

Communications to the Editor

Simultaneous Electrochemical and Fluorometric Monitoring of Zinc Tetraphenylporphyrin Deposited on Indium Oxide and Pyrolytic Graphite Electrodes

Sir:

Recently there has been considerable interest in electrocatalysis, particularly of oxygen reduction. For example, much research is being done on the catalytic role of various porphyrins,¹⁻⁶ phthalocyanines, and similar molecules⁷⁻¹⁶ deposited onto electrode surfaces, typically graphite. Although the mechanisms of their catalysis are at present unknown, it seems likely that the structures of adsorbed layers are important. The extent of surface coverage and the geometric arrangement of the molecules are difficult to determine because such small amounts of material are present. We are now studying the possibilities of using fluorescence as a probe for these and other substances while they are bound to an electrode surface and are actually engaged in electrochemical activity. Fluorometric measurements are very sensitive and can be carried out with relatively simple apparatus. Moreover, they offer information about the environment surrounding the molecule of interest, and through polarization studies, one can obtain data on relative orientations of species with respect to a surface.

Arden and Fromherz^{17,18} have detected fluorescence from a species spaced away from semiconductor electrodes by several Langmuir-Blodgett layers and have modulated its fluorescence by changing the oxidation state of a surface-bound quencher. Iwasaki et al.¹⁹ observed fluorescence from electroactive species in the diffusion layer near an electrode by internal reflection spectroscopy. We believe that the experiments reported below are the first to show selective fluorometric detection of surface-deposited species actually involved in electrode reactions. These results offer encouragement to the idea that fluorescence techniques could be of value in realistic electrochemical situations.

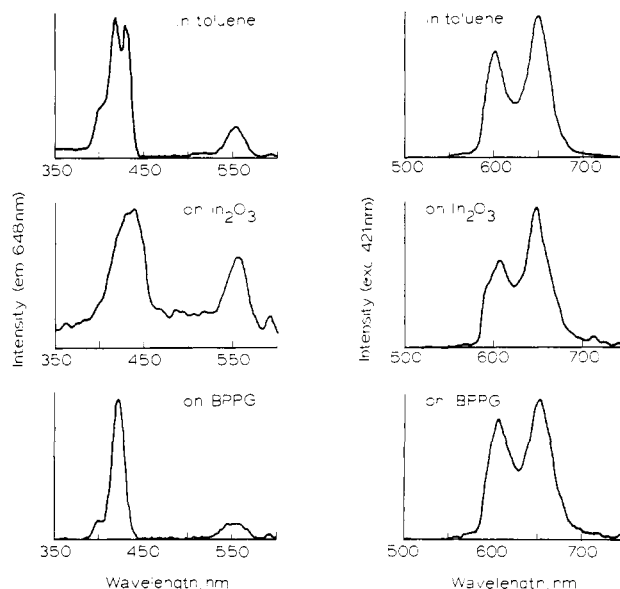


Figure 1. Excitation (left) and emission (right) spectra of ZnTPP under different conditions: in toluene, $\sim 5 \times 10^{-6}$ M; on In_2O_3 -CG, $\sim 8 \times 10^{-10}$ mol/cm²; on BPPG, $\sim 4 \times 10^{-9}$ mol/cm². All except the toluene solution are in 1 M HCl.

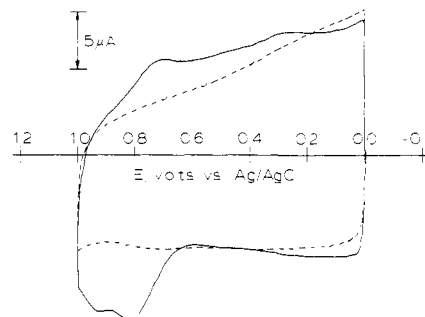


Figure 2. Cyclic voltammogram of In_2O_3 -CG (---) and 8×10^{-10} mol/cm² ZnTPP on In_2O_3 -CG (—), scanned at 0.1 V/s from 0.0 V.

At present, we are studying the structure of zinc tetraphenylporphyrin (ZnTPP) applied to the surface of an indium oxide coated glass (In_2O_3 -CG) or a basal plane pyrolytic graphite (BPPG) electrode. Luminescence is observed straightforwardly from species in close interaction with the electrode. This finding is surprising, at least with respect to graphite, because it runs counter to the expectation that excited species near an electrode would be strongly quenched by the electrode.

A three-electrode cell capable of being monitored fluorometrically comprises a quartz fluorescence cuvette (10-mm path length) containing an Ag/AgCl reference electrode, a Pt wire auxiliary electrode, and a 8×60 -mm In_2O_3 -CG working electrode in 1 M HCl electrolyte. The cell is placed into the sample compartment of a computer-controlled spectrophotofluorometer²⁰ to obtain fluorescence spectra. The In_2O_3 -CG strip is positioned manually such that its front face makes an angle of ca. 45° to the excitation beam. ZnTPP is applied to the substrate, either by using a 10- μL syringe to deliver a 2-3- μL aliquot of a 0.4 mM solution in toluene onto a ~ 1 -cm² area of the electrode and

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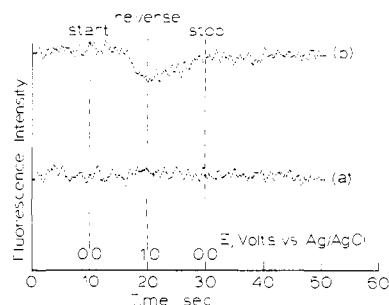


Figure 3. Modification of the fluorescence intensity (λ_{exc} 421 nm, λ_{em} 648 nm) of $\text{In}_2\text{O}_3\text{-CG}$ (a) and $\sim 8 \times 10^{-10}$ mol/cm² ZnTPP on $\text{In}_2\text{O}_3\text{-CG}$ (b) as the applied potential is scanned from 0.0 to 1.0 V and back. Trace (a) illustrates only the absence of any change in intensity due to the substrate. The dip in (b) represents a loss in intensity of about 20%. The zero of the background trace has been moved for clarity.

evaporating to dryness under a stream of N_2 or by soaking the end of the strip in the solution for several minutes and rinsing off the excess with distilled water.

