine groups with surface acid chloride sites.

Fluorescence of Hydrolytic Product of Pt/∿(NH₂)₄TPP Surface. The reaction conditions used in this paper for BCl silanization of Pt/PtO surfaces were deliberately "wet" (see Experimental) in contrast to the anhydrous procedures used above for glassy carbon and by us previously for metal oxides. In moist laboratory air, some polymerization of the BCl silane may occur, so that multimolecular layers of redox substances become bonded to the electrode surface. In such a multilayer film, the arrangement of the polymeric structure may cause some of the immobilized redox molecules to be electrochemically silent. This is an important question with polymer-coated electrodes on which little quantitative data is available. Accordingly, we hydrolytically

cleaved the porphyrin from Pt/$\sim$(NH$_2$)$_4$TPP surfaces into a limited volume of acid and determined its fluorescence intensity. Figure 4 shows that the hydrolysate fluorescence spectrum is nearly identical to that of a standard (NH$_2$)$_4$TPP solution. Cyclic voltammetry of the Pt/$\sim$(NH$_2$)$_4$TPP surface before hydrolysis affords an electrochemical coverage Γ_{elec} for comparison with that calculated from the fluorescence intensity data, Γ_{fluor}; Table II shows that the two coverages agree quite well.

The geometrical area requirements for (NH$_2$)$_4$TPP estimated from models[3b] are ca. 1.2 x 10^{-10} and 3.5 x 10^{-10}mole/cm^2 for coplanar and perpendicular orientations, respectively, of the porphyrin ring with respect to the Pt surface. On either account, the porphyrin coverages in Table II are more than monomolecular as expected for attachment to a polymeric BCl silane matrix. Between 3 and 8 monolayer-equivalents of porphyrin are attached to the BCl silane polymer and are quantitatively electroactive. Larger quantities have not been successfully attached by this particular silanization procedure. A technique for attaching thicker layers of amine redox substances to Pt, using spin-coating of BCl silane, is described below.

If a Pt/$\sim$(NH$_2$)$_4$TPP surface is viewed under fluorescent light, no visible emission from the surface is seen, although the amount of porphyrin suffices to give a visualized emission in the hydrolysate. We observed[24] (but did not report) a similar phenomenon during fluorescence studies of dansylsulfonamide attached to Pt with a different silane. We have reported[25] that the photolability characteristic of certain ruthenium complexes dissolved in solution vanishes upon their immobilization on Pt using silane chemistry; the surfaces are photostable. These three qualitative observations suggest that excited state lifetimes are generally shortened by the silanization-attachment to Pt. The excited state quenching may occur via energy

transfer through weak spectral overlap with the Pt electrode absorption. A far more interesting eventuality would be electron transfer quenching, since in it an electron transfer event akin to that operative in the electrochemical reactions of these molecules occurs at a rate competitive with excited state emission lifetimes. We suggest that quantitation of the quenching effect might be an avenue to electrode kinetic studies.

Reflectance Spectra of Pt/∿(NH$_2$)$_4$TPP Electrodes. BC1 silanized glassy carbon surfaces to which (NH$_2$)$_4$TPP has been attached exhibit a faint porphyrin coloration but are not very suitable for sensitive electronic spectroscopy. Reflectance spectra of Pt/∿(NH$_2$)$_4$TPP surfaces, which have a golden tint to the eye, are on the other hand readily obtained. A reflectance spectrum of Pt/∿(NH$_2$)$_4$TPP (Γ_{elec} = 4.1 x 10^{-10} mole/cm^2) is compared in Figure 5A to a transmission spectrum of a solution containing the same number of porphyrin molecules per unit beam area . The Soret λ_{max} are virtually identical (see Table III), reflecting weak (or equal) interactions between the ground and excited porphyrin states and the Pt electrode, a result consistent with the general equality of $E_{surf}^{o'}$ and $E_{soln}^{o'}$ values (Table I). A weak porphyrin-electrode interaction does exist; the surface spectrum is broadened toward longer wavelengths. Similar results are obtained for Pt/∿(Cu)(NH$_2$)$_4$TPP (Figure 5B). One interpretation of this broadening effect would invoke charge transfer interaction of the excited state with the metal conduction band[26].

For interactions between electrode and porphyrin to be weak, it is important that the Pt/∿(NH$_2$)$_4$TPP surface be properly solvated. A reflectance spectrum with the surface in contact with air is severely broadened and red shifted as compared to the DMSO solvated surface.

Quantitative Aspects of Pt/∿(NH$_2$)$_4$TPP Reflectance Spectra. The quantity of attached (NH$_2$)$_4$TPP is known unequivocally from the analysis of Table II, so the

reflectance spectral intensity can be analyzed. In reflection from a surface coated with a thin absorbing film, of the available quantitative models[27,28] that by Hansen[28] is most readily applied to the present situation.

$$A = \frac{n_2 \; \alpha_2 \; d_2}{2.3 \; n_1 \; R_o \; \cos \theta} \quad <E^2>^o_2 \qquad (2)$$

α_2 is the absorption coefficient of the porphyrin layer of thickness d_2 (i.e., $\ln(I_o/I) = \alpha_2 d_2 = 2.3 \times 10^3 \; \epsilon \Gamma$ where ϵ is molar absorptivity), and d_2 is taken as small compared to the thickness of the standing, reflecting wave[29] set up at the electrode/solution interface. The node of this wave is slightly below the surface plane; for visible light reflected normally from Pt the mean square intensity of the standing wave at the surface plane[27] $<E^2>^o_2 = 0.26$. Using literature parameters[30], and assuming that R_o is unaffected by the porphyrin, eq. 2 simplifies to

$$A = 0.58 \times 10^3 \; \epsilon \Gamma \qquad (3)$$

Values of ϵ thus derived (Table III), are larger than those of their unattached analogs. A better comparison of attached and unattached intensities can be based on band areas expressed as oscillator strengths[33] $f = 4.32 \times 10^{-9} \int \epsilon \, d\bar{\nu}$, which (Table III) again indicates a higher absorption probability for the attached versions. Oscillator strengths for the unattached porphyrin Soret peak are very large, approaching the hypothetical limit of 2. The attached versions have f_{surf} > 2, which may indicate (i) we have seriously overestimated n_2 (unlikely), (ii) R_o is substantially decreased by the porphyrin layers, (iii) we have underestimated reflectance intensity in the long wavelength spectral tail, or (iv) the $(NH_2)_4$TPP ring has a preferred orientation with respect to the Pt surface. The last would not be surprising since the porphyrin is connected to the surface by two amine groups. The Soret transitions are polarized in the plane of the porphyrin ring[34], so a larger f_{surf} implies that more porphyrins are oriented with absorption

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vector parallel to the electric vector of the (normal incidence) incoming

light (i.e., with the porphyrin ring parallel to the Pt) than are oriented

perpendicular to the surface.

Reflectance Spectroelectrochemistry. Virtually all of the spectroscopy to

date on modified electrodes has been ex situ, i.e., XPS, IETS,

fluorescence, etc.   In a cyclic voltammogram such as in Figure 2 there

is no real question that the voltammetry reflects reduction and oxidation

of attached porphyrin, however, electrochemical potentials usually

                                                    have limited struc-

tural information content. For more chemically involved electron transfer

reactions, supplementary in situ spectroscopy would often be of value. The

reflectance spectral experiment is suited to such observations with attached,

potent chromophores like the porphyrins.

