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## Semiconductor Electrodes. 50. Effect of Mode of Illumination and Doping on Photochemical Behavior of Phthalocyanine Films

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The behavior of photoelectrochemical (PEC) cells composed of SnO<sub>2</sub> or Pt electrodes with coatings of different phthalocyanines (Pc), H<sub>2</sub>Pc, ZnPc, MgPc, CuPc, and InPcCl, was investigated. Spectral sensitization at the SnO<sub>2</sub>/Pc interface leads to photooxidation currents, while efficient photoreduction occurs at the Pc/solution interface through bulk generation of charge carriers. The presence of both anodic and cathodic photocurrents leads to different net photocurrent responses for back and front side illumination, especially with thicker films. The efficiency of the reduction process was sensitive to the potential of the redox couple in solution and maximized when  $E_{\text{redox}}$  was about 0.37 V for H<sub>2</sub>Pc, ZnPc, and MgPc. A dramatic improvement of the photoelectrochemical behavior of the coating results from doping with an electron acceptor (e.g., *o*-chloranil) and quantum yields as high as 4.6% were measured for Pt/H<sub>2</sub>Pc electrodes.

### Introduction

In this work we continue our studies of the photoelectrochemical behavior of phthalocyanine films on semiconductor electrodes.<sup>1-3</sup> These investigations, as well as numerous previous studies of organic materials as sensitizers or as semiconductors,<sup>4,5</sup> have demonstrated the production of photocurrents in photoelectrochemical (PEC) cells upon irradiation of such electrodes. Phthalocyanines have been of particular interest because they are stable, highly absorbing, and can be chemically modified to yield a wide range of redox potentials and colors; references to many of the previous studies of these are contained in ref 1-3.

A persistent problem with the use of organic and organometallic compounds as sensitizers for semiconductors is the relatively low efficiency for conversion of incident radiation to electron flow (e.g., compared to band gap irradiation of the substrate inorganic semiconductor). This can be attributed to the low efficiency of conversion of excitons to separated electron-hole pairs and to the low mobility and rapid trapping of carriers in the sensitizer films. The phthalocyanines show a tendency toward aggregation and polymerization in the solid state.<sup>4d</sup> This could lead to a better overlap of the  $\pi$  orbitals between chromophores and improve the photogeneration and conduction of charge carriers.

For most inorganic semiconductors, because of the strong interactions among atoms in the lattice, the photogeneration of a free electron-hole pair is a direct process and follows immediately the absorption of a photon.<sup>5-8</sup>

For molecular solids, the lattice forces are of the van der Waals type and only a small overlap will develop between the orbitals of adjacent molecules. The energetics of carrier formation may be described in terms of localized electrons and holes, while the mobilities are best described in terms of the band approximation. Frenkel excitons constitute the first intermediate after photoexcitation in organic crystals and these will only generate the carriers by interaction with the surface or with traps.<sup>5,6</sup>

The band gap energy for  $\alpha$ -H<sub>2</sub>Pc is 2.11 eV<sup>5d</sup> and the observation of photocurrent with excitation up to 1.5 eV emphasizes the indirect nature of photocarrier formation.<sup>5e</sup> Photogeneration of carriers appears to be promoted by the presence of impurities or adsorbed gases in the phthalocyanines;<sup>7</sup> these behave as dopants in the Pc lattice.

We report here the PEC behavior of several phthalocyanines (H<sub>2</sub>Pc, CuPc, InPcCl, ZnPc, MgPc) deposited on SnO<sub>2</sub> and Pt substrates and in electrolytic contact with different solutions to gain better understanding of the interfacial processes. Doping with *o*-chloranil was also undertaken.

### Experimental Section

**Materials.** Films of the phthalocyanines (Pc) purchased from Eastman (Rochester, NY), were prepared by vacuum sublimation (10<sup>-5</sup> to 10<sup>-6</sup> torr) as reported previously.<sup>1,2</sup> The thickness of the layer was estimated by spectrophotometry either directly on the substrate or after dissolution of the film in a concentrated sulfuric acid solution. Tin oxide films on glass and Pt were used as substrates for vacuum deposition; the platinum disk (~0.025 cm<sup>2</sup>) was polished with 3 and 1 Metadi II diamond paste (Buehler LTD, Lake Bluff, IL). The SnO<sub>2</sub> (350  $\Omega$ /square) was washed in H<sub>2</sub>SO<sub>4</sub>, thoroughly rinsed in water before being treated 24 h in boiling 2-propanol, and dried at 150 °C; contact to the tin oxide was made with silver paint (Acme Chemicals, New Haven, CT) to a copper wire. The *p*-hydroquinone (H<sub>2</sub>Q), *p*-benzoquinone (BQ, Eastman Chemicals), and *o*-chloranil (*o*-Chl, Sigma Chemical) were purified by sublimation under reduced pressure. All other chemicals were used without further purification. Deion-

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(4) See, e.g., (a) H. Gerischer and F. Willig, *Top. Curr. Chem.*, **61**, 31-84 (1976); (b) M. D. Archer, *Photochem.*, **8**, 571-90 (1977); (c) A. Kirsch-De Mesmaecker, P. Leempoel, and J. Nasielski, *Nouv. J. Chim.*, **3**, 239-45 (1979); (d) T. M. Mezza, C. L. Linkous, V. R. Shepard, N. R. Armstrong, and M. Kenney, *J. Electroanal. Chem.*, **124**, 311-20 (1981), and references therein.