Fluorescence spectra indicate that the ZnTPP applied to the electrode in this manner does not merely crystallize and adhere to the surface. Excitation and emission spectra of various forms of ZnTPP are shown in Figure 1. Experimental spectra of the solution phase are very comparable to previously reported ones for both absorption²¹⁻²⁴ and fluorescence.^{25,26}

Work with crystalline material is hampered by artifacts caused by full absorption of the excitation beam and reabsorption of emission, but we find that purified crystalline powder dusted onto glass and either immersed in 1 M HCl or left in air shows a long-wavelength emission peak at 658 nm, which is red shifted by about 10 nm from the value observed in toluene or with the electrodes.²⁷

No evidence of demetalation of the ZnTPP is observed, even though demetalation in solution by HCl is a known reaction.²⁸ Our spectra have none of the features distinctive to metal-free porphyrin (H_2TPP), i.e., excitation peaks near 515, 550, 595, and 650 nm and emission peaks at ca. 660 and 720 nm.^{27,28} An authentic sample of H_2TPP applied to the electrodes does show these features.

The ability to observe a fluorescence signal from ZnTPP applied to BPPG as indicated by preliminary experiments is particularly noteworthy. Similar systems are of great interest from a technological standpoint, and a simple monitoring method for adsorbates in operating cells would be valuable to kinetic studies.

Cyclic voltammograms of the adsorbed ZnTPP shown in Figure 2 exhibit two closely spaced oxidation peaks at ca. 820 and 900-1000 mV vs. Ag/AgCl. The two corresponding reduction peaks occur near 700 mV and between 150 and 300 mV. The magnitudes of the peak currents of the two oxidations do not exhibit the same dependences on scan rate, v . The 820-mV peak, which does not shift more than 10 mV as v increases from 100 to 250 mV/s, grows linearly with v . This indicates that the electroactive species is bound to the surface.²⁹ The peak potential of the second oxidation shifts to a more positive value by ca. 60 mV as v changes from 100 to 300 mV/s and exhibits a more complex dependence on v . Previous studies of ZnTPP in aprotic solutions^{43,24} show that successive reversible, one-electron ring oxidations occur at 0.8 and 1.1 V vs. SCE. The difference between

the peak potentials, 0.3 V, is much larger than that observed in the present experiments. Our results could suggest that the electroactive material is undergoing essentially the same electrode process, but in at least two different environments. At present, the precise nature of the electrode process is not clear, and it is not essential to our purpose here to define it. It is chemically reversible since one can run cyclic voltammograms repeatedly with only minor changes in response; however, the splittings between anodic and cathodic peaks show that slow kinetics exist, either in charge transfer or in chemical changes to the molecular structure. Data presented below show that oxidation is fast, but re-reduction is quite slow. The simplest explanation is that a cation radical is formed by oxidation and that it is stabilized by its interaction with the electrode against chemical attack. Other more complicated possibilities involving reversible alteration of the molecular structure may be more likely.

If 8×10^{-10} mol of ZnTPP ($2 \mu\text{L}$) are applied to a 1-cm² portion of the electrode and dried, the amount oxidized during the potential scan is close to 2×10^{-10} equiv (as determined by estimating the area under the anodic peak). If about 1 cm² of the electrode is soaked for ca. 10 min in the solution and the excess is rinsed off with water, then only ca. 6×10^{-11} equiv are oxidized; if the excess is allowed to dry, again 2×10^{-10} equiv are electroactive. The deposition, though, is not irreversible. If the electrode is rinsed well with toluene, the cyclic voltammogram obtained is identical with that of a fresh electrode.

Simultaneous electrochemical and fluorometric experiments provide evidence that at least a portion of the fluorescent material on the surface is also electroactive. The peak fluorescence intensity is diminished as the potential is scanned past the oxidations as shown in Figure 3(b). This attenuation is equal to approximately one-fifth of the original peak intensity, a fraction that correlates well with the ratio of electroactive equivalents estimated from the voltammetric response to the number of moles applied by syringe.^{30,31} After completion of the potential scan, the fluorescence intensity does not revert completely to its initial value in this figure because of slow re-reduction; however, there is some irreversible loss of material with time.

Excitation and emission spectra of the ZnTPP on an electrode being held at 1000 mV show qualitative differences, as well as an overall attenuation of peaks by about one-quarter, from those obtained with the electrode at open circuit.³⁰

On BPPG, the fluorescence intensity of the ZnTPP is also attenuated by oxidation. Further investigation of this system is currently being conducted.

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(30) In recent work, we have observed attenuation exceeding 50%. The residual fluorescence may have a contribution from the oxidized form.

(31) Whether the fluorescence observed from the ZnTPP on a substrate is emitted from a layer directly adjacent to the surface is not entirely clear at present. Using a syringe to apply the solution to the electrode does not result in uniform surface coverage, and multilayer regions must exist. However, fluorescence is observed even if the electrode is soaked for several minutes in the ZnTPP solution and rinsed with distilled water, a method which seems to result in greater uniformity and closer to monolayer coverage.

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The Π and Σ_{N} Electronic States of the Succinimidyl Radical. Can Nitrogen-Centered Radicals Have Σ_{N} Ground States? An *ab Initio* Study

Sir:

The succinimidyl radical **1** was first proposed as an intermediate almost 40 years ago,¹ but its chemical properties remained a