The reflectance spectrum of a Pt/$\sim$(NH$_2$)$_4$TPP surface in contact with

DMSO solvent is the same whether the electrode is at open circuit or potentio-

statted at 0 volts vs. SSCE. Application of E = -1.3 volts vs. SSCE (as observed

by the cyclic voltammetry to be sufficient to reduce the porphyrin to its radical anion)

for 5 minutes changes the reflectance spectrum to that in Figure 5C. The peak

at 453 nm is probably not the simple radical anion, but is instead a protonated

form.   Reduction of Pt/$\sim$(Cu)(NH$_2$)$_4$TPP to its radical

anion (Figure 5B) is not accompanied by protonation. In the radical anion,

the Soret peak collapses, and appears split.

The cobalt-metallated surfaces provide better illustrations of the

power of in situ spectroelectrochemistry. Pt/$\sim$Co(NH$_2$)$_4$TPP and C/$\sim$Co(NH$_2$)$_4$TPP

surfaces exhibit very unusual electrochemical behavior. Figure 6 compares

typical cyclic voltammograms for Pt/$\sim$Co(NH$_2$)$_4$TPP and for a CoTPP

solution. The quasi-reversible dissolved Co(TPP) wave for Co(III/II) at

E_{soln}° = +0.1 volt vs. SSCE is vanishingly small on the Pt/$\sim$Co(NH$_2$)$_4$TPP

electrode; it can be observed by differential pulse voltammetry, at the reversible potential (+0.12), but is only 1-5% as large as the Co(II/I) surface wave at -0.86 v. vs. SSCE. The second unusual feature of the Pt/~Co(NH$_2$)$_4$TPP voltammogram is that the charge underneath the cathodic surface wave at the Co(II/I) potential is <u>larger</u> than that of the anodic member. The exact value of Q_{cath}/Q_{anod} depends on the electrode's potential scanning history; in Figure 6 it is 1.8. If only the potential region immediately around the Co(II/I) wave is scanned, Q_{cath}/Q_{anod} = 1.0 .

We have observed[7] qualitatively similar behavior for cobalt metallated (NH$_2$)$_4$TPP attached to activated glassy carbon electrodes, and Jester has hypothesized[35] that the cobalt becomes axially coordinated by carbon surface ligands, probably carboxylate, which centrally underlie the cobalt porphyrin site.

Reflectance spectroelectrochemistry of Pt/~Co(NH$_2$)$_4$TPP was useful in exploring this proposal. In this case Figure 6(A) shows that after potentiostatting at +0.4 volt vs. SSCE for a few minutes; the 452 nm λ_{max} reflectance spectrum agrees well with that (450 nm) for a solution of Co(III)TPP obtained in an optically transparent thin layer cell at the same potential. At -0.3 volt vs. SSCE the absorbance decreases at 452 mn and grows at 435 nm which is near λ_{max} for a solution of Co(II)TPP (433 nm). The change however is exceedingly slow; the spectrum shown (Curve B) was taken <u>after several minutes of potentiostatting</u> and a significant Co(III) porphyrin shoulder is still apparent. At a potential of -1.1 volt vs. SSCE, the surface spectrum changes immediately to Curve C, the Pt/~Co(I)(NH$_2$)$_4$TPP state. Returning to -0.4 volt vs. SSCE, an immediate restoration of the Co(II) spectrum (Curve D) is obtained, now without any shoulder for Co(III) porphyrin. Finally, application of +0.4 volt vs. SSCE restores the Co(III) spectrum as in Curve A. This last reaction occurs slowly, but not as slow as the Co(III)→Co(II) transformation.

The reflectance spectroelectrochemistry shows that the Co(III/II) reac-

tion does occur on the Pt/~Co(NH$_2$)$_4$TPP surface, at a potential between +0.4
and -0.3 volt vs. SSCE, but it is much too slow to contribute a noticeable
current peak in a cyclic voltammogram. The reaction occurs rapidly at potentials
sufficient to reduce the porphyrin to the Co(I) state; in Figure 6, Q$_{cath}$ corres-
ponds to a Co(III/I) reaction.

Our rationalization of the slow Co(III/II) reaction rests on the expecta-
tion[36] that cobalt is six coordinate in the Pt/~Co(III)(NH$_2$)$_4$TPP state but five
coordinate as Pt/~Co(II)(NH$_2$)$_4$TPP, so dissociation of an axial ligand will
accompany electron transfer. Such a change in coordination by pyridine was estab-
lished on carbon by Jester[35]. If the axial ligand is carboxylate, co-immobilized
on the Pt surface with the porphyrin, such axial dissociation would be very slow.
Re-association would be comparatively faster, and we spectrally observe that the
Co(II/III) transformation is faster than Co(III/II).

Spin Coating of BCl Silane on Pt. Electrodes coated with polymeric redox
substances[21,37-43] offer possibilities of many interesting applications includ-
ing electron transfer mediation at semiconductor photoanodes, for which polymer-
ized silylferrocenes[44,45] have been used. To expand the scope of polyferrocene
coated electrodes, we have spin coated films of BCl silane onto oxidized Pt
surfaces (see Experimental). The relative reactivities of the chlorosilyl and
acid chloride groups are such that PtOSi surface bonding and siloxane polymer-
ization can occur without exhaustive hydrolysis of the acid chloride groups so
that reagents such as aminophenylferrocene can amide-bond to the pre-formed
siloxane polymer matrix. The shiny brownish surface thus prepared shows an
intense Fe 2p$_{3/2}$ XPS peak at 708 e.v. (characteristic of ferrocene) and a Pt
4f band which is very weak or absent depending upon the thickness of the
polymeric film.

Cyclic voltammetry of the film shows a charge for the oxidation of
aminophenylferrocene which varies, with the amount of spin coated BCl silane,

from 10^{-9} to as large as 2×10^{-7} mole/cm.^{2}. In acetonitrile, symmetric voltammetric waveshapes observed at lower coverages, grow tails (Figure 7A) at high coverages. In Figure 7A, electrochemical charge is being transported through a film equivalent to at least ca. 500 monolayers of aminophenylferrocene. Exchange of electrons between adjacent sites is the most likely mechanism for this, but the exchange itself is not necessarily rate controlling[39c].

In aqueous $LiClO_4$ (and $HClO_4$), the anodic current peak becomes quite sharp (Figure 7B), and in aqueous H_2SO_4 both anodic and cathodic peaks are sharp (Figure 7C). E_{FWHM} = 28 mv. for Figure 7C whereas surface waves for redox polymers typically have E_{FWHM} = 100-200 mv. The sharp current peaks mean that the ratio of activities of the oxidized and reduced surface molecules changes relatively little over the course of exhaustive electrolysis of the surface layer. This is a phase-like property, as we have pointed out in connection with the behavior of plasma polymerized vinylferrocene films in aqueous $LiClO_4$[42]. The present results demonstrate that phase-like behavior can occur in quite diverse types of ferrocene polymer matrices and is moderated both by choice of solvent and electrolyte. Presumably, the important factor in this activity phenomenon is whether the polymer matrix becomes significantly swollen by solvent in its various oxidation state/electrolyte counterion forms. Finally, we note that the proper choice of solvent and electrolyte allows switching between ferrocene and ferricenium surface states over a rather narrow range of potentials. Considering the redox film as a molecular surface state (layer), a phase-like property yields a very narrow energy band, a factor of possible utility in applications to semiconductor electrodes.

