mediator ions might be so completely encapsulated by the surrounding polymer chains that no particular orientation would be required for the electron transfer to occur. The formation of the precursor complex would then be limited by the activation energy necessary to cross this shell of polymer chains separating the mediator reaction site from the incoming co-reactant. The height of the energy barrier would be essentially a function of the charge and size of the reactants and if it were high enough the overall rate constant would no longer depend upon the redox driving force. Clearly, additional kinetic measurements (involving the use of mediator couples that differ not only in standard potential but also in charge and size and for which data on homogeneous self- and cross-reaction kinetics are available) are needed to distinguish between these possibilities.

Acknowledgment. Dr. K. Shigehara supplied the polylysine copolymer and contributed many helpful suggestions. This work was supported in the USA by the US Army Research Office and in France by the Centre National de la Recherche Scientifique. We are grateful to the North Atlantic Treaty Organization for a Collaborative Research Grant.

Registry No. $Co(tpy)_2^{2+}$, 18308-16-2; $Mo(CN)_8^{3-}$, 17845-99-7; $W(CN)_8^{3-}$, 17568-76-2; $Mo(CN)_8^{4-}$, 17923-49-8; $W(CN)_8^{4-}$, 18177-17-8; graphite, 7782-42-5.

Electrochemical Modulation of Fluorescence from Zinc Tetraphenylporphyrin on Electrode Surfaces

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Abstract: Zinc tetraphenylporphyrin (ZnTPP) has been studied as deposits on pyrolytic graphite, indium oxide coated glass, and thin films of gold. Deposits were made (a) by drying of an aliquot of solution in toluene that had been loaded onto a defined area by syringe or (b) by dipcoating from toluene solution. The dipcoating method provided apparently uniform coverages in the range $1–4 \times 10^{-10}$ mol/cm^2. Syringe-coating gave coverages that were larger by an order of magnitude. On graphite, only 1% of the molecules in a dipcoated deposit are electroactive, but oxidation of those sites results in strong quenching of luminescence from the deposit. The excitation spectrum of the luminescence on graphite and gold at low coverages features a very weak contribution from the Soret transition. At heavier coverages the transition reappears. On indium oxide, the degree of electroactivity is higher than on graphite, and similar degrees of quenching can be obtained upon oxidation, but there are no unusual spectral modifications in thin layers. A model for the structure of ZnTPP deposits is proposed on the basis of these observations.

Introduction

As research on electrode processes has become concerned with finer degrees of detail, a demand has developed for spectroscopic tools capable of characterizing interfacial structure. A large volume of research has been directed toward this end.[1] The more successful methods for observations in situ involve optical absorption,[2-5] changes in reflectivity,[6-8] or Raman scattering.[9-11] Useful information can also be gathered from observations of electrode surfaces by various ion- and electron-beam techniques,[1] but these methods do not allow study in situ.

Our concern here is with the development of fluorescence spectroscopy as a means for probing interfacial structure. There are several reasons for interest in the approach. First, there is already a large volume of experience with fluorescent probes, particularly in the labeling of microstructures in biological systems.[12-19] The probes are useful in defining local pH, polarity, fluidity, molecular rotational freedom, intermolecular spacings, and molecular orientation. Much of this kind of information cannot be obtained from existing optical tools for examining electrode surfaces. Second, fluorescence can be observed in the time domain, and the kinetics of fluorescence quenching, which are very well understood, can be used to examine a host of transport phenomena and bimolecular interactions. This aspect makes possible the observation of molecular events in electrochemical systems on a nanosecond time scale, which is simply not accessible to purely electrochemical modes of observation, or even to other spectroelectrochemical modes as they presently exist. Finally, fluorescence techniques are exquisitely sensitive. Detection

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of species in submonolayer amounts is not difficult.[20,21] This feature has value in observations of an interfacial zone, where there is never more than the equivalent of a few monolayers of any species. In fact, it makes spectroelectrochemical monitoring of an interface possible with standard fluorescence spectrometers, while optical methods based on absorption usually require special apparatus with enhanced sensitivity.

Only a few reports have been made of fluorescent probes near electrodes. Fromherz and Arden placed dye-labeled Langmuir–Blodgett monolayers onto oxide semiconductor electrodes and observed the sensitization of photoelectrochemistry at the semconductor by light absorbed initially in the dye.[22-25] Relative quenching of dye fluorescence was used to define the dynamics of electron transfer from the excited dye to the semiconductor. Honda and co-workers excited luminescence near a tin oxide electrode by light trapped by internal reflection within the electrode and its substrate.[26] The evanescent excitation wave extending into the solution was able to interact with chromophores within ~1000 Å from the surface; hence modifications in the near-surface concentration profile of fluorescein could be followed as it underwent electrooxidation. In an earlier communication, we reported that zinc tetraphenylporphyrin (ZnTPP) deposited on indium oxide-coated glass (IOCG) or on predominantly basal plane surfaces of pyrolytic graphite (BPPG) electrodes was electroactive and luminescent.[27] We also showed that the luminescence was modulated as the ZnTPP underwent electrooxidation and rereduction. That report was the first to show luminescence from a species bound sufficiently intimately to an electrode surface to undergo faradaic electrochemistry, and the results were surprising in view of the general expectation that excited molecules at electrodes other than semiconductors would be rapidly quenched, either by energy transfer or by the reversible electron-exchange mechanism.[28-31] More recently, Majda[32] has used the dynamics of luminescence quenching to evaluate the rate of charge migration by electron exchange between tris(2,2′-bipyridine) complexes of Ru(II) and Ru(III) in polymeric modifying layers on Pt electrodes. Similar work has been reported by Buttry and Anson.[33] In these cases, the electroactive, luminescent complexes were bound within films ~2000 Å in thickness on the Pt surface.

