

absorptions which we observe for the mnt compounds.²⁹

Multiple-state emissions from spin-orbit split excited states have been found for most of the previously reported luminescent Ir(I) and Rh(I) complexes.^{11,30} The key experimental evidence cited for multiple-state emission was often the temperature dependence of emission lifetimes below 77 K. For many of the compounds no significant spectral changes were observed. We note that the 12 and 77 K emission spectra of complex Ib are essentially superimposable. All of our data can be interpreted in terms of a single emitting electronic state; however, the possibility of multiple-state emission still exists in a situation where either only one state is responsible for the bulk of the observed emission or the emitting excited states (which must be in thermal equilibrium) have nearly identical emission spectra. Further studies of the temperature dependence of emission lifetimes seems to be in order for these systems.

Finally, environmental rigidity appears to be required to observe luminescence from the Rh, Ir, and Pt mnt compounds. This is a general result for planar d⁸ complexes and a solvent relaxation study has been reported.³¹ We have also noticed a counterion effect on emission intensity. At room temperature, the TBA⁺ salts of the Ir complexes display brighter luminescence than the PPN⁺ salts. An extreme example of this effect is found in complex IIb, which as the TBA⁺ salt exhibits bright luminescence at room temperature whereas no luminescence could be detected for the PPN⁺ salt. The origin of this curious effect is unknown, but it may relate to the structural rigidity of the lattices in the TBA⁺

(29) One possibility is that the highest occupied molecular orbital (formally assigned as a metal d orbital) has considerable ligand π character. This would lead to lower extinction coefficients (due to the reduced effect of spin-orbit coupling) and larger singlet-triplet splittings (due to increased electron correlation).

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(31) Andrews, L. J. *J. Phys. Chem.* **1979**, *83*, 3203-3209.

and PPN⁺ salts. This observation is under continuing study.

Conclusion

We have discovered a new series of luminescent d⁸ complexes which have highly structured emission and excitation spectra. With the mnt compounds reported here, we have greatly extended the number and variety of d⁸ complexes exhibiting emission, and have developed a class of compounds ideally suited to detailed spectroscopic study. The luminescing excited state is essentially undistorted from the planar ground-state geometry and is assigned to be ³(d- π^* (mnt)). The vibrational structure is attributed to progressions in the mnt C=C vibration and other vibrations associated with the metal-mnt moiety. While the mnt complexes do not luminesce in fluid solution, studies to develop the photochemistry of these systems are continuing.

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Registry No. IaTBA, 84623-79-0; IaPPN, 84623-80-3; IaK, 84623-81-4; IbPPN, 84642-22-8; IbTBA, 84623-91-6; IcTBA, 84623-85-8; IcPPN, 84642-23-9; IdPPN, 84623-83-6; IdTBA, 84623-89-2; Ie(PPN)₂, 84642-25-1; IeTBA, 30845-95-5; IePPN, 84642-26-2; IIbTBA, 29985-53-3; IIbPPN, 84642-28-4; IIdAsPh₄, 63159-12-6; IIdTBA, 29985-52-2; IIdPPN, 84642-27-3; IIIf, 84623-88-1; IIIf, 80316-84-3; IIIf, 84623-87-0; IIIf, 84623-86-9; [Pt(PPh₃)₂(mnt)], 62637-80-3; (TBA)₂[Pt(Mnt)₂], 42401-87-6; TBA[Ir(CO)₂Br₂], 73190-78-0; Pt(dppm)Cl₂, 52595-94-5; Pt(COD)Cl₂, 12080-32-9.

Supplementary Material Available: Complete listing of electronic emission and low-energy excitation maxima (2 pages). Ordering information is given on any current masthead page.

Vibrational Spectroscopy of the Electrode-Solution Interphase. 2. Use of Fourier Transform Spectroscopy for Recording Infrared Spectra of Radical Ion Intermediates

Stanley Pons,*† T. Davidson,† and A. Bewick‡

Contribution from the Departments of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2, and The University, Southampton, Hampshire, SO9 5NH U.K.