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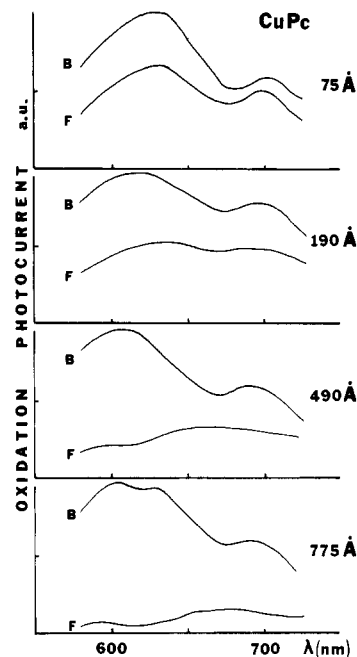
ized water was doubly distilled from alkaline potassium permanganate solution. The cobalt(II) complexes were prepared as described by Chen et al.<sup>8</sup> and electrolyzed to generate a 1:1 solution of Co(II)/Co(III) complex.

**Apparatus.** A conventional three-electrode, single-compartment cell was used for the electrochemical measurements. The cell, painted black, was equipped with an optical window to allow irradiation of the electrode. A saturated calomel electrode (SCE) served as reference and a large area Pt foil as the counterelectrode. All solutions were deoxygenated with nitrogen prior to the measurements. The electrochemical experiments were performed with a PAR Model 173 potentiostat and a Model 175 programmer (Princeton Applied Research Corp., Princeton, NJ) and recorded on a Houston Instrument X-Y 2000 recorder (Austin, TX). The light source was either a 1.5-mW Spectra Physics Model 132 He-Ne laser or a 2500-W Xe lamp and power supply (Schoffel Instrument Co., Westwood, NJ) combined with lenses and a Jarrel Ash monochromator (Waltham, MA) to give a light flux of 0.4 mW at 620 nm. The light flux was measured with an EG and G Model 550 radiometer and all the photocurrent spectra were corrected for the spectral distribution of the light source and the absorption of the solution. In some cases, action spectra were obtained by modulated irradiation and phase-sensitive detection techniques with a PAR Model 192 variable-frequency chopper and a PAR Model 5024 lock-in amplifier.

**Methods.** The advantages of optically transparent electrodes have been described frequently. Phthalocyanine films vacuum deposited on SnO<sub>2</sub> can be photoexcited through either side of the coating and in this paper it will constantly be referred to as front-side (FS) and back-side (BS) irradiation. Back-side irradiation implies that the light passes first through the SnO<sub>2</sub> electrode and then reaches the coating; this results in a predominant excitation at the substrate/Pc interface. In the front side mode, excitation of the film occurs directly and generates the e<sup>-</sup>h<sup>+</sup> pairs mainly at the Pc/electrolyte interface; with Pt the excitation was always by front-side irradiation.

Most of the photoelectrochemical studies on Pc films have involved phase-sensitive detection techniques. These cannot always be used because of the slow transient response of the electrode as pointed out earlier.<sup>9</sup> Most of the experiments described here involve the direct measurement of the photocurrent at a potential determined by the couple in solution. At this potential no dark current flows and the photocurrent corresponds to the short circuit photocurrent of a cell consisting of the Pc electrode and a large area counterelectrode acting as a quasi-reference. Thus, unless mentioned otherwise, the potential of the Pc electrode is equal to that of a Pt electrode immersed in a solution containing about equal concentrations of both halves of the redox couple.

Homogeneously doped samples are difficult to prepare by vacuum sublimation and even surface doping is very difficult to control by this technique.<sup>10</sup> Surface doping was thus achieved from solution. Known amounts of *o*-chloranil were dissolved in toluene or cyclohexene (2.5–3.5 mg of *o*-Chl/25 mL) and 0.1 mL of this solution was allowed to evaporate on the sublimed phthalocyanine layer. Before use, every doped electrode was placed under reduced pressure for at least 15 min. Better results were obtained with toluene rather than cyclohexane probably because toluene evaporates more slowly and slightly dis-



**Figure 1.** Action spectra for SnO<sub>2</sub>/CuPc electrodes of various thickness in 10 mM H<sub>2</sub>Q, 0.1 M Na<sub>2</sub>SO<sub>4</sub>, phosphate buffer, pH 6.8. Excitation mode: B, back side; F, front side.  $V = 0.2$  V SCE.

solves the organic layer allowing deeper penetration of the *o*-Chl.