Further details and applications of spin coated BC1 and other siloxane polymer films will be presented in another report.

.

TABLE I

ELECTROCHEMICAL DATA FOR BC1-SILANE ATTACHED AMINOPHENYLFERROCENE AND $(NH_2)_4TPP$

Entry	Electrode	Solvent	$E°'_{surf}$, vs. SSCE[a]	ΔE_p, mv.[b]	$\Gamma \times 10^{10}$, mole/cm^2	$E°'_{soln}$
1	C/~NH$_2$PhCpFeCp	CH$_3$CN	+0.46	10	4.5	+0.40[d]
2	Pt/~NH$_2$PhCpFeCp	CH$_3$CN	+0.43	23-176	60-1500	+0.40[d]
3	Pt/~(NH$_2$)$_4$TPP	DMSO	-1.11, -1.49	20	5.7	-1.08, -1.45[c]
4	C/~(NH$_2$)$_4$TPP	DMSO	-1.10, -1.48	25, 20	2.5	-1.08, -1.45[c]
5	C/~(NH$_2$)$_4$TPP	CH$_3$CN	-1.24, -1.62	40	4.5	
6	C/~(Co)(NH$_2$)$_4$TPP	DMSO	-0.85	50	4.1	-0.82[c]
7	C/~(Ni)(NH$_2$)$_4$TPP	DMSO	-1.19, -1.75	15	3.6	-1.18, -1.75[c]
8	C/~(Cu)(NH$_2$)$_4$TPP	DMSO	-1.18, -1.64	-	3.8	-1.20, -1.68[c]
9	C/~(Zn)(NH$_2$)$_4$TPP	DMSC	-1.37, -1.73	-	3.2	-1.31, -1.72[c]

a. Average potential of cathodic and anodic peaks.

b. Difference in potential of cathodic and anodic peaks.

c. Felton, R.H. and Linschitz, H., J. Amer. Chem. Soc. 1966, 88, 1113.

d. Solution analog is 4-acetainidophenylferrocene.

TABLE II

COMPARISON OF ELECTROCHEMICAL AND FLUORIMETRIC COVERAGES

OF $(NH_2)_4$TPP ON Pt/$\sim$$(NH_2)_4$TPP ELECTRODES

Determination	Electrode Area, cm^2	Hydrolysate[a] conc., M	Γ_{fluor}, mole/cm^2 [b]	Γ_{elec}, mole/cm^2 [b]
1	0.84	1.8×10^{-7}	9.7×10^{-10}	10.5×10^{-10}
2	1.15	2.5	7.6	7.7
3	1.15	1.8	10.5	10.3

a. From hydrolysate solution of fluorescence intensity, solution volume is in 4-6 ml range.

b. Correction for Pt electrode microscopic roughness (ca. 1.5)[20] has not been made to these values; it is probably inappropriate at multilayer coverages.

TABLE III

REFLECTANCE SPECTRAL INTENSITIES FOR Pt$\sim$(NH$_2$)$_4$TPP ELECTRODES

ALL IN DMSO SOLVENT

Solution[a]	Electrode	Γ_{elec}, mole/cm^2	A at λ_{max}	λ_{max}	ε_{max}, l./mole-cm.	f^b
-	Pt$\sim$(NH$_2$)$_4$TPP	5.4×10^{-10}	0.100	442	3.2×10^5	3.2
-	Pt$\sim$(NH$_2$)$_4$TPP	4.1×10^{-10}	0.074	440	3.1×10^5	3.2
(NH$_2$)$_4$TPP	-	-	-	439	2.1×10^5	1.6
-	Pt$\sim$(Cu)(NH$_2$)$_4$TPP	3.8×10^{-10}	0.074	432	3.4×10^5	2.3
Cu(NH$_2$)$_4$TPP	-	-	-	425	2.6×10^5	1.5
-	Pt$\sim$(Co^{III})(NH$_2$)$_4$TPP	3.3×10^{-10}	0.070	450	3.6×10^5	2.9
Co^{III}(NH$_2$)$_4$TPP^c	-	-	-	450	1.4×10^5	1.0
-	Pt$\sim$(Co^{II})(NH$_2$)$_4$TPP	3.3×10^{-10}	0.056	435	2.9×10^5	3.2
Co^{II}(NH$_2$)$_4$TPP^c	-	-	-	433	1.1×10^5	1.3
-	Pt$\sim$(Co^{I})(NH$_2$)$_4$TPP	3.3×10^{-10}	0.038	442	2.0×10^5	-
Co^{I}(NH$_2$)$_4$TPP^c	-	-	-	434	0.75×10^5	-

TABLE III

continued: footnotes

a. Transmission spectra of standard solutions.

b. Calculated from $f = 4.32 \times 10^{-9} \int \epsilon d\bar{\nu}$

c. Due to solubility problems, $Co(NH_2)_4TPP$ gave difficulties in preparing an adequate standard solution, so the $Co(NH_2)_4TPP$ concentration was measured assuming that f for $Co^{II}(NH_2)_4TPP$ is equal to f for $Co^{II}TPP$.

REFERENCES

1. Present address (a) Naval Research Laboratory, Washington, DC; (b) Florida Atlantic University, Boca Raton, Florida.

2. Watkins, B. F.; Behling, J. R.; Kariv, E. and Miller, L. L. J. Amer. Chem. Soc. 1975, 97, 3549.

3. (a) Lennox, J. C. and Murray, R. W. J. Electroanal Chem. 1977, 78, 395. (b) Rocklin, R. D. and Murray, R. W. J. Electroanal. Chem. 1979, 100, 271.

4. Fujihira, M., Tamura, A., Osa, T. Chem. Letters 1977, 361.

5. Koval, C. A. and Anson, F. C. Anal. Chem. 1978, 50, 223.

6. Evans, J. R., Kuwana, T., Henne, M. T. and Royer, G. P. J. Electroanal. Chem. 1977, 80, 409

7. Lennox, J. C. and Murray, R. W. J. Amer. Chem. Soc. 1978, 100, 3710.

8. Lenhard, J. R. and Murray, R. W. J. Electroanal. Chem. 1977, 78, 195.

9. Brown, A. P., Koval, C. and Anson, F. C. J. Electroanal. Chem. 1976, 72, 379.

10. Smith, D. F., Willman, K., Kuo, K. and Murray, R. W. J. Electroanal. Chem. 1979, 95, 217.

11. Elliott, C. M. and Murray, R. W. Anal. Chem. 1976, 48, 1247.

12. Moses, P. R., Wier, L. M., Lennox, J. C., Finklea, H. O., Lenhard, J. R. and Murray, R. W. Anal. Chem. 1978, 50, 576.

13. Treibs, A. and Haberle, N. Liebigs Ann. Chem. 1968, 718, 183.

14. Wightman, R. M., Scott, R. L., Reilley, C. N., Murray, R. W. and J. N. Burnett, Anal. Chem. 1974, 46, 1492.

15. Murray, R. W., Heineman, W. R. and O'Dom, G. W. Anal. Chem. 1967, 39, 1666.

16. Lenhard, J. R., Rocklin, R., Abruna, H., Willman, K., Kuo, K., Nowak, R., and Murray, R. W. J. Amer. Chem. Soc. 1978, 100, 5213.