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Abstract: High-quality infrared spectra of the radical ions of benzophenone, anthracene, and tetracyanoethylene were recorded during electrolysis of the substrates at a platinum electrode by using a specular reflection apparatus and a Fourier transform infrared spectrometer. Evidence of adsorption of benzophenone was indicated, whereas simple ion spectra were observed for anthracene and tetracyanoethylene. Versatility of the technique is discussed.

The investigation of heterogeneous and homogeneous electrode processes by infrared coupled spectroelectrochemical techniques has been reported. Thus work on the electrosorption of methanol on platinum electrodes¹ and adsorbed hydrogen on platinum^{2,3} and studies of the platinum-acetonitrile interface,⁴ adsorption of acrylonitrile,⁵ and changes in the water structure at metal electrodes^{3,6} have been completed.

The use of Fourier transform infrared spectrometers has proven to be a convenient rapid method for obtaining infrared spectral

differences between two polarization potentials at an electrode interface.⁴ We report here the ease with which the vibrational spectra of free-radical ions may be observed by using this technique. Traditionally, it has been rather difficult to obtain free-

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(3) A. Bewick and K. Kunimatsu, *Surf. Sci.*, **101**, 131 (1980).

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(5) A. Bewick and C. Gibilaro, in preparation.

(6) A. Bewick and J. W. Russell, in preparation.

* University of Alberta.

† The University.

radical ion spectra in the infrared region for the obvious reasons of sample handling and the large IR absorptions of the solvents commonly used when generating ion radicals. Conventional techniques used to observe such spectra include cocondensation of the parent molecule and alkali metal atoms onto infrared transparent windows,⁷ examination of mulls of prepared salts of stable radical ions,⁸ and crossed molecular beam cocondensation techniques.⁹⁻¹¹ If the radicals of interest can be generated electrochemically, then it is likely, by using the technique described herein, that their infrared spectra may be recorded with minimal experimental effort. The traditional problem of strong solvent absorption is minimized by using reasonably thin layers of solution and efficient software subtraction routines available with most commercial FT IR instruments.

Experimental Section

FT IR Spectroscopy and Electrochemical Generation of Ions. Spectra were recorded on a Nicolet 7199 Fourier transform infrared spectrometer with a type A mercury-cadmium-telluride solid-state cooled (77 K) detector. Light was polarized by a Cambridge optical polarizer mounted before the cell. Potential programs were generated at the electrode by a HI-TEK DT2101 potentiostat and PPR1 waveform generator. The spectra were recorded after near steady-state conditions had been reached at the appropriate potential. Potential step widths were 4 s at each level. Synchronization between the application of the potential step and the beginning of the spectral data collection was made by tapping the TTL signal accompanying the beginning of data collection at the Nicolet A/D converter and applying the signal to a 74190 down counter. Thus the waveform generator could be triggered at chosen sweep increments. Spectra reported herein were recorded at 4-cm⁻¹ resolution at a nominal mirror velocity of 1.5 cm s⁻¹. Further details are given elsewhere.¹²

Solvents and Chemicals. Acetonitrile (Caledon HPLC grade, 0.003% water) was used without further purification. Benzophenone (Aldrich) was vacuum sublimed twice before use. Anthracene (Aldrich) was used as received, and tetracyanoethylene was recrystallized twice from chlorobenzene. All solutions were degassed with argon before use.

Tetrabutylammonium tetrafluoroborate (TBAF)¹³ was used as supporting electrolyte in all solutions.

Cell and Electrodes. The cell body was constructed from glass; full details have been given elsewhere.¹² A platinum mirror disk electrode (6-mm diameter) was mounted in a Kel-F cylinder (9-mm diameter) and the electrode inserted through a syringe barrel mounted on one end of the cell. The electrode cylinder extended through the interior of the cell to the opposite side, which was constructed of a plate of infrared transparent material (silicon, Irtran-4) oriented parallel to the mirror electrode face. The electrode was adjusted so that only a very thin layer of electrolyte solution was present between the electrode face and the window. Infrared radiation was directed through the window and solution and reflected off the electrode face and back through the solution and window to the detector.

Secondary and reference electrodes were located in the cell as well. The reference was Ag/Ag⁺ (0.01 M; tetrabutylammonium tetrafluoroborate (0.10 M) in acetonitrile).