## Results

**Spectral Sensitization.** The illumination of SnO<sub>2</sub>/Pc electrodes generates a photocurrent whose spectral dependence agrees very well with the absorption spectrum of the dye layer.<sup>2,9</sup> This behavior has been observed for all the phthalocyanines investigated here: H<sub>2</sub>Pc, CuPc, ZnPc, MgPc, and InPcCl. However, the extent of agreement between photocurrent and absorption depends upon the irradiation conditions, the potential of the electrode, and the thickness of the dye layer.<sup>5e,11</sup> The dependence of the FS action spectra with thickness for a SnO<sub>2</sub>/CuPc electrode in the presence of H<sub>2</sub>Q, shown in Figure 1, represents typical Pc-film behavior. Although the sample thickness does not affect the shape of the BS action spectrum, with FS excitation a decrease in intensity and a gradual flattening of the spectrum with increasing thickness occurs. The magnitude of the oxidation photocurrent is almost constant with the thickness within the range investigated with BS excitation; in the FS mode, however, a maximum value is reached at about 100 Å followed by a rapid drop of the photooxidation current. The photoeffect observed under those conditions is characteristic of a spectrally sensitized anodic current for a SnO<sub>2</sub> electrode with a small number of active dye layers close to the SnO<sub>2</sub>/Pc interface.<sup>3,12</sup> Similar behavior has been observed for SnO<sub>2</sub>/InClPc electrodes.

**Effect of Redox Couple.** The previous results pertained to solutions containing only a reductant, e.g., H<sub>2</sub>Q. The spectra are quite different when both forms of the redox couple (e.g., H<sub>2</sub>Q and BQ) are present in about equal amounts in the solution. The action spectrum is especially sensitive to the thickness of the dye layer and the electrode potential.

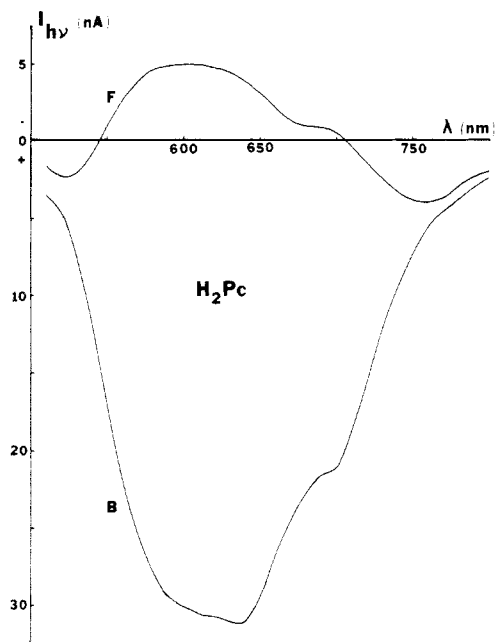
Upon BS illumination a 2900-Å SnO<sub>2</sub>/H<sub>2</sub>Pc electrode exhibits the usual spectral distribution in an H<sub>2</sub>Q/BQ

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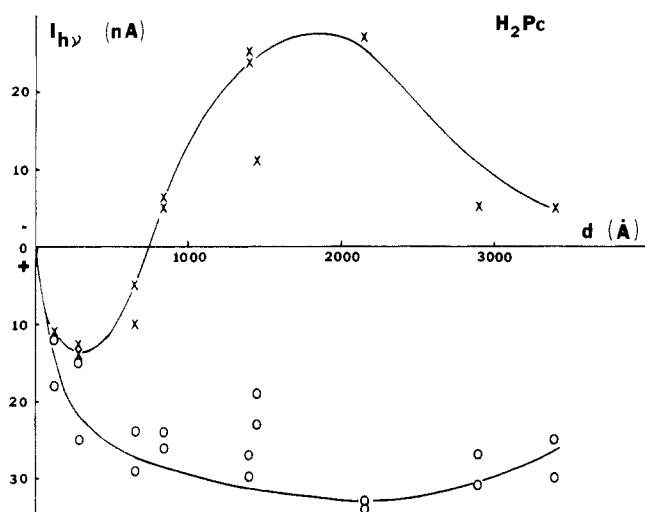
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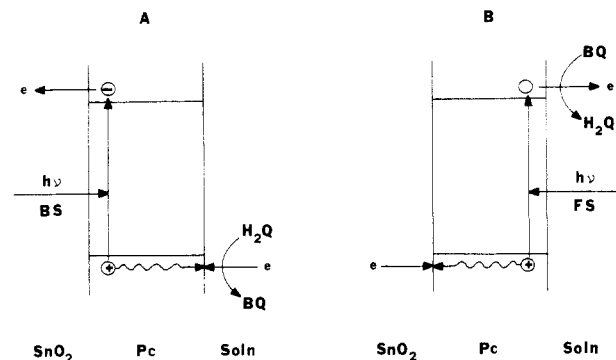


**Figure 2.** Action spectrum for a 2900-Å  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode in 5 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , phosphate buffer, pH 7. Excitation mode: B, back side; F, front side.  $V = 0.04$  V SCE.