17. Rocklin, R., unpublished results, University of North Carolina, 1979.

18.   Brown, A. P. and Anson, F. C. Anal. Chem. 1977, 49, 1589.

19.   Small amounts of attachment may occur without BCl silanization via carbon surface acid anhydride or carbonyl as Schiff base. We did not observe polymerization of aminophenylferrocene as seen for aminoferrocenes by Oyama, N., Yap, K. B. and Anson, F. C. J. Electroanal. Chem. 1979, 100, 233.

20.   Lenhard, J. R. and Murray, R. W. J. Amer. Chem. Soc. 1978, 100, 7870.

21.   Fischer, A. B., Wrighton, M. S., Umana, M. and Murray, R. W. J. Amer. Chem. Soc. 1979, 101, 3442.

22.   Facci, J. and Murray, R. W., J. Electroanal. Chem., in press.

23.   The slight λ_{max} difference may be due to unhydrolyzed amide bonds in the $(NH_2)_4$TPP hydrolysate.

24.   White, H. S. and Murray, R. W. Anal. Chem. 1979, 51, 236.

25.   Abruna, H. D., Meyer, T. J. and Murray, R. W. Inorg. Chem. 1979, 18, 3233.

26.   Gerischer, H. Dis. Faraday Soc. 1974, 58, 219.

27.   McIntyre, J. D. E. Advances in Electrochemistry and Engineering, Vol. 9, P. Delahay and C. Tobias, Editors, John Wiley & Sons, New York, NY, 1973, Chap. 2.

28.   Hansen, W. N. Symp. Faraday Soc. 1970, 4, 27.

29.   Because of this, absorption by the porphyrin is not appropriately described by a double pass transmission model.

30.   Refractive indices n_1 = 1.48 for incident medium (DMSO) and $n_2 \approx 2.0$ for silane-porphyrin layer (estimated from ellipsometric data[31]), substrate reflectivity R_o = 0.6 for Pt in 400-500 nm range[32], and angle of (normal) incidence cos θ = 1.0 .

31.   Bartell, L. S. and Churchill, D. J. Phys. Chem. 1961, 65, 2242.

32.   American Institute of Physics Handbook, 3rd edition, 1972.

33.   McGlynn, S. P., Vanquickenborne, L. G., Kinoshita, M., and Carroll, D. G. Introduction to Applied Quantum Chemistry, Holt, Rinehart and Winston, 1972, New York.

References page 3

34.   Bergeron, J. A., Gaines, G. L. and Bellamy, W. D. J. Colloid. Interface Sci. 1967, 25, 97.

35.   Jester, C. P., Rocklin, R. D. and Murray, R. W., J. Electrochem. Soc., in press.

36.   Scheidt, W. R. Accts. Chem. Res. 1977, 10, 339.

37.   Merz, A. and Bard, A. J. J. Amer. Chem. Soc. 1978, 100, 3222.

38.   Wrighton, M. S., Palazzotto, M. C., Bocarsly, A. B., Bolts, J. M., Fischer, A. B. and Nadjo, L. J. Amer. Chem. Soc. 1978, 100, 7264.

39.   a) Nowak, R., Schultz, F. A., Umana, M., Abruna, H. and Murray, R. W. J. Electroanal. Chem. 1978, 94, 219; b) Ibid., Anal. Chem. 1980, 52, 315;

    (c) Lenhard, J. R., Daum, P., Rolison, D. R., and Murray, R. W. J. Amer. Chem. Soc. 1980, 102, 0000.

40.   (a) Miller, L. and VanDeMark, M. J. Amer. Chem. Soc. 1978, 100, 639; (b) VanDeMark, M. and Miller, L. ibid, 1978, 100, 3223; (c) Miller, L. and VanDeMark, M. J. Electroanal. Chem. 1978, 88, 437.

41.   (a) Kaufman, F. B. and Engler, E. M. J. Amer. Chem. Soc. 1979, 101, 547; (b) Kaufman, F. B., Schroeder, A. H., Engler, E. M., Kramer, S. R. and Chambers, J. Q. ibid, 1980, 102, 483.

42.   (a) Daum, P. and Murray, R. W. J. Electroanal. Chem. 1979, 103, 289; (b) Ibid, submitted for publication.

43.   Oyama, N. and Anson, F. J. Amer. Chem. Soc. 1979, 101, 739.

44.   Wrighton, M. S., Austin, R. G., Bocarsly, A. B., Bolts, J. M., Haas, O., Legg, K. D., Nadjo, L. and Palazzotto, M. C. J. Amer. Chem. Soc. 1978, 100, 1602.

45.   Bolts, J. M., Bocarsly, A. B., Palazzotto, M. C., Walton, E. G., Lewis, N. S. and Wrighton, M. S. J. Amer. Chem. Soc. 1979, 101, 1378.
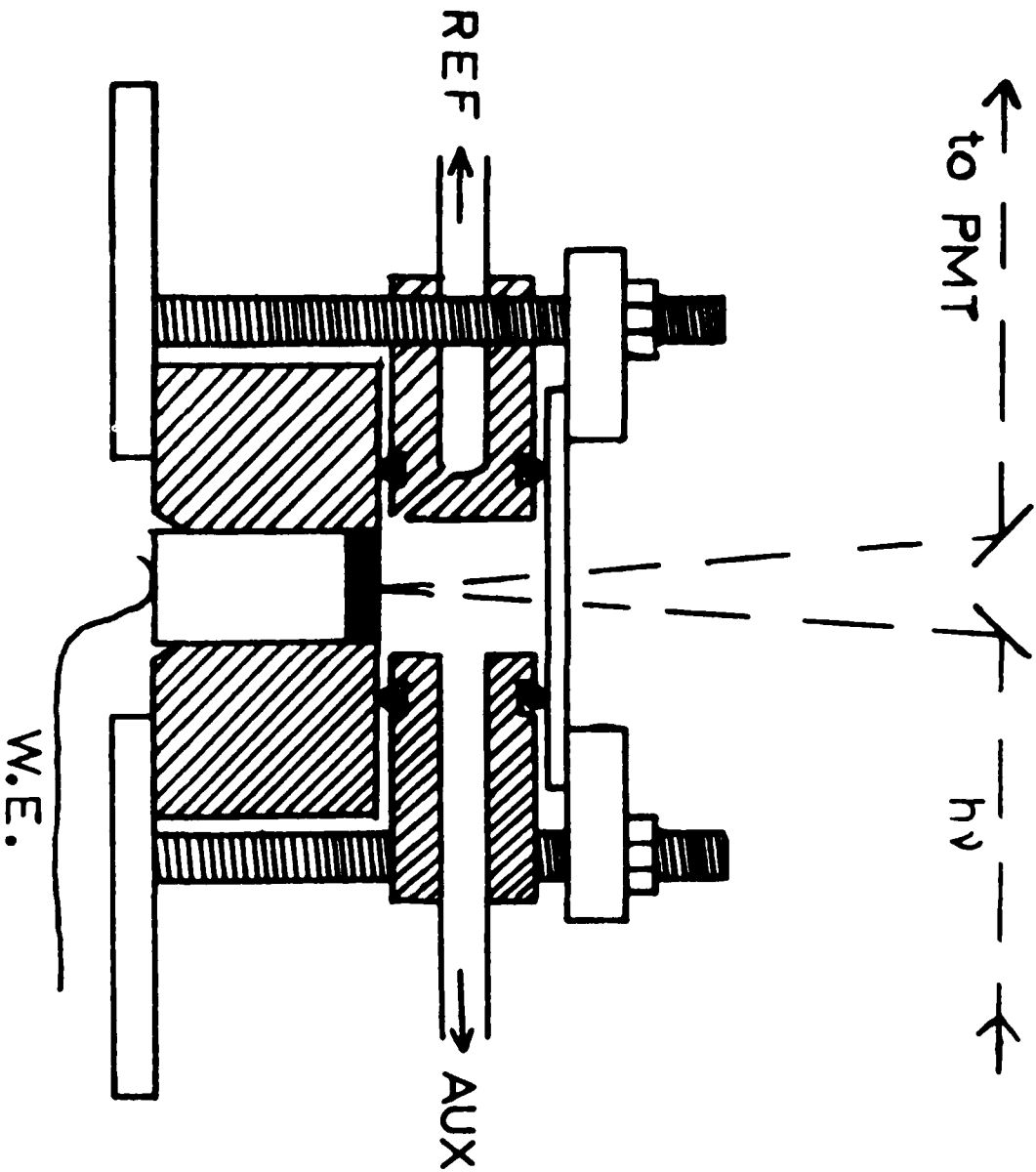
FIGURE LEGENDS