Results

The differential reflectance FT IR spectrum of a 10 mM solution of benzophenone in acetonitrile (0.1 M TBAF) at a platinum mirror electrode is shown in Figure 1b. The potential limits were -1.75 and -2.50 V vs. the Ag/Ag⁺ reference. The light was polarized such that the plane of the electric field vector was perpendicular to the surface of the electrode (p polarized with respect to the plane of incidence). The thickness of the solution layer was 1.0 μm. The corresponding transmission spectrum of benzophenone in the same cell arrangement is shown in Figure 1a. As will be discussed later, bands extending downward (Figure 1b) correspond to increased absorbance at -2.75 V, while peaks

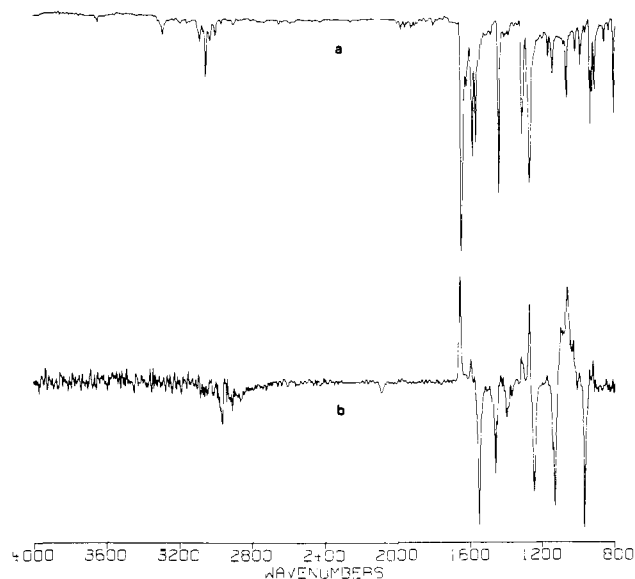


Figure 1. (a) Transmission spectrum of benzophenone. (b) Differential FT IR spectrum of benzophenone between -1.75 and -2.50 V.

Table I. Comparison of Absorption Bands of Benzophenone and Benzophenone Ketyl Radical^a

| benzophenone | | benzophenone ketyl | |
|--------------|-----------|--------------------|-----------|
| ref 15 | this work | ref 16 | this work |
| 1666 (vs) | 1660 (vs) | 976 (s) | 970 (vs) |
| 1610 (m) | 1600 (m) | 1019 (m) | 1025 (w) |
| 1317 (s) | 1319 (m) | 1143 (vs) | 1147 (vs) |
| 1277 (vs) | 1277 (vs) | 1150 (vs) | 1155 (s) |
| 917 (m) | 922 (m) | 1260 (vs) | 1249 (vs) |
| | | 1288 (m) | 1288 (w) |
| | | 1396 (s) | 1394 (m) |
| | | 1560 (s) | 1555 (vs) |

^a Relative band-intensity nomenclature: vs = very strong, s = strong, m = medium, w = weak.

extending upward correspond to decreased absorbance at this potential. Thus the downward extending bands correspond to absorbance due to the anion radical, while the upward extending bands correspond to disappearance of the substrate benzophenone as it is reduced to form the anion radical. Table I lists absorbance bands observed and compares them with literature values. Slight differences in wavenumber values are attributed to solvent effects (the literature values were determined in carbon tetrachloride (benzophenone) and tetrahydrofuran (benzophenone ketyl anion radical)). There is a very good correlation between this work and reported values, except for the weakest bands. No attempt was made to enhance the signal to noise by further signal averaging. The reported spectra were the average of 40 scans (about 5 min).

The band at 1464 cm⁻¹ in Figure 1b has not been previously reported for the benzophenone ketyl anion radical. If the solution thickness is increased to 200 μm and the benzophenone in the thin layer of solution is 90% reduced to the ketyl structure, the difference spectrum has a greatly enhanced intensity, and it is not possible to detect the band at 1464 cm⁻¹. The 1464-cm⁻¹ band is also absent from the spectrum if the light polarization is changed by 90° to the s-polarized form. A comparison of the p-polarized spectrum with an s-polarized spectrum is shown in Figure 2. We note changes in band widths and intensities of the bands as a function of polarization and wavelength.