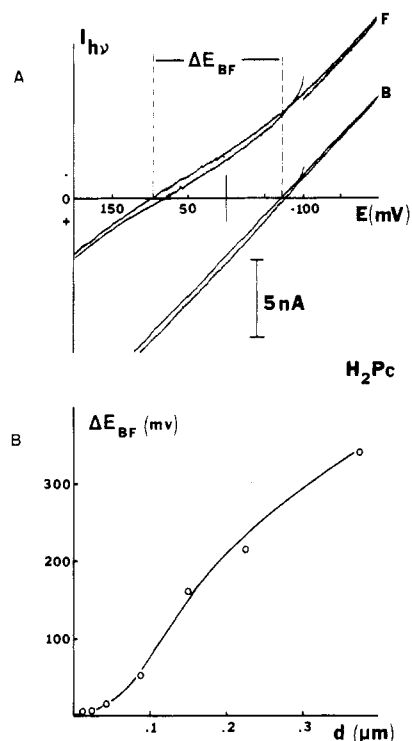


**Figure 3.** Dependence of sensitized photocurrent on thickness for  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes in 5 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , phosphate buffer, pH 6.9. Excitation mode: O, back side; X, front side. Xe lamp,  $\lambda = 620$  nm.

solution (Figure 2). However, in the FS mode, a photo-reduction is observed as well as a photooxidation and the sign of the steady-state photocurrent is wavelength dependent. Similar behavior has been observed for a metal/chlorophyll *a*/metal sandwich cell upon pulsed excitation.<sup>11</sup> In our case, in the FS excitation mode, a wavelength where the absorbance is high induces photoreduction of the benzoquinone, while a net photooxidation current is the result of illumination at a wavelength where light penetrates to the  $\text{SnO}_2/\text{H}_2\text{Pc}$  interface. The same conclusion can be reached by changing the sample thickness and illuminating it in the wavelength range of the absorption maximum of the phthalocyanine (Figure 3). No unusual behavior is observed in the BS mode. The photooxidation current increases in a fairly proportional way with the amount of light absorbed by the film and attains a limiting value for a thickness close to 350 Å; at this thickness more than 40% of the light is absorbed in the film. With films thicker than 3000 Å, the photoanodic



**Figure 4.** Scheme of electron transfer at  $\text{SnO}_2/\text{Pc}$  electrode upon (A) back-side excitation and (B) front-side excitation.

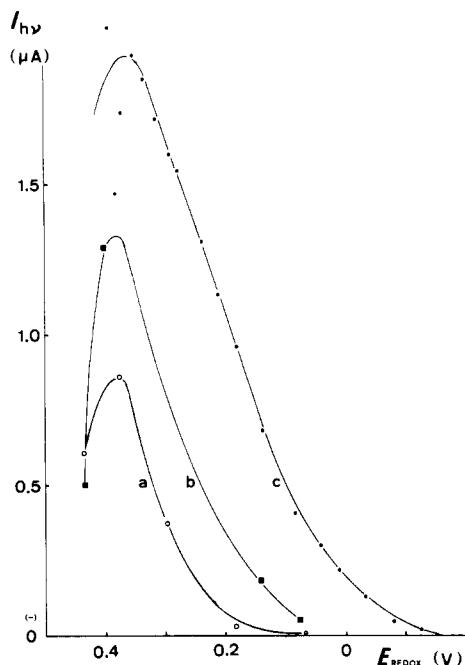


**Figure 5.** A. Photocurrent-potential curve for a 1400-Å  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode in 5 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$  phosphate buffer, pH 6.9. Excitation mode: B, back side; F, front side. Xe lamp,  $\lambda = 620$  nm. Chopped illumination at 90 Hz. B. Thickness dependence of the zero potential difference upon back- and front-side excitation. Same conditions as A.

current with BS illumination decreases.

The photoelectrochemical behavior of the  $\text{SnO}_2/\text{Pc}$  electrodes is different in the FS mode. While both modes of excitation lead to a photooxidation current for very thin samples, the FS illumination induces a photoeffect in which the photocurrent changes from oxidation to reduction as the thickness is increased (Figure 3). The photoreduction currents are much more sensitive to film thickness than the BS photooxidation currents. These results can be explained by the scheme shown in Figure 4.

A competition exists between the processes at the two interfaces;  $\text{Pc}/\text{solution}$  and  $\text{SnO}_2/\text{Pc}$ , which yield opposite photoeffects.<sup>1,2</sup> For thin samples and net current is imposed by the most efficient interface (photooxidation at pH 7) but, as the thickness is changed, both types of photocurrents occur and the net current is governed by the mode of irradiation. This can also be shown by the potential dependence of the photocurrent and the change of the zero-photocurrent potential difference ( $\Delta E_{\text{BF}}$ ) with