This paper is the sequel to our earlier communication on fluorescence and electrochemistry of surface layers of ZnTPP on electrodes. It contains results from a large number of experiments designed to define (a) the nature of the deposits formed by ZnTPP on indium oxide and basal-plane pyrolytic graphite; (b) the electrochemistry of the deposited molecules; (c) the spectroscopy of ZnTPP in the deposited state and its implications concerning the intimacy of interaction between the emitting ZnTPP and the electrode; and (d) and basis for electrochemical modulation of the luminescence. The conclusions are of interest not only for their relevance to the general prospects for monitoring surface layers in simultaneous electrochemical/fluorescence experiments, but also because they concern the nature of deposits of porphyrins on electrodes, a matter related to electrocatalysis by these species and related compounds.[34-49]

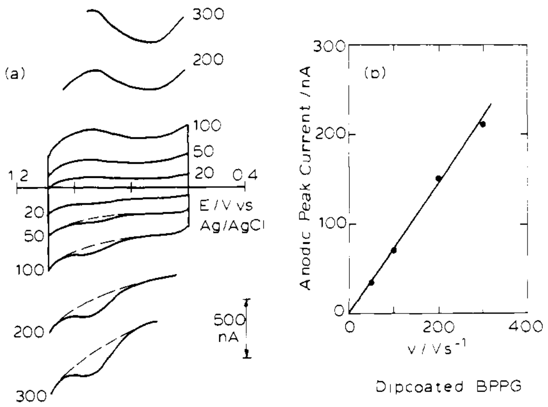

Figure 1. (a) Steady-state cyclic voltammograms of ZnTPP dipcoated onto BPPG. Electrolyte was 0.1 M H_2SO_4. Dipcoating was done from 0.4 mM toluene solution of ZnTPP. Cathodic currents are up. Numbers by curves are scan rates in mV/s. Recorder slew is not shown at switching potentials in voltammograms at 200 and 300 mV/s. (b) Anodic peak current vs. scan rate for voltammograms in (a). Currents were measured against dashed baselines in (a).

Experimental Section

A sample of zinc tetraphenylporphyrin (ZnTPP) that had been obtained from Sigma Chemical Company and purified by treatment with dichlorodicyanobenzoquinone[50] was kindly provided by S. Schmidt and G. B. Schuster of this department. Metal-free tetraphenylporphyrin (H_2TPP) was purchased from Aldrich Chemical Co. and used without further purification.

The electrodes were either disks of basal plane pyrolytic graphite (BPPG), indium oxide-coated glass (IOCG, Varilight Co., Cincinnati, OH) cut into 8 × 30-mm strips, or gold. Gold electrodes of 300–400 Å thickness were prepared by deposition in vacuo through a mask, directly over a 70-Å chromium anchor layer, which had previously evaporated through the same mask onto a clean 12 × 25-mm glass slide. The active electrode area was slightly greater than 0.2 cm^2.[49] BPPG, obtained from Union Carbide Corp. (Grade HPG), was cut into disks 6 mm in diameter and ca. 0.5 mm thick with the basal planes oriented largely parallel to the faces of the disks. The disks were fastened to a gold electrode using silver paint or conducting epoxy; the edges of the disks were sealed with melted paraffin.

To apply a surface layer of ZnTPP, two different techniques were used. Initially, so that the total amount of material deposited was known, a 1 or 2 μL aliquot of ca. 0.4 mM ZnTPP in toluene was transferred with a 10-μL syringe to a 0.25, 1, or 0.2 cm^2 area of the electrode (BPPG, IOCG, or gold). This method resulted in the formation of visible purple ridges, similar in color to the ZnTPP powder, which surround a yellow film. The alternate procedure was intended to provide coverage of

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greater uniformity. It involved dipping the substrate into the ZnTPP solution for ca. 10 s, removing it, and allowing it to dry in a vertical position. For BPPG, the disks were dipped prior to attachment to the gold electrode and sealing. After air-drying, the back and sides of the glass substrate were wiped clean with a cotton-tipped applicator saturated with toluene, in order to prevent interference from fluorescence of ZnTPP not on the actual electrode surface. On IOCG, a light yellow, uniform film, is then perceptible on IOCG. On the other substrates, the color is imperceptible.

Early fluorometric and electrochemical measurements were obtained with a three-electrode cell comprising a 10-mm square quartz fluorescence cuvette containing an aqueous Ag/AgCl/KCl(sat'd) reference electrode, a coiled Pt wire as auxiliary electrode, and the working electrode in either 0.1 M H_2SO_4 or 0.1 M or 1 M HCl electrolyte. A custom-built potentiostat and digital waveform generator were used to control the applied potential.

Fluorescence spectra were obtained using a computer-controlled spectrophotofluorometer[51] with a bandpass of 2.5 nm in both excitation and emission beams. Double monochromators in the two optical beams assured the high efficiency of stray light refjection that appears essential to this work. The excitation source was a 1 kW xenon arc, and detection was carried out by a thermoelectrically cooled Hamamatsu R928 photomultiplier, whose output was registered in the analog domain. In recording spectra, signal averaging was carried out in software by aggregating 250–1250 successive readings of the 12-bit A/D converger monitoring the analog current follower that served as a photocurrent transducer. The working electrode was positioned manually in the cell and held by a Teflon holder, so that the front face of the electrode made an angle of ca. 45° to the excitation beam. In the luminescence/electrochemistry experiments, the photocurrent-to-voltage converter was monitored by a Nicolet digital oscilloscope.