Figure 3, a and b, shows the spectrum of anthracene and the difference spectrum of anthracene between -1.5 and -2.5 V, respectively. The light was p polarized and the solution thickness was 14 μm. The solvent and other parameters were the same as noted above for benzophenone.

Figure 4, a and b, shows the results for the tetracyanoethylene (TCNE) system. The modulation region was +0.25 to -0.25 V. The solution thickness was 17 μm.

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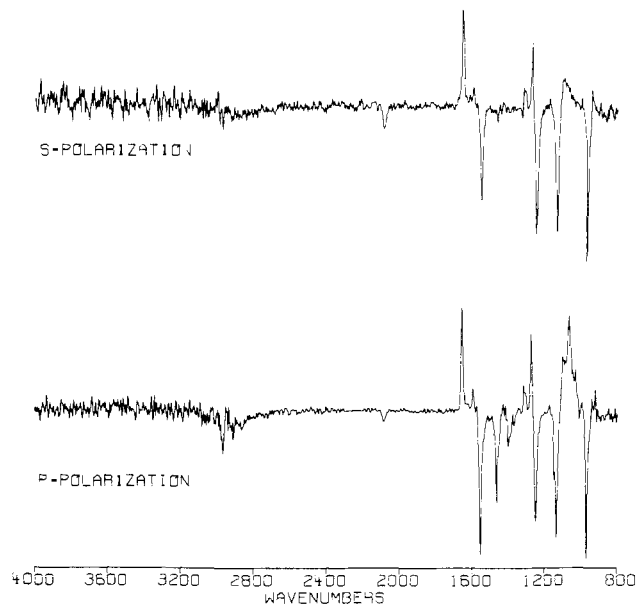


Figure 2. Differential spectrum of benzophenone with s- and p-polarized light.

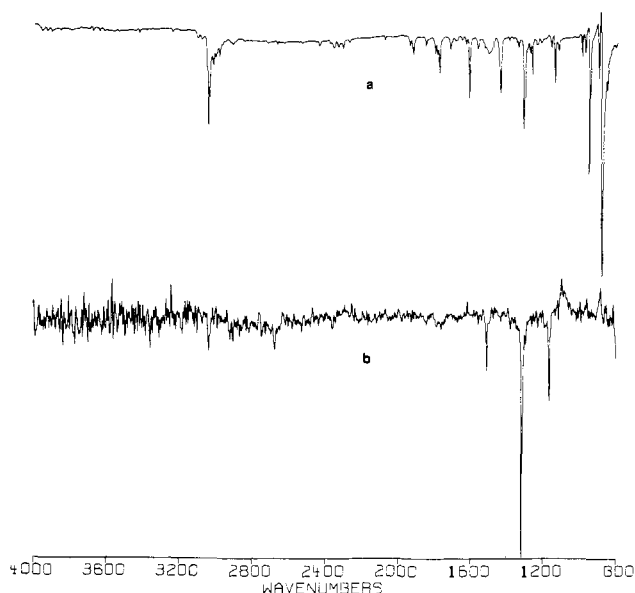


Figure 3. (a) Transmission spectrum of anthracene. (b) Differential FT IR spectrum of anthracene between -1.5 and -2.5 V.

Discussion

Care must be taken when interpreting difference spectra. In Figures 3 and 4, where the extinction coefficients of the products (the anion radicals of anthracene and tetracyanoethylene) are apparently much greater than the reactants,¹¹ the results are quite straightforward. The resulting difference spectra closely resemble pure absorption spectra of the species formed at the more negative potential. In spectra where the extinction coefficient of reactant and product are about the same (Figure 1), the spectra may be more complex. A discussion of these effects has been presented elsewhere.¹²

There are several considerations that need to be made when interpreting the results of experiments that use polarized light for reflection studies at metal interfaces. First, s-polarized light has an almost zero electric field intensity at the surface of the metal especially at IR wavelength and therefore cannot interact with dipole oscillators of any orientation that might exist at that surface, i.e., s-polarized radiation is "blind" to adsorbed species. Second, p-polarized light will interact with dipole oscillators encountered in solution, and also dipole oscillators at the metal surface oriented