Figure 1.   Cell for reflectance spectroelectrochemistry. Quartz window, 1 cm.

of deareated supporting electrolyte/solvent. Cross-hatched is Teflon,

solid is modified Pt electrode.

Figure 2.   Cyclic voltammetry of $\underline{BCl}$-silanized electrode. Curve A:

$C/\!\!\sim\!\!NH_2PhCpFeCp$ in 0.1 $\underline{m}$ Et_4NClO_4/CH_3CN at 200 mv./sec., $\Gamma = 4.5 \times$

10^{-10} mole/cm^2, $S = 9.3$ µa/cm^2; dashed curve same as Curve A except

carbon electrode was not silanized, $S = 7$ µa/cm^2; Curve B: $Pt/\!\!\sim\!\!(NH_2)_4TPP$

in 0.1 $\underline{M}$ Et_4NClO_4/DMSO at 100 mv./sec., $\Gamma = 5.7 \times 10^{-10}$ mole/cm^2,

$S = 14$ µa/cm^2, points are fit of surface activity theory[10] to experiment,

$r = r_\bullet = r_R = -4.04$ and -6.74×10^9 for the two waves; Curve C:

$C/\!\!\sim\!\!(NH_2)_4TPP$ in 0.1 $\underline{M}$ Et_4NClO_4/DMSO at 200 mv./sec., $\Gamma = 2.5 \times 10^{-10}$

mole/cm^2, $S = 7$ µa/cm^2.

Figure 3. N 1s XPS of a $\underline{BCl}$-silanized Pt/PtO surface after reaction with

3,5-dinitrobenzoyl chloride. Counts are expressed as 1×10^3 counts/

division. Band at left is nitro (B.E. $= 406.6$ e.v.), band at right

is porphyrin nitrogen plus amide nitrogen (overlap) at B.E. $\underline{ca}$.

400 e.v. Relative band areas are 1.9 after correction of 400 e.v.

band for typical adsorbed level of reduced N 1s. No nitro correction

necessary as indicated by control experiment.

Figure 4.   Fluorescence spectra ($\lambda_{exc} = 439$ nm) in HCl (conc.) of $Pt/\!\!\sim\!\!(NH_2)_4TPP$

hydrolysate solution (——) and of 2.0×10^{-7} $\underline{M}$ standard $(NH_2)_4TPP$

solution (----). I_F axis is % of intensity of the standard solution

For this example, (determination 2 from Table II) $(NH_2)_4TPP$ hydrolysate
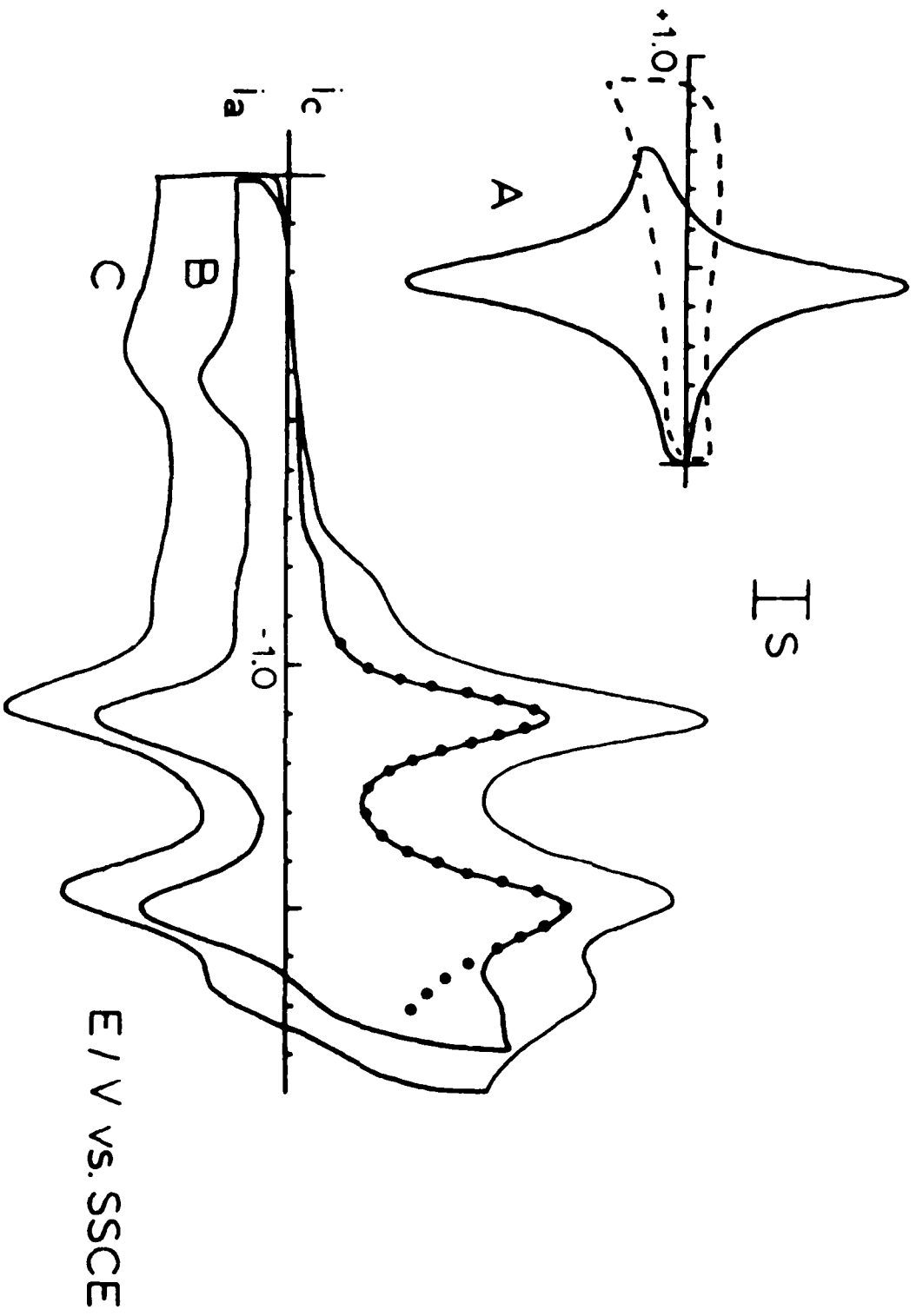
concentration is 2.5×10^{-7} M.