More recent experiments were performed using a custom-built Teflon cell with quartz windows. A precision rotator (Oriel no. 1641) added the capability of precise angular placement of the electrode surface relative to the incident light beam. Absorption spectra were obtained with a Cary Model 219 spectrophotometer.

Results and Discussion

The method of deposition of ZnTPP onto a substrate affects the type of film formed. The differences in films, together with differences arising from the various substrates (BPPG, IOCG, or gold), are manifested both spectroscopically and electrochemically. We organize the initial discussion on the basis of substrate.

1. Pyrolytic Graphite. Electrochemistry. ZnTPP on BPPG is electrochemically active, but only in part. When a dip-coated electrode is placed into 0.1 M H_2SO_4, an oxidation/reduction couple is seen with $E^{\circ\prime} = 0.95$ V vs. Ag/AgCl, as shown in Figure 1a. The peaks have widths at half maximum near 100 mV and are on a sloping baseline which appears to be a background-limiting process catalyzed by ZnTPP. The peak separation is less than 30 mV and the peak potentials do not change as the scan rate is increased over more than an order of magnitude. Also, the peak currents show linear dependences on the scan rate (Figure 1b). These features indicate that ZnTPP applied in this manner exhibits behavior characteristic of a surface-bound species, with fairly fast heterogeneous electron-transfer kinetics.

The consequences of cycling the potential past 1.2 V are twofold. A second anodic peak is seen at ca. 1.25 V on a very steep baseline, but no corresponding cathodic peak is clearly discernible. Upon further cycling between 0.6 and 1.1 V, one can no longer detect the peaks for the less extreme couple. However, after returning the electrode to 0.6 V and leaving it at open circuit for several minutes, the couple at 0.95 V again becomes evident. If the electrolyte is replaced during this time, the peaks do not reappear. This behavior suggests that the ZnTPP is removed from the surface, either by its own second oxidation or by the limiting background reaction, and that it can be redeposited from solution, as ZnTPP, by allowing the electrode to stand at a potential more negative than ~1 V.

The two anodic peaks may reflect different sites at which molecules of ZnTPP may deposit, but they more probably reflect the two known one-electron oxidations of ZnTPP, which have been reported to occur in aprotic media at 0.79 V and 1.10 V vs. SCE.[52] This interpretation implies that the radical cation[52-56] would be formed as the stable product of the oxidation at 0.95 V. At first glance, it might be surprising that such a species could have such a long lifetime in aqueous media. However, the literature contains reports that porphyrin π-cation radicals are stable in the presence of nucleophiles. Moreover, Green[57] has recently demonstrated that films of the related molecule, zinc phthalocyanine, oxidize completely in a reversible process requiring one electron per molecule. The product is formally a film of radical-ion salt, into which charge-compensating anions are drawn during the oxidation. The oxidized films are stable for long periods in contact with aqueous solutions. Green's results suggest that oxidized sites in a ZnTPP film could be reasonably stable under like conditions.

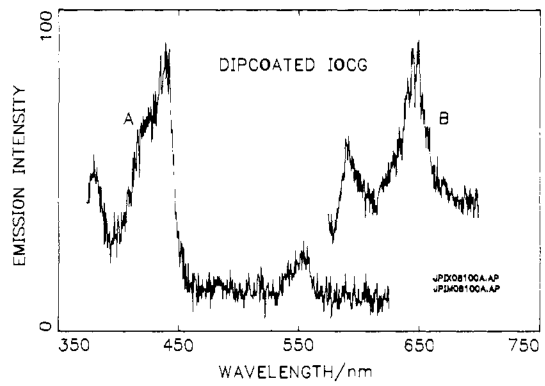

Figure 2. Uncorrected excitation (A) and emission (B) spectra for ZnTPP dipcoated onto IOCG from 0.3 mM toluene solution. Spectra were recorded while the sample was immersed in 0.1 M HCl. Excitation spectrum is for emission at 646 nm. Emission spectrum is for excitation at 438 nm. Essentially the same spectra are obtained for either IOCG or BPPG coated by syringe. Spectra are offset vertically for clarity.

The amount of electroactive material present on the electrode, estimated by integrating the area under the oxidation or reduction peak and assuming a one-electron reaction, is 3.5×10^{-12} mol/cm^2. This figure is much smaller than the amount of material applied to the surface, which was determined separately as follows. Disks of BPPG were dipcoated from a 0.413 mM solution of ZnTPP, exactly as for electrochemistry. The edges were then wiped with a tissue dampened in toluene, and the ZnTPP was redissolved from the disks by soaking in toluene. The resulting solution was diluted to 10 mL and assayed by absorption spectrometry at 423 nm. The results showed that ZnTPP was coated at 3.7×10^{-10} mol/cm^2, so that only about 1% of the material was electroactive. A large portion of the deposit is probably contained in the compact zones that become visible as "ridges" on more heavily coated electrodes. Apparently, only a small fraction of material in close contact with electrochemically active parts of the surface can actually undergo electroreaction. The active amount of 3×10^{-12} mol/cm^2 corresponds to one molecule per 5000 Å^2 of geometric surface area.