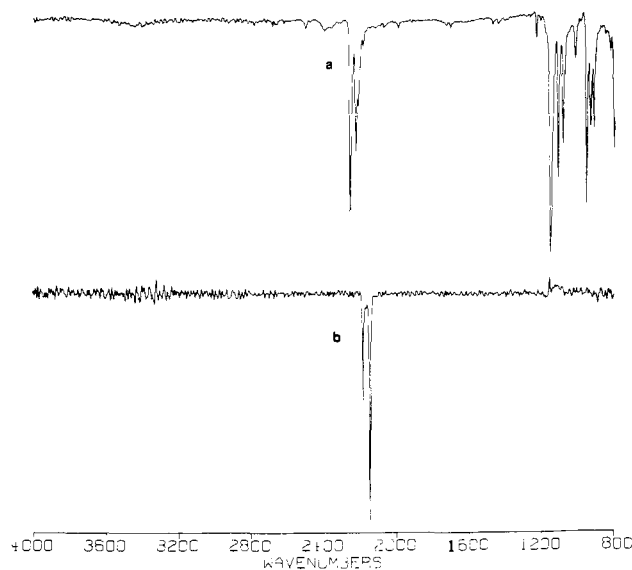


Figure 4. (a) Transmission spectrum of TCNE. (b) Differential FT IR spectrum of TCNE between $+0.25$ and -0.25 V.

such that the derivative of the dipole moment with respect to the normal coordinate ($\partial\mu/\partial Q$) has a nonzero component perpendicular to the electrode surface, i.e., p-polarized radiation can interact with adsorbed species but such interaction will depend upon the orientation of the molecule.⁶ Third, for s-polarized light, the spectra observed may possess features from (a) absorption by species present in the bulk solution as the IR beam is transmitted through it, reflected off the electrode, and transmitted back through the solution again and (b) internal reflectance absorption at the interface between the inner face of the window and the bulk solution. This latter effect is rather complex and can lead to severe distortion of the normal spectra, especially at reflection angles near the Brewster angle of the window. Many examples of this phenomenon have been reported,¹⁴ and it is apparent that for the purposes herein, it is very difficult to obtain quantitative data from spectra obtained with s-polarized light.

Thus there are two simple ways in which to distinguish between the spectra of intermediates that are adsorbed at the electrode surface and species dissolved in the thin layer of solution. First, in this cell, adsorbed species will absorb only p-polarized radiation, whereas species in solution will not preferentially absorb either polarization state. Second, at short electrolysis times, the spectrum can have contributions from both adsorbed and nonadsorbed species, while at longer electrolysis times, there will be a larger contribution by the nonadsorbed species with no increase in the intensity of bands arising from any adsorbed species. It is also important to note that, in general, only vibrational modes of the adsorbate unperturbed by adsorption will be expected to absorb at the same frequency as those of the corresponding dissolved species; other bands may be shifted due to changes in vibrational modes accompanying interaction with the atoms in the metallic surface. In the case of benzophenone both of these possibilities are observed, and it is clear that the anion radical is present in both the adsorbed and the nonadsorbed state. Two new bands, a strong absorption at 1464 cm^{-1} and a weaker absorption at 1340 cm^{-1} , are observed for the adsorbed anion radical. The former is almost certainly the carbonyl stretch of the adsorbed species (shifted from 1555 cm^{-1}), and the latter is at the position expected for the combination band from the carbonyl stretch and the symmetrical stretch of the aromatic ring.¹⁶ It is to be concluded, therefore, that the anion radical on the electrode surface is adsorbed via the carbonyl group, as would be expected. Voltam-

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metric measurements using a Pt electrode also support the conclusion that adsorbed anion radical is present: simulations of the voltammogram are best fitted to the experimental curves when adsorption of the product of electron transfer is considered.