**Figure 6.** Dependence of the photoreduction current on the solution potential. Front-side illumination. (a) 2400-Å  $\text{SnO}_2/\text{H}_2\text{Pc}$ , Xe lamp,  $\lambda = 620$  nm, 10 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , buffered solutions. The solution potential was modified by pH changes. (b) 1500-Å  $\text{Pt}/\text{H}_2\text{Pc}$ , He-Ne laser, couples used (by increasing redox potential):  $\text{Co}(\text{bpy})_3^{2+/3+}$ ,  $\text{Co}(o\text{-phen})_3^{2+/3+}$ ,  $\text{Co}(5\text{-nitro-}o\text{-phen})_3^{2+/3+}$ ,  $\text{Fe}^{2+/3+}$ , all 10 mM and prepared as described in the Experimental Section; 0.1 M  $\text{H}_2\text{SO}_4$ . (c) 2950-Å  $\text{Pt}/\text{H}_2\text{Pc}$ , He-Ne laser, 10 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{H}_2\text{SO}_4$ , unbuffered solutions, the solution potential was modified by pH changes with  $\text{NaOH}$ .

thickness upon BS and FS excitation (Figure 5).

As shown in Figure 5a, a dramatic spectral modification appears in the action spectrum as the potential of the electrode is changed. For a potential equivalent to the one determined by the redox couple in solution (i.e., +50 mV for  $\text{H}_2\text{Q}/\text{BQ}$  at pH 7), the action spectrum of a 1400-Å  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode resembles the one in Figure 2, the photocurrent in the FS mode being either an oxidation or a reduction depending upon whether the absorbance of the  $\text{H}_2\text{Pc}$  is low or high. At sufficiently positive potentials, no photoreduction current is observed and the BS action spectrum is similar to the absorption spectrum of the coating. However, in the FS mode, the spectral distribution of the current is affected by a strong filter effect, since the  $\text{SnO}_2/\text{H}_2\text{Pc}$  is the primary interface involved in the photooxidation process. However, at negative potentials only photoreduction currents are observed, since the  $\text{Pc}/\text{solution}$  is the primary interface involved in the photoeffects. Here the BS action spectrum presents a filter effect.

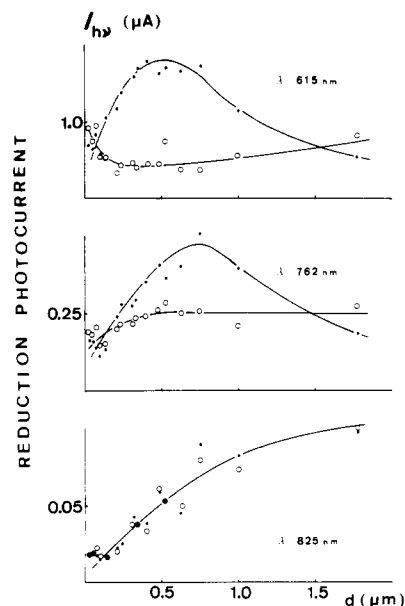
**Effect of Redox Potential.** Phthalocyanines like  $\text{H}_2\text{Pc}$  or  $\text{ZnPc}$  behave as p-type semiconductors.<sup>1,13,14</sup> Although spectral sensitization with Pc coatings has been observed,<sup>1,2,9</sup> the photooxidation currents are small and only ring-stacked phthalocyanines show efficiencies and characteristics which might be of interest in PEC devices.<sup>4d</sup> However, as shown in Figure 6, higher photoreduction currents can be generated with  $\text{SnO}_2/\text{Pc}$  or  $\text{Pt}/\text{Pc}$  electrodes by using very simple phthalocyanines such as  $\text{H}_2\text{Pc}$ ,  $\text{ZnPc}$ , or  $\text{MgPc}$ . The magnitude of the photoreduction current is very sensitive to the redox potential of the couple

**TABLE I:** Oxidation Peak Potential for Hydroquinone on  $\text{Pt}/\text{Pc}$  Electrodes<sup>a</sup>

pH	Pt	$E_{\text{pa}}$ , mV		
		MgPc ( $I_c =$ 4.95 eV) <sup>b</sup>	ZnPc ( $I_c =$ 5.10 eV) <sup>b</sup>	$\text{H}_2\text{Pc}$ ( $I_c =$ 5.20 eV) <sup>b</sup>
6.5	290	290	415	1145
4.5	412	410	460	995
2.6	470	475	520	575
1.3	507	567	610	587

<sup>a</sup> Buffered solution, 0.1 M  $\text{Na}_2\text{SO}_4$ ; scan rate, 10 mV/s.

<sup>b</sup>  $I_c$  is the photoelectric work function after ref 6 and 20.



**Figure 7.** Thickness dependence of the sensitized photocurrent for  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes in 10 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , trichloroacetate buffer, pH 1.3. Excitation mode: O, back side; •, front side Xe lamp,  $\lambda = 615, 762,$  and  $825$  nm.  $V = 0.38$  V vs. SCE.