Syringe-coated samples show electrochemistry essentially identical with that of dip-coated electrodes. The amount of electroactive material remains at the value seen for dip-coated substrates (3×10^{-12} mol/cm^2), even though syringe-coating produced substantially larger nominal coverages of ZnTPP. Typically the coating involved 1 μL of 0.4 mM ZnTPP in toluene, so that the coverage was 1×10^{-9} mol/cm^2.

When 0.1 M HCl is used as the supporting electrolyte, the cyclic voltammograms are different than in H_2SO_4. The baseline slopes more steeply and the second oxidation peak is observed at ca. 1.1 V. The first anodic peak is fairly well-defined and shows a linear

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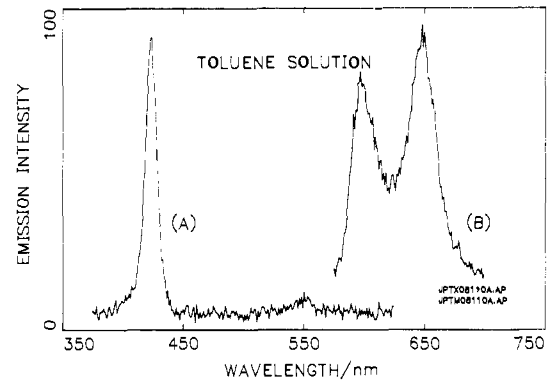

Figure 3. Uncorrected excitation (A) and emission (B) spectra of 50 mM ZnTPP in toluene solution. Excitation spectrum is for emissions at 646 nm. Emission spectrum is for excitation at 423 nm. Spectra are offset vertically for clarity.

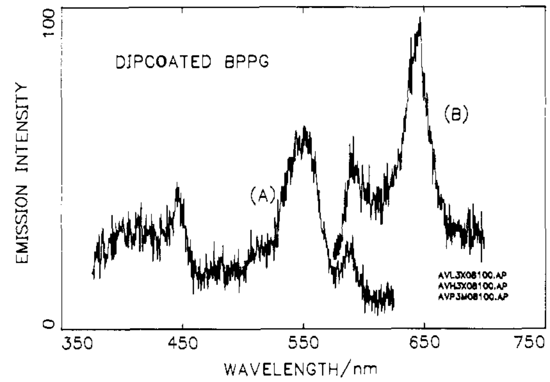

Figure 4. Uncorrected excitation (A) and emission (B) spectra for BPPG dipcoated from 0.4 mM toluene solution. Excitation spectrum is for emission at 646 nm. Emission spectrum is for excitation at 550 nm. Each spectrum is an average of three scans. Spectra are offset vertically for clarity.

dependence on the scan rate, indicating that it orginates from a surface-bound species. Slow kinetics also apply, since the anodic peak potential shifts by almost 50 mV as the scan rate is increased by an order of magnitude.

Luminescence. Emission can be observed from ZnTPP on the surface of BPPG, regardless of the method of application. However, the spectral characteristics differ for the two conditions. When the ZnTPP is applied via syringe, the excitation spectrum is similar both to that reported by Tanimura et al.[58] for an amorphous film of ZnTPP deposited in vacuo onto quartz and to that of ZnTPP applied by either technique to IOCG (Figure 2). The red shift and broadening of the Soret band, characteristic of the condensed state,[39,46] is readily seen upon comparison to the solution spectra (Figure 3). These effects are caused by interactions between identical molecules in the solid phase.[59,60] It has been reported that in films of 100–1000 Å thickness on quartz and platinum surfaces, deexcitation of the upper excited state, S_2 (populated by absorption in the Soret band), is accomplished solely by internal conversion to S_1. For ZnTPP on IOCG, or applied by syringe to BPPG, this does seem to be true, since the ratio of the fluorescence intensity of the Soret band to that of the visible band in the excitation spectrum is approximately equal to the ratio of absorbed light in these same bands in the absorption spectrum of ZnTPP on IOCG.

When dip-coated BPPG is used, the Soret band is drastically quenched relative to the visible bands, as shown in Figure 4. Moreover, it is red-shifted from the position shown by ZnTPP in solution. This behavior is also observed with ZnTPP applied by syringe to a gold substrate at a level of 2×10^{-9} mol/cm^2. These results do not arise from chemical degradation of the ZnTPP, because redissolved deposits showed normal luminescence of ZnTPP. Luminescence could not be seen at all for dip-coated samples on gold, which were assayed as having coverages similar to those on dip-coated BPPG, nor could it be seen for syringe-coated gold at $<1 \times 10^{-9}$ mol/cm^2. The loss of emission at such low coverages is in accord with the findings of Cotton et al.[61] that the fluorescence interference is eliminated in Raman measurements of porphyrins adsorbed on silver.

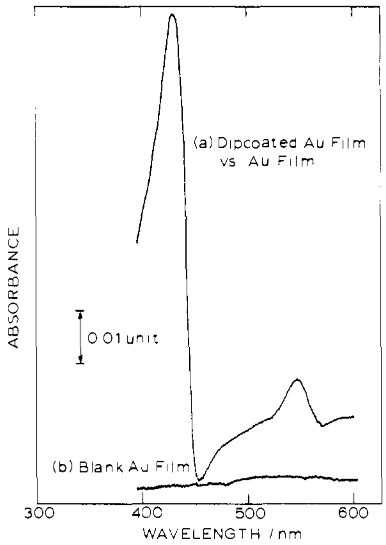

Figure 5. (a) Absorption spectrum of ZnTPP deposited by dipcoating onto a gold film from 0.4 mM toluene solution. (b) Blank spectrum for an uncoated gold film.