Figure Legends, p. 2

Figure 5.   A: Reflectance spectrum of $\Gamma_{elec} = 4.1 \times 10^{-10}$ mole/cm^2

Pt/$\sim\!\!\sim$(NH$_2$)$_4$TPP surface in contact with 0.1 $\underline{M}$ Et$_4$NClO$_4$/DMSO (———);

transmission spectrum of 1 cm cell containing 4.1 x 10^{-7} $\underline{M}$ solution

of (NH$_2$)$_4$TPP in DMSO (----); B: Reflectance spectrum of Pt/$\sim\!\!\sim$(NH$_2$)$_4$TPP

in contact with 0.1 $\underline{M}$ Et$_4$NClO$_4$/DMSO at 0 volts vs. $\cup$SCE (——);

same except -1.4 volt $\underline{vs}$. SSCE applied potential (-.-.); transmission

spectrum of Cu(NH$_2$)$_4$TPP in DMSO (----); C: Reflectance spectrum of

Pt/$\sim\!\!\sim$(NH$_2$)$_4$TPP in contact with 0.1 $\underline{M}$ Et$_4$NClO$_4$/DMSO at 0 volt vs. SSCE

(———); same except after $\underline{ca}$. 5 minutes at -1.3 volt vs. SSCE (----).
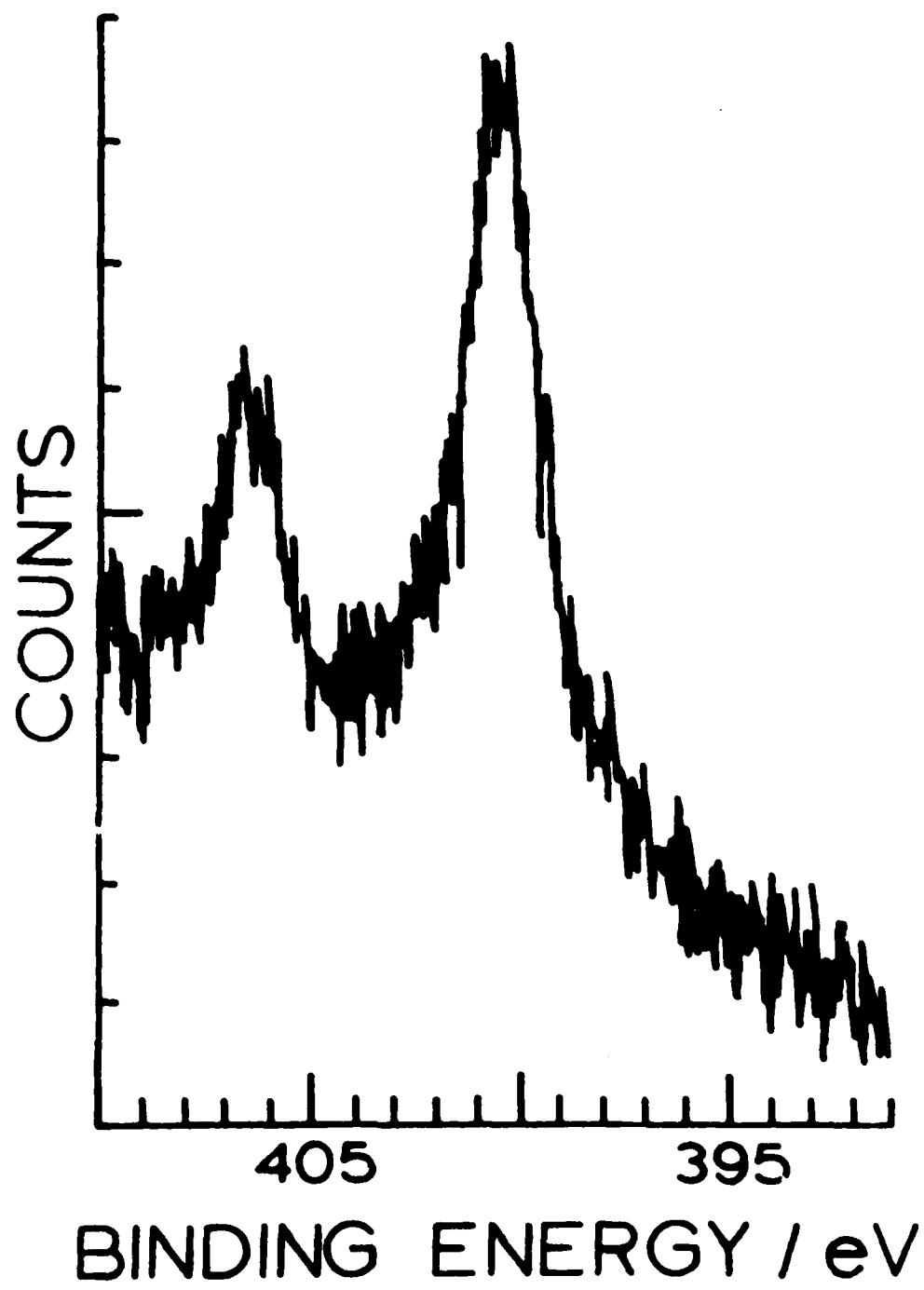
Absorbance axis for B and C uncalibrated.

Figure 6.   Reflectance spectroelectrochemistry of a Pt/$\sim\!\!\sim$Co(NH$_2$)$_4$TPP surface

in 0.1 $\underline{M}$ Et$_4$NClO$_4$/DMSO. From the cyclic voltammetry (———), Γ_{elec}

$= 4.1 \times 10^{-10}$ mole/cm^2 (from the Co(I$\rightarrow$II) anodic wave), and

$Q_{cath}/Q_{anod} = 1.8$. S = 10 μa/cm^2. The dashed curve (----) is a

Co(TPP) DMSO solution at a glassy carbon electrode. 100 mv./sec.

The reflectance spectra were taken at the potentials (A-D) indicated

on the voltammogram of Pt/$\sim\!\!\sim$Co(NH$_2$)$_4$TPP, in that order. The line

at 433 nm is λ_{max} for Co(II)(NH$_2$)$_4$TPP in DMSO solution; the 450 nm line

is λ_{max} for Co(III)(NH$_2$)$_4$TPP in DMSO solution, both from thin layer

spectroelectrochemistry.

Figure 7.   Cyclic voltammograms of aminophenylferrocene coupled to spin coated,

polymerized $\underline{BCl}$ silane film on Pt. Curve A: 0.1 $\underline{M}$ Et$_4$NClO$_4$/CH$_3$CN, 2

mv./sec., S = 6.5 μa/cm^2; Curve B: 0.1 $\underline{M}$ LiClO$_4$/H$_2$O, 2 mv./sec., S =

7.0 μa/cm^2; Curve C: 0.1 $\underline{M}$ H$_2$SO$_4$/H$_2$O, 1 mv./sec., S = 7.0 μa/cm^2.