The differential reflectance spectrum recorded during the reduction of tetracyanoethylene (TCNE) in acetonitrile at a platinum electrode is shown in Figure 4. The positive bands due to disappearance of the TCNE substrate at the more negative potential are not visible. This is because the sensitivity of the transmission scale has been decreased to accommodate the full amplitude of the bands at 2187 and 2148 cm^{-1} . The band at 2148 cm^{-1} is almost 10^4 times larger than is predicted from a simple Beer's law calculation for the total amount of TCNE anion that has been found during the potential step. The weaker band at 2187 cm^{-1} corresponds closely to an assignment made by Devlin et al. to the $\text{C}\equiv\text{N}$ stretch, which has been charge transfer enhanced by formation of a complex between the anion radical and

a surface platinum atom. The stronger band increases markedly with an increase in the cell thin-layer gap and is therefore due to solution free $\text{C}\equiv\text{N}$ fundamental stretch, enhanced most likely by the formation of an electron donor-acceptor complex between the anion radical and neutral TCNE. The point is under investigation.

Conclusions

The technique described is a very powerful new method for the rapid recording of the spectra of radical ion intermediates produced during electrochemical reactions. The method is capable of detecting spectra from short-lived species that could not otherwise be obtained.

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Registry No. Platinum, 7440-06-4.

Electrochemical Stability of Catechols with a Pyrene Side Chain Strongly Adsorbed on Graphite Electrodes for Catalytic Oxidation of Dihyronicotinamide Adenine Dinucleotide

Hans Jaegfeldt,*[†] Theodore Kuwana,[†] and Gillis Johansson[‡]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Analytical Chemistry, University of Lund, Lund, Sweden. Received March 11, 1982

Abstract: The electrochemical stability and reactivity of 4-[2-(1-pyrenyl)vinyl]catechol (PSCH₂) and 4-[2-(1-pyrenyl)ethano]catechol (PECH₂) strongly adsorbed on graphite electrodes were investigated as a function of the applied potential at pH 7.0. The surface coverage of these compounds ranged from 0.1×10^{-9} to 2.7×10^{-9} mol/cm². The "modified" electrodes exhibited deactivation which could be explained by second-order reactions between the catechols and the electrochemically produced quinones coupled with a second-order reaction between the quinones. The ethano compound showed a much larger decay rate, probably because of free rotation around the saturated bond connecting the pyrene part and the catechol group. The deactivation was apparently not associated with desorption of the compounds. The catechols in the oxidized form could catalytically oxidize NADH. The overpotential for NADH oxidation was thus decreased from 410 to 150 mV vs. SCE at pH 7.0. However, the catalytic current was found to decrease exponentially with increasing number of scans. The rate of this deactivation of the catalytic electrode was found to be inversely proportional to the coverage of immobilized mediator. The deactivation could be explained by a chemical coupling reaction between the mediator and NADH, forming a complex which gradually blocked off the surface of the electrode. The probable nature of the complex makes it unlikely that "capping" of active sites, e.g., the 2, 5, and 6 positions, on the catechol ring would effectively prevent the blocking and, hence, deactivation of the catalytic electrodes.

Introduction

The coenzyme nicotinamide adenine dinucleotide (NADH) is oxidized directly at different electrode materials only with high overvoltages.¹ The overvoltage at pH 7 is about 1.1 V at a carbon² and 1.3 V at a platinum electrode.³ Attempts have been made to link the electrochemical oxidation of the coenzyme to the analysis of substrates for clinical purposes.^{4,5} About 300 dehydrogenases are known which are dependent on NADH or NADPH as redox transfer agents. Electrodes modified to oxidize NADH more easily should therefore open up new applications both in analysis and in biotechnology.

Surface modifications have been proposed as a means of reducing the overvoltage of the electrochemical oxidation of NADH. Blaedel and Jenkins⁶ reduced the overvoltage with 0.2 to 0.45 V

vs. SCE with an electrochemical pretreatment of the electrode. They assumed that hydroxyl, carbonyl, and quinone groups produced by the oxidative pretreatment of the electrode caused this decrease of overvoltage. It has been shown in this laboratory that a catalytic electrode could be produced by the separate covalent attachment of 1,2-hydroquinones to the surface of pyrolytic graphite.⁷ That work demonstrated the possibility of producing catalytic electrodes by the covalent incorporation of electron-transfer mediating groups onto the surface of the electrode. Recently, Degrand and Miller⁸ modified a vitreous carbon

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* Permanent address: Analytical Chemistry, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden.

[†] The Ohio State University.

[‡] University of Lund.