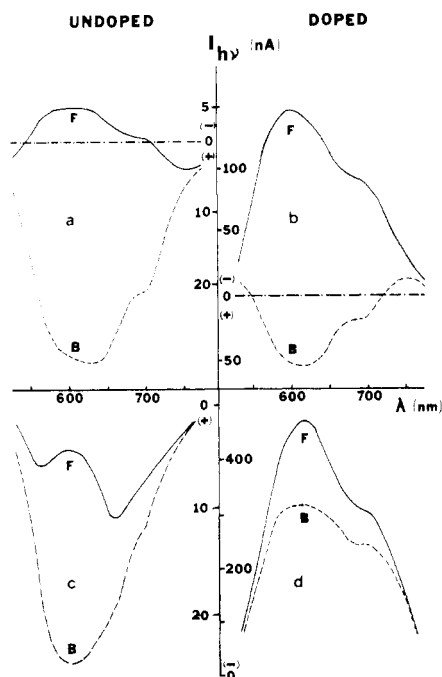
present in solution. All photocurrents described in Figure 6 were obtained with a solution containing equimolar amounts of oxidant and reductant; the potential of the solution was changed either by using different redox couples or by changing the pH of the medium when  $\text{H}_2\text{Q}/\text{BQ}$  was used. The behavior was very similar under different experimental conditions, e.g., different film thicknesses, different substrates for the coatings, and different redox couples. The magnitude of the photocurrents in Figure 6 are not related to the pH but rather to the redox potential of the solution. If a pH effect exists, it has no direct effect upon the Pc layer or the  $\text{SnO}_2$ , at least not in such a way as to modify the photocurrents.

The photopotential,  $\Delta E$ , essentially is independent of  $E_{\text{redox}}$  in the 0–350-mV range, but decreases very rapidly outside these limits. The lack of increase in  $E$  with  $E_{\text{redox}}$ , while the photoreduction is enhanced, is the result of a parallel increase in the dark currents, oxidation as well as reduction. The couples are known to be more reversible on Pc electrodes as their redox potentials become more positive<sup>13</sup> and the potential for the oxidation of  $\text{H}_2\text{Q}$  on Pt and Pc are nearer each other as  $E_{\text{redox}}$  increases (Table I).

For a solution potential more positive than 100 mV, a  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode does not show any photoanodic current for any thickness of the organic layer (Figure 7). The FS action spectrum is related to the absorption spectrum of the coating while, in the BS excitation mode, the photocurrent is affected by a filter effect. Furthermore,

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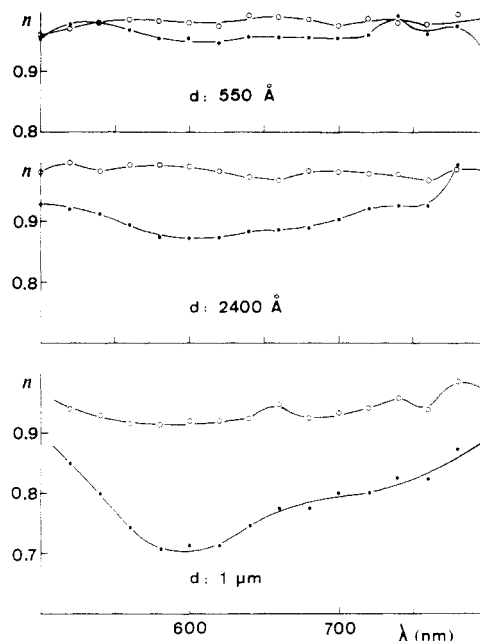
(14) F.-R. F. Fan and L. R. Faulkner, *J. Chem. Phys.*, **69**, 3334–40 (1978).



**Figure 8.** Action spectrum for  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes in 5 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , phosphate buffer, pH 7. Excitation mode: B, back side; F, front side;  $V = 0.04$  V vs. SCE. Electrodes: 2900 Å  $\text{SnO}_2/\text{H}_2\text{Pc}$  (a) undoped, (b) *o*-chloranil/toluene doped, 650 Å  $\text{SnO}_2/\text{H}_2\text{Pc}$ , (c) undoped, (d) *o*-chloranil/toluene doped.

for a Pt/Pc electrode, no photooxidation of solution species has ever been measured under our experimental conditions even for fairly negative couples and even for coatings as thin as 1100 Å. These observations show that the photoanodic current at  $\text{SnO}_2/\text{Pc}$  occurs through spectral sensitization, while the photocathodic current occurs via processes at the Pc/solution interface, independent of the back contact. Note that the BS photocurrent never disappears, even when essentially no light reaches the front interface (for example, at 615 nm for a 1- $\mu\text{m}$  coating). The three wavelengths shown in Figure 7 are associated with different absorption coefficients of the Pc layer. For small absorbances (at 825 nm), as light penetrates deep into this film, the FS and BS photocurrents are similar even for very thick samples. However, for the other samples, the magnitude of the photoeffect depended upon the excitation mode, when the film was thick relative to the penetration depth of the light.