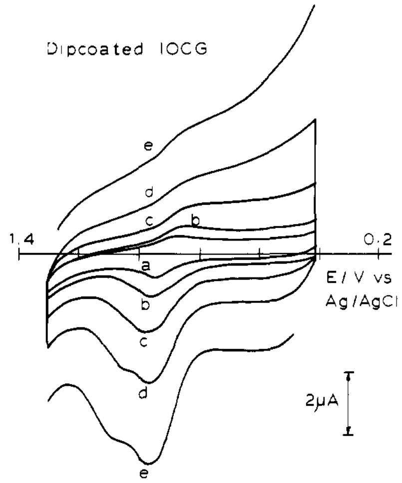

Figure 6. Steady-state cyclic voltammograms at dipcoated IOCG in 0.1 M HCl. Cathodic currents are up. (a)–(e) are for scan rates of 10, 20, 50, 100, and 200 mV/s.

Since the absorption spectrum of ZnTPP on gold has, as its most prominent feature, the Soret band (Figure 5), the selective suppression of this band in excitation spectra of deposits on gold and carbon implies that some form of deexcitation of S_2, other than internal conversion to S_1, occurs. One possibility is an electronic coupling of the excited molecule with the substrate, resulting in a Förster-type energy transfer to the electrode.[28-31] Alternatively, it is possible that electron transfer from S_2 occurs more readily than from the ground state, or that S_2 excitons diffuse much more rapidly into quenched sites. Any sort of transfer, whether energetic or electronic, would have to be extremely fast. We are not aware of optical artifacts[30] that could produce the observed effects, considering the apparent distance scales involved.

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This point will be considered below.

2. Indium Oxide Coated Glass. Electrochemistry. The electrochemistry of ZnTPP on IOCG is more complex than on BPPG. As shown in Figure 6, two anodic peaks and one very broad cathodic peak are seen at fast scan rates with the electrode in contact with 0.1 M HCl. The first oxidation, at ca. 0.95 V, does not appear to change its peak potential as the scan rate increases. A more positive peak grows and becomes distinguishable from the first at scan rates greater than 100 mV/s; at 500 mV/s, its peak potential is ca. 1.15 V. The scan rate dependences of the peak currents for these two oxidation are ambiguous, due to the proximity of the two peaks and the sloping baseline. However, the second peak appears to grow superlinearly with scan rate. This behavior might indicate that oxidation proceeds at two types of sites or with two modes of charge compensation, such that the energetics were slightly different. The rapid growth of the more difficult process with scan rate would then suggest that the system is capable of organizing itself so that the lower-energy product is ultimately produced from the higher-energy one. These results are reminiscent of behavior reported by Majda[62] for the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ system in poly(styrenesulfonate) films. His detailed results were interpreted in this dual-channel scheme with slow reorganization to produce communication between channels.

Even at slow scan rates, the separation between the anodic and cathodic peaks is much larger (100 mV at 20 mV/s) than on BPPG and increases with scan rate. Thus the overall kinetics of charge transfer are rather slow. Exchanging the electrolyte after the return scan, in the manner described above for BPPG electrodes, does not cause a significant loss of electrochemical reponse; hence it appears that the processes do not involve desorption and reuptake.

Electrodes dipcoated from 0.4 mM toluene solutions showed coverages ranging from 0.5 to 2 × 10^{-10} mol/cm^2, as determined by spectrophotometric assay of the redissolved deposits. The amount of electroactive material was typically 8 × 10^{-11} mol/cm^2; hence 30–100% of the deposit was electroactive. This is a much larger fraction than on BPPG. The qualitative features of electrochemistry of syringe-coated samples covered at 5–10 times heavier levels were the same as for dipcoated samples, but as for BPPG, the absolute amount of electroactive material remained at 8 × 10^{-11} mol/cm^2, regardless of the coating method or loading level.

In 0.1 M H_2SO_4, dipcoated electrodes showed much lower degrees of electroactivity, typically 1–2 × 10^{-11} mol/cm^2. Moreover, the electrochemical reponse was lost more rapidly than with 0.1 M HCl upon repeated cycling. These differences are probably related to structural aspects of charge-compensation by anions in the oxidized films and dynamics of anion movement within the deposits. Similar differences were seen by Green[57] in studies of electrochromic oxidations of zinc phthalocyanine films.

Luminescence. The excitation and emission spectra of ZnTPP deposited onto IOCG either by syringe or by dipping are shown in Figure 2. These exhibit uncomplicated condensed-phase characteristics. That the deposited ZnTPP does not merely crystallize and adhere to the surface when applied by either technique is clear from the difference between the spectra of the deposited material and those of crystalline ZnTPP dusted onto glass. The emission spectrum of the crystalline samples, either in air or immersed in 1 M HCl, exhibits a shift of the long wavelength peak by ca. 280 cm^{-1} from the peak emission of ZnTPP deposited on a substrate or in toluene. The excitation spectrum of the powder is distorted by full absorption of the exciting light, so that useful information is not available.