Apparent coverage (measured by baseline current extrapolation) of

ferrocene is $\Gamma \approx 1.5 \times 10^{-7}$, 1.5 x 10^{-8}, and 3.0 x 10^{-8} moles/cm^2,

respectively. E_{FWHM} (anodic) = 200, 55 and 28 mv, for Curves A-C

respectively.

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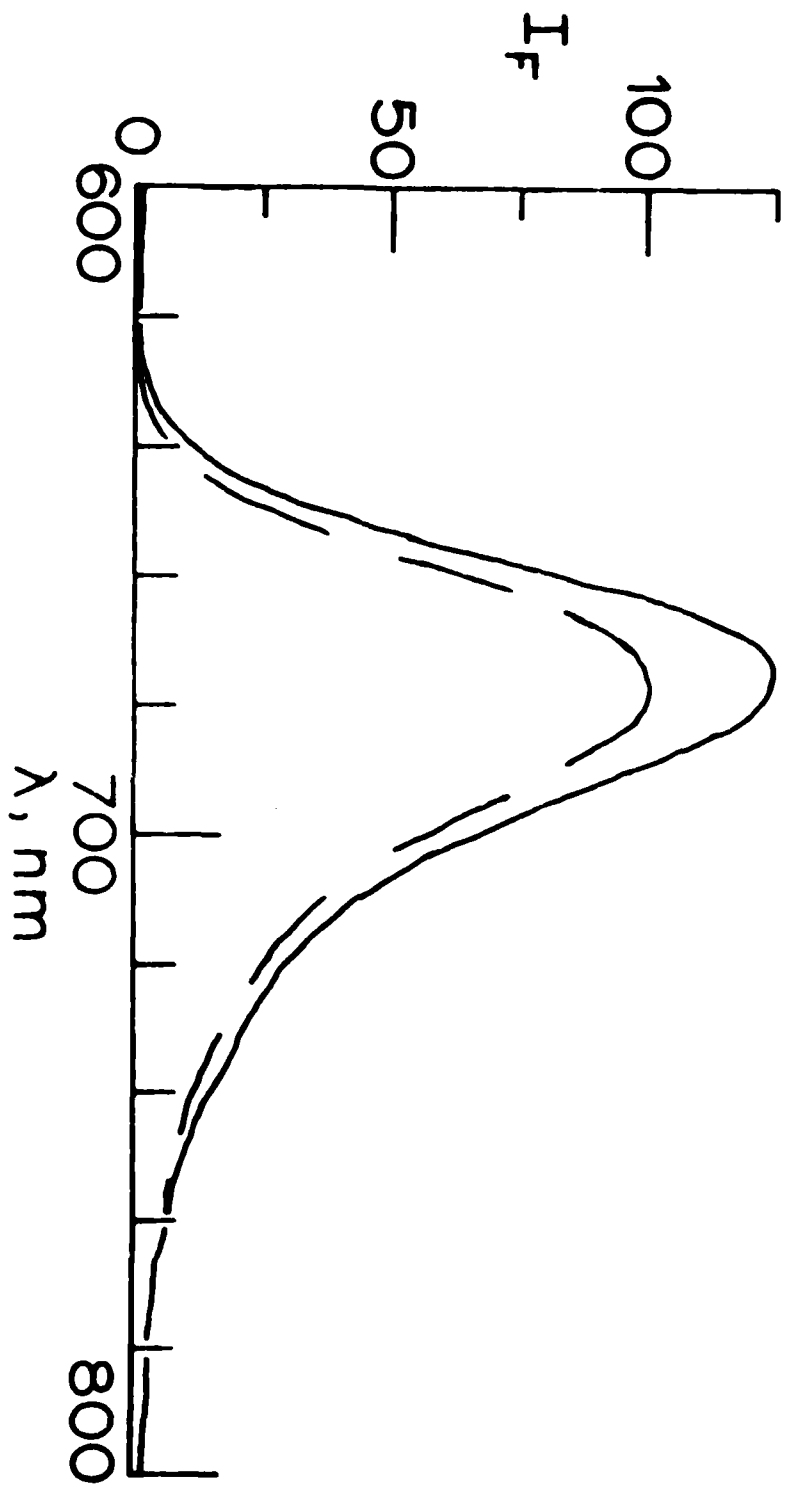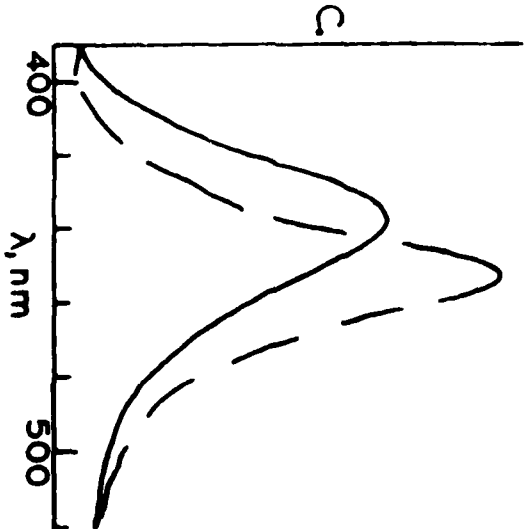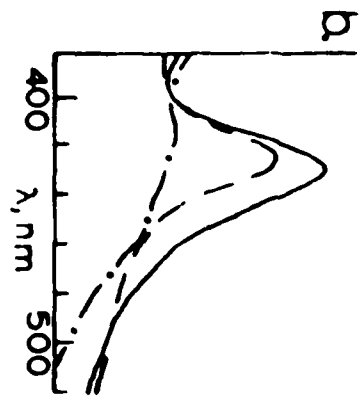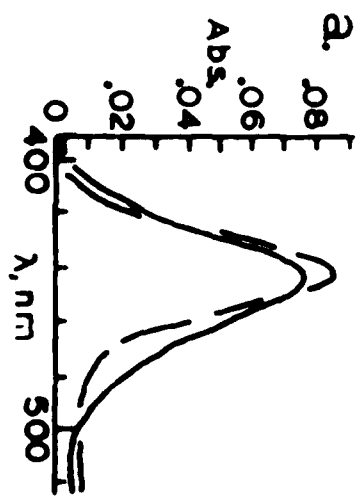
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to PMT