**Effect of the Doping.** The effect of electron acceptors like  $\text{O}_2$  or *o*-chloranil upon the conductivity and photoconductivity of phthalocyanine is well-known.<sup>15-18</sup> Surface doping by solvent evaporation as carried out here, although easily controllable, did not give reproducible results. However, after doping, every electrode exhibited an enhanced reduction photocurrent by a factor ranging from 2 to 20 in the FS excitation mode. Under our experimental conditions, no clear correlations were found between the efficiency of the doping and the thickness of the sample, although thick layers were usually affected most. More porous phthalocyanine films seemed to show larger doping effects; this is understandable in terms of a better distribution of dopant acceptor species at the grain bound-



**Figure 9.** Wavelength dependence of the light exponent.  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes, front-side excitation, Xe lamp, in 10 mM  $\text{H}_2\text{Q}/\text{BQ}$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , trichloroacetate buffer pH 1.3.  $V = 0.38$  V vs. SCE:  $\bullet$ , undoped samples;  $\circ$ , doped samples.

aries within the organic layer. Parallel to the enhancement of the photocurrent, the dark current also increases upon doping, sometimes in such a way that the competition between the photoreduction and the dark oxidation decreases the open circuit photovoltage.

The change of the action spectrum of 650- and 2900-Å-thick  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes upon doping with *o*-chloranil/toluene is shown in Figure 8. A complete inversion of behavior can be observed; the photooxidation current, which was predominant, becomes a minor component and the Pc/solution interface responds more efficiently to the photoexcitation while a filter effect develops in the BS mode. Qualitatively this is equivalent to the modifications of the behavior for the photoelectrode when more positive redox couples are used. In general, *o*-chloranil-doped electrodes behave similarly to undoped ones, but show higher reduction currents.

The steady-state reduction photocurrent for  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrodes was almost linearly dependent upon light intensity at all wavelengths for thin coatings. This linearity, represented by  $n$  (where  $i$  varies as  $I^n$ ), was unaffected by doping. For thicker coatings, however, a pronounced wavelength dependence was observed as shown in Figure 9. For a 1- $\mu\text{m}$ -thick film for example, rather small  $n$  values were found close to the absorption maximum of the layer and the plot of  $n$  vs.  $\lambda$  resembled an upside-down absorption spectrum of phthalocyanine. This was even clearer in a plot of  $n/\alpha$ . Under pulsed light excitation, transient photocurrent spikes were observed upon excitation and extinction at 620 nm. After *o*-chloranil doping, the wavelength dependence of the light exponent,  $n$ , and the spikes of the transient photocurrent were absent and the photocurrent was greater by a factor of 15. Further treatment of the electrode with the *o*-chloranil/toluene solution only slightly improved the photocurrent.

## Discussion

**Photoeffect in the Absence of Dopants.** In the presence of only reductant in solution, the action spectrum matches the absorption characteristics of the sample when light is incident on the  $\text{SnO}_2/\text{Pc}$  interface (BS mode). Illumina-

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tion through the front side of the electrode produces an inverse relationship between action and absorption spectra, because the phthalocyanine layer acts as an internal filter, the weakly absorbed wavelengths having a relatively larger contribution than strongly absorbed ones. The presence of the filter effect in the FS mode indicates that the photoactive region lies mainly at the  $\text{SnO}_2/\text{Pc}$  interface, when an oxidant is absent in the solution and that the generation of the anodic photocurrent is not through a bulk process.

If the participation of bulk-generated carriers to the photooxidation process is neglected, the rate of charge carrier generation at a distance  $x$  from the illuminated interface is proportional to  $\exp(-\alpha x)$ , where  $\alpha$  is the absorption coefficient of the Pc film.<sup>14</sup> The photocurrent is proportional to the number of photons absorbed within the photoactive region. Since there is no filter effect in the BS excitation mode, the photocurrent is (in faradays  $s^{-1}$ ) is given by

$$i_{\text{BS}}^{\text{ox}} = -\phi_{\text{ox}} I_0 [1 - \exp(-\alpha A)] \quad (1)$$

where  $A = d$  if  $d \leq l_{\text{ox}}$ ,  $A = l_{\text{ox}}$  if  $d \geq l_{\text{ox}}$ ,  $\phi_{\text{ox}}$  is the photooxidation quantum yield,  $I_0$ , the light intensity,  $d$ , the thickness of the film, and  $l_{\text{ox}}$  the thickness of the photoactive region for the photooxidation.

In the FS excitation mode, however, the light is first filtered before reaching the back interface and eq 1 becomes

$$i_{\text{BS}}^{\text{ox}} = -\phi_{\text{ox}} I_0 \exp\{-\alpha(d - A)\} [1 - \exp(-\alpha A)] \quad (2)$$

From the experimental data of Figure 1 and eq 1 and 2, the active layer thickness for  $\text{CuPc}$ ,  $l_{\text{ox}}$ , is calculated to be close to 100 Å. This is of the order of the grain size for  $\text{CuPc}$  on n-Si (estimated to range between 50 and 100 Å).<sup>3</sup> As in the case of  $\text{H}_2\text{Pc}$ ,<sup>5e</sup> the photoactive layer is limited by the size of the microcrystallites constituting the organic phase.<sup>5e</sup> The electron injection into the  $\text{SnO}_2$  phase will be followed by hole movement to the solution interface and injection into the solution in the presence of reductants, such as  $\text{H}_2\text{Q}$  or  $\text{I}^-$ . The effect of thickness on the magnitude of the photoeffect is important in terms of spectral sensitization of wide band gap semiconductors. In most cases, spectral sensitization originates from the portion of the dye layer nearest the semiconductor.<sup>4a,9,12</sup> This results in a very inefficient absorption of light for thin layers and limitations because of resistance effects (carrier mobility) as the organic layer thickness grows.<sup>19</sup> Our results are in agreement with this model and show that the critical thickness, beyond which the absorbed light does not result in an increase of current, is a function of the thickness of the photoactive layer and the grain size in the coatings.