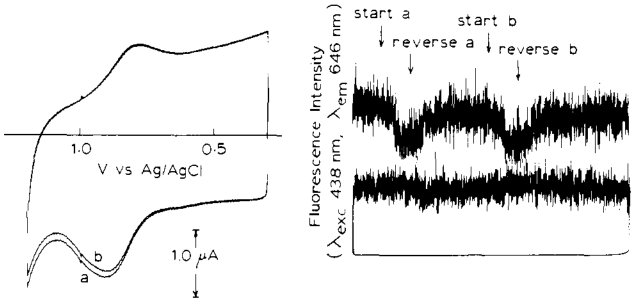

Figure 7. Two cycles of voltammetry (left) with simultaneous recording of luminescence intensity vs. time (right). The sample is dipcoated IOCG in 0.1 M HCl. In the voltammograms, cathodic currents are up. Sweep rate = 50 mV/s. Baseline at right obtained as described in text.

Furthermore, the similarities between the emission spectrum from toluene solution and spectra of the deposited species seem to have nothing to do with solvation of the ZnTPP by the coating solvent on the surface. The emission spectrum of a solution of ZnTPP in methanol is quite different from that in toluene, with a very intense peak at 603 nm and a less intense peak at 656 nm (vs. a weak 600-nm peak and strong 646-nm peak in toluene). However, if the IOCG is dipcoated from this methanolic solution, the resulting fluorescence spectra are identical with those obtained using a toluene dipping solution.

Coverages. The total amount of ZnTPP applied to the electrode by dipping was determined essentially as described above for BPPG substrates. Two trends were observed with these rinsing studies. First, increasing the concentration of the dipping solution increases proportionally the amount of ZnTPP actually deposited on the electrode. Samples dipped in solutions of ZnTPP at 0.413, 0.212, and 0.106 mM had coverages of 3.8 × 10^{-10}, 1.8 × 10^{-10}, and 1.1 × 10^{-10} mol/cm^2, respectively. The relative standard deviations of the mean were about 10%. The precision of these determinations seemed to be limited by the definition of covered area after wiping of the edges and the backs of samples. That the wiping process is effective is shown by the facts (a) that unwiped electrodes exhibited a fluorescence intensity corresponding to three or four times as much ZnTPP present than those that had been wiped on the edges and the back and (b) that an electrode which had been wiped on all faces shows no ZnTPP fluorescence at all.

The second trend was that unused electrodes tended to have more ZnTPP present than ones which had undergone electrochemical experiments after being dipped into the same solution. Losses ranged from 2% to 42%, depending on the electrolyte and the extent of usage.

Demetallation. Evidence of the demetallation of ZnTPP by HCl, a well-known solution-phase reaction,[63] is observed when the dipcoated IOCG is immersed in 1 M HCl. One then observes a strong, broad emission peak at ca. 675 nm that increases in intensity with time. Simultaneously there are decreases in the intensities of the two characteristic ZnTPP emission peaks at 595 and 646 nm, until after several minutes, they have all but disappeared. Stripping of both the ZnTPP and the In_2O_3 layer from the glass substrate accompanies the demetallation. Spectra of the 1 M HCl solution in which a ZnTPP-coated electrode has been immersed for 20 min and removed are identical with those obtained when an H_2TPP-coated electrode is treated in the same manner. This is also the same spectrum obtained when a small amount of H_2TPP is dissolved in 1 M HCl. These solution spectra of H_2TPP in HCl are quite different than those of H_2TPP in toluene or H_2TPP deposited on a substrate,[58] but left in air. However, if 0.1 M HCl is used, there is no evidence of demetallation of ZnTPP. There is some decrease in the overall fluorescence intensity with time, but no growth of an emission peak at 675 nm is observed. Demetallation is not seen, even in 1 M HCl, if the ZnTPP is applied to the IOCG via syringe rather than by dipping. The molecules in compact phases apparently interact sufficiently strongly with each other to prevent reaction with the HCl.

3. Simultaneous Electrochemical and Fluorometric Experiments. The results of a typical simultaneous cyclic voltammetric/fluorometric experiment using a dipcoated electrode are shown in

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[62] Majda, M.; Faulkner, L. R. Presented at the 161st Meeting of the Electrochemical Society, Montreal, May 9–14, 1982, paper no. 621; manuscript in preparation.

[63] Levanon, H.; Neta, P. *Chem. Phys. Lett.* **1980**, *70*, 100.

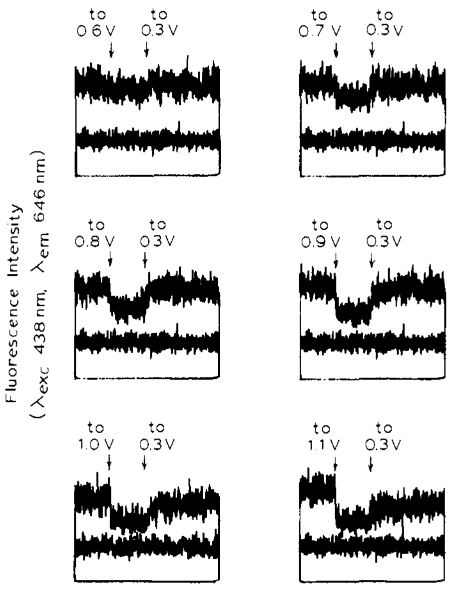

Figure 8. Luminescence intensity vs. time during steps of 10 s duration for dipcoated IOCG in 0.1 M HCl.

Figure 7. The intensity of the peak fluorescence is clearly attenuated by more than 50% as the potential is scanned past the oxidation peak. This is a fairly reversible effect, as the intensity returns nearly to the initial value within a minute, although some irreversible loss of intensity is evident. The baseline photocurrent shown in Figure 7 was obtained by blocking the emission beam of the spectrometer with a shutter. Earlier, we showed that the effect is not caused by a modulation of scattered light from the electrode as the potential is changed. Degrees of modulation in these experiments typically range from 20%, on syringe-coated electrodes, to nearly unity, on dipcoated electrodes. We have not seen significant differences in the depth of modulation on dipcoated BPPG vs. IOCG.