hν

COUNTS

405   395

BINDING ENERGY / eV

I_F

100

50

0

600

700

800

λ, nm

C   B   A

i_a i_c

E vs NaSCE

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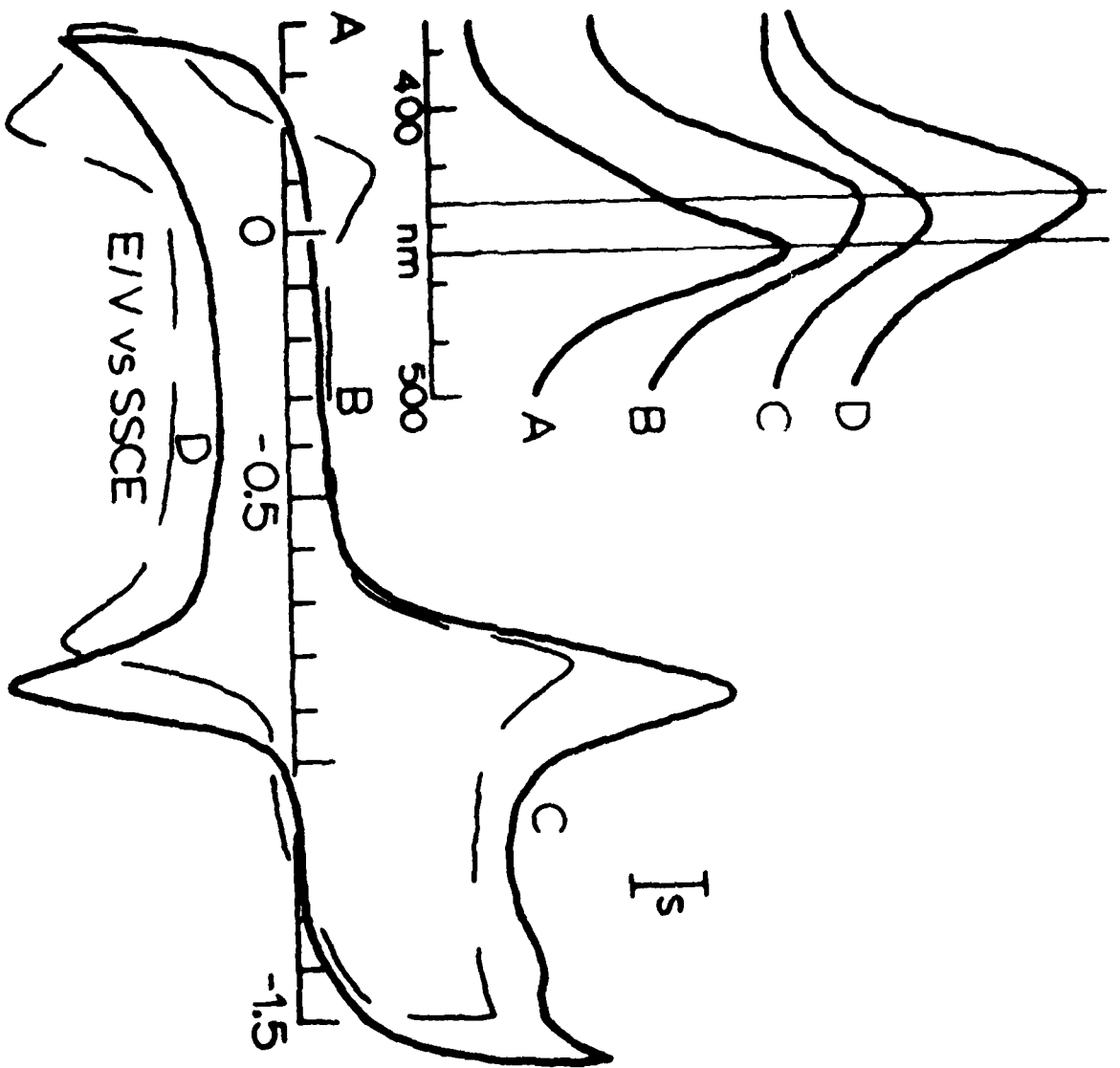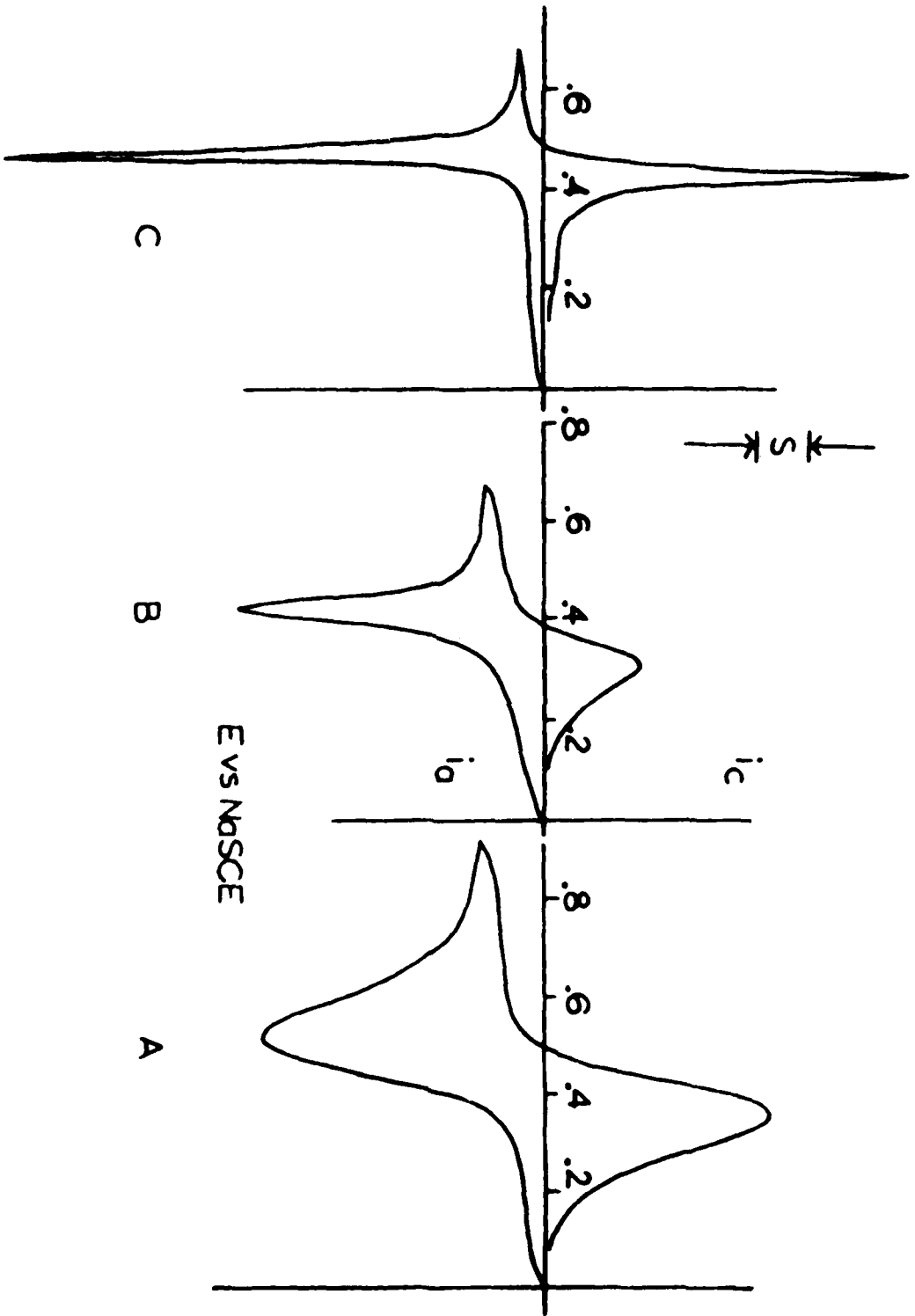
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Department of Chemistry
University of Southampton
Southampton 509 5NH England   1

Dr. Janet Osteryoung
Department of Chemistry
State University of New
  York at Buffalo
Buffalo, New York 14214   1

Dr. R. A. Osteryoung
Department of Chemistry
State University of New
  York at Buffalo
Buffalo, New York 14214   1

Mr. James R. Moden
Naval Underwater Systems
  Center
Code 3632
Newport, Rhode Island 02840   1

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