The slow return to preoxidation intensity values, suggests that the rereduction is slower than the oxidation. As shown in Figure 8, the fluorescence intensity, monitored as a function of time as the applied potential is stepped to various values, both preceding and following the anodic peak, begins to diminish when the step potential reaches 0.7 V. The almost instantaneous drop in intensity and much slower return to initial intensity upon rereduction is particularly noticeable in those experiments where the potential is stepped past the oxidation peak at 0.95 V.

4. A Model for the System. The observations described above allow one to construct a physical model of the surface layers at a useful level of detail. A number of striking features, particularly for deposits on BPPG, must be rationalized.

First is the point that only one molecule per 5000 Å^2 of nominal surface area ($\sim 3 \times 10^{-12}$ mol/cm^2) is electroactive, whether the electrode is loaded to $3-4 \times 10^{-10}$ mol/cm^2 by dipcoating or by syringe. This level of coverage corresponds to 50 Å^2 per molecule, which would permit one close-packed monolayer of molecules oriented with the porphyrin planes normal to the surface or about 10 monolayers with the planes parallel to the surface. The fact that only about 1% of the molecules are electroactive implies two things: (1) A large part of the deposited material is not situated in positions conducive to direct electrooxidation. (2) The "holes" produced by oxidation are not mobile. If they were, propagation of charge by electron exchange would lead to full electrooxidation of the deposit.[57]

Point 1 further implies that the bulk of the deposit is either (a) in the form of compact domains that are energetically difficult to oxidize because they require admission of charge-compensating anions into a lattice or (b) not in contact with a part of the electrode where the faradaic reaction can occur. Point 2 could be true because (c) the oxidizable sites are isolated defects in a deposit largely comprising unoxidizable domains or (d) the kinetics of exchange are intrinsically slow. Given the reversibility of the oxidation on moderately fast times scales, it is difficult to see why exchange kinetics would be slow; therefore we trend to believe that the electroactive sites are chemically distinct from the others in a manner that discourages exchange. That is, the bulk of the sample seems simply unoxidizable, probably because it exists in compact phases. These phases might be compact surface layers, or they could be more isolated blocks of the crystalline or amorphous units that, in sufficient size, and at large coverages, become visible as "ridges."

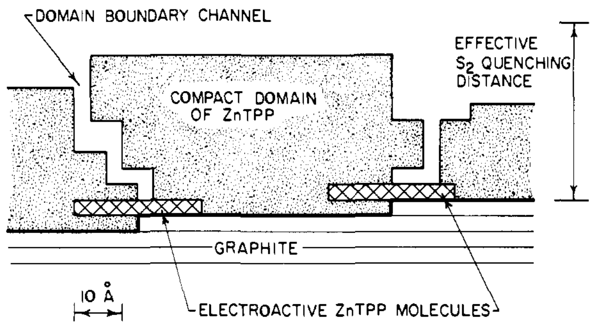

Figure 9. Schematic view of the model for dipcoated BPPG. The view of syringe-coated BPPG is similar, except the compact domains would extend past the effective S_2 quenching distance by 100 Å or more.

Another approach to a model can be made through observations about the luminescence. The most striking feature is the distinctive excitation spectrum for dipcoated deposits on BPPG, where the Soret band is selectively quenched. In contrast, BPPG coated by syringe at a three-times larger level ($10-12 \times 10^{-10}$ mol/cm^2) displays luminescence with an excitation spectrum essentially the same as that observed for IOCG or glass coated by either method. The selective quenching of the Soret band seems very likely to be rooted in an electronic coupling between the Soret oscillator and the graphite, as one would expect for a system in which the ZnTPP molecules were spaced no more than a few tens of ångstroms from the graphite.[28-31] The severity of the effect suggests that essentially all molecules that can *absorb light leading to luminescence* on dipcoated BPPG are in intimate communication with the surface. The absence of the selective quenching with syringe-coated BPPG indicates that luminescence can be excited at sites fairly remote from the surface. Since ZnTPP coated on gold at an equivalent level shows the selective quenching of the Soret transition, it appears that the gold can influence emission from more remote sites than graphite can. The selective quenching is not expected for ZnTPP on glass or IOCG because their bandgaps are too wide.

These thoughts lead to a view (Figure 9) of dipcoated BPPG as comprising compact, unoxidizable domains of ZnTPP situated essentially uniformly over the whole surface, not extended more than a few tens of ångstroms out from the surface, and offering defects, perhaps at the edges of domains or at dislocations in the graphite, where a small fraction of the molecules can be oxidized. Compact, uniform deposition of all molecules over the nominal surface area would produce a layer about 30 Å thick. Syringe-coated BPPG can be envisioned in similar terms, although the compact domains would have to extend fairly far from the surface. A coverage of 12×10^{-10} mol/cm^2 would correspond to about 120 Å thickness in a uniform layer, and its seems likely that such a thickness would provide the necessary remoteness for most of the molecules. The fact that the amount of electroactive ZnTPP remains at 3×10^{-12} mol/cm^2 may indicate that the electroactive species are adsorbed at dislocations on the graphite surface. Access for charge-compensating anions could be provided by diffusion along domain boundaries.[57]

The higher degrees of electroactivity observed for deposits on IOCG is generally consistent with this view if, as expected, the microscopic roughness of the indium oxide layer (produced by chemical vapor deposition) exceeds that of the graphite.

Another noteworthy point is that small degrees of oxidation (1% on dipcoated BPPG) can produce much larger decreases in relative fluorescence intensity. Figures of 20–80% are typical.

The incomplete extinction of luminescence upon oxidation shows that some emission comes from molecules that are not electroactive, but the depth of modulation implies that the oxidized electroactive centers have a large quenching radius. If these centers are spread evenly over the surface, they would be separated from each other, on the average, by 50–80 Å. Thus any point of excitation in a dip-coated layer on BPPG would be within 40 Å of such a quenching center. It is entirely reasonable that an exciton resulting from light absorption would be quenched over such a distance by one-step resonance transfer. There is also the prospect of exciton migration among unoxidizable molecules. To the extent that this process occurs, the need for a strong resonance interaction between exciton and quenching center would be reduced. These considerations lead to a realization that none of the modulated luminescence may actually arise from electroactive sites.

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Porphyrins. 44.[1] Electronic States of Co, Ni, Rh, and Pd Complexes

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Abstract: Iterative extended Hückel (IEH) calculations are presented with the aim of understanding the near-UV, visible, and near-IR absorption spectra and the emission properties of Co, Rh, Ir, Ni, Pd, and Pt porphyrins. UV–visible spectra are reviewed for 30 such complexes; new near-IR spectra are presented for Co^{II}, Ni^{II}, and Pd^{II} complexes of octaethyl- and tetraphenylporphyrin (OEP and TPP). We also report that three Co^{III} complexes and one Pt^{IV} complex show no emission. While the calculations do not well predict shifts of the visible spectra, they are able to explain quenching by transitions at lower energy than the usual ring phosphorescent state $^3T_1(\pi,\pi^*)$ and fluorescent state $^1Q(\pi,\pi^*)$. These states are as follows: (d,π^*) in Co^{I} porphyrin; (π,d) in Co^{II}, Ni^{IV}, and Pd^{IV} porphyrins; and $^3(d,d)$ in Co^{III} and Ni^{II} porphyrins. No quenching states are predicted for the strongly phosphorescent Rh^{III} and Pd^{II} porphyrins. In the near-IR absorption, bands identified as transitions to (d,π^*) were earlier reported for Co^{I} porphyrin; in this paper we report bands in Co^{II} porphyrins corresponding to $^2(\pi,d)$. We also locate absorptions in the near-IR corresponding to the $^2T_1(\pi,\pi^*)$ state of Co^{II}(OEP) and the $^3T_1(\pi,\pi^*)$ states of Pd^{II}(OEP), Pd^{II}(TPP), and Pt^{IV}(TTP)Cl$_2$ [TTP = mesotetratolylporphyrin]. We have not yet located $^1(d,d)$ bands in Co^{III} or Ni^{II} porphyrins; nor $^1(\pi,d)$ in Co^{III} and Pd^{IV} porphyrins; nor $^1(d,\pi)$ in Ni^{II} porphyrins. The $^1(\pi,d)$ state of Ni^{IV} and Pd^{IV} porphyrins is expected to the red of 1100 nm, the limit of our current studies; the other states may be found in the near-IR with careful study but perhaps are hidden under the $^1Q(\pi,\pi^*)$ bands.

The enzymatically important Fe porphyrins exhibit very dramatic spectral changes as a function of ligands and oxidation state,[2] which reflect the changing electronic structure of their ground and excited states. The porphyrin complexes of the congener metals, Ru and Os, also show dramatic spectral changes with change of ligands. The systematics of the spectral changes in complexes Os(OEP)LL′ have been discussed by the authors[3] with some comparisons given to Fe and Ru.[4] The iterative extended Hückel (IEH) calculations used in those papers provide a good qualitative picture for the electronic structure of these complexes: The smaller d orbitals of Fe have a relatively small crystal field splitting between the lower energy orbitals d_{xy}, d_{xz}, d_{yz} and the higher energy orbitals d_{z^2}, $d_{x^2-y^2}$; hence ligands on Fe porphyrins can give rise to low, intermediate, and high spin complexes by modulating this splitting.[5] For the Ru and Os porphyrins, the crystal field splitting of the 4d and 5d orbitals is much larger, so that d_{z^2} and $d_{x^2-y^2}$ are never populated. Nonetheless ligands can strongly influence the absorption and emission spectra and the redox properties by shifting the energy of the filled d_{xy}, d_{xz}, d_{yz} orbitals relative to the energy of the four orbitals of the ring [$a_{1u}(\pi)$, $a_{2u}(\pi)$, $e_g(\pi^*)$],[6] which are responsible for the lower energy porphyrin excited states.

In this paper we use the same model to consider the electronic structure of Co, Ni, Rh, and Pd porphyrins. Since the calculated structures for Ru and Os porphyrins were quite similar,[4] we expect a similarity between Rh and Ir porphyrins and between Pd and Pt porphyrins, and we have not done calculations on the heavier metals.

In the complexes considered here the metals have configuration d^6, d^7, and d^8. An experimental generality we wish to address concerns the fact that the emission properties do not depend on electron configuration. The known published studies can be summed up as follows: (i) Co and Ni complexes show no emission whether d^6, d^7, or d^8; (ii) Rh as d^6 and Pd and Pt as d^8 show strong phosphorescence and weak fluorescence.[6–9] [Ir as d^6 has had little

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