The addition of an oxidant, e.g., BQ, into the solution increases the cathodic photocurrent. Equivalent equations as (1) and (2) can be written for the reduction process, where the primary process occurs at the front interface:

$$i_{\text{BS}}^{\text{red}} = \phi_{\text{red}} I_0 [1 - \exp(-\alpha B)] \quad (3)$$

$$i_{\text{BS}}^{\text{red}} = \phi_{\text{red}} I_0 \exp\{-\alpha(d - B)\} [1 - \exp(-\alpha B)] \quad (4)$$

where  $B = d$  if  $d \leq l_{\text{red}}$  and  $B = l_{\text{red}}$  if  $d \geq l_{\text{red}}$  and  $\phi_{\text{red}}$  and  $l_{\text{red}}$  are defined for the reduction process. Suitable combinations of eq 1-4 allow the simulation of the data of Figure 3 and yields the following values:  $\alpha = 7 \times 10^4 \text{ cm}^{-1}$ ,<sup>14</sup>  $\phi_{\text{ox}}$ ,  $4 \times 10^{-4}$ ;  $\phi_{\text{red}}$ ,  $1 \times 10^{-4}$ ;  $l_{\text{ox}}$ , 350 Å;  $l_{\text{red}}$  1000 Å.

The photoactive layer of 350 Å for  $\text{H}_2\text{Pc}$  agrees fairly well with the values already published, which range from

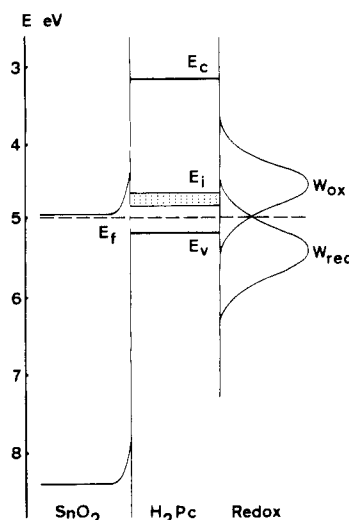


Figure 10. Energy band diagram for a  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode in a redox electrolyte having an equilibrium potential of 0.3 V vs. SCE.

200<sup>5e</sup> to 400 Å,<sup>17,20</sup> lengths comparable to the grain size. However, an  $l$  value of 1000 Å seems unreasonable, since it exceeds the grain diameter and because it is not obvious that  $l_{\text{ox}}$  and  $l_{\text{red}}$  should be different, unless the mechanism for charge carrier generation is different for the photo-reduction processes, or the oxidant penetrates a certain depth into the film. This assumption is further substantiated by some other experimental results.

Pulse photoconductivity action spectra suggest that the quantum efficiencies for carrier generation are independent of wavelength. Our measurements, under steady-state illumination, with a 1- $\mu\text{m}$   $\text{SnO}_2/\text{H}_2\text{Pc}$  confirm roughly these observations for a wavelength range extending from 400 to 850 nm.

Moreover, the data presented in Figure 7 for three wavelengths absorbed differently by the samples, are not consistent with a surface process. For a couple like  $\text{H}_2\text{Q}/\text{BQ}$  at pH 1.3, which has a rather positive redox potential (0.38 V vs. SCE), fairly high reduction currents are generated upon FS illumination and the photocurrent vs. thickness plot is strongly wavelength dependent. With 615-nm photons (a strongly absorbed wavelength) the current saturates for a thickness of 3500 to 7500 Å before the resistance affects the efficiency. With 762-nm light and even more for 825-nm light (medium and weakly absorbed wavelengths), the maximum photoresponse is reached for much thicker samples. The thickness dependence of the BS photocurrent does not correlate well with a simple filter effect as in the case of  $\text{CuPc}$  (see Figure 1). These results suggest that the primary photoprocess leading to the reduction current is not localized at the Pc/solution interface but mainly occurs in the bulk of the organic phase. In the phthalocyanines, the carrier generation process is known to be extrinsic and is strongly affected by adsorbed molecules.<sup>22</sup> Bulk generation, although shown to exist,<sup>21</sup> is not generally considered for a polycrystalline sample.<sup>5e</sup> However, it can be visualized as a photocarrier generation process at the grain boundaries coupled with charge transport within the organic phase.

The interface between the redox solution and a  $\text{SnO}_2/\text{H}_2\text{Pc}$  electrode can be represented as in Figure 10. In this case the potential of the solution was chosen equal to the assumed flat-band potential of  $\text{H}_2\text{Pc}$ ,  $\sim 0.3 \text{ V}^{13}$  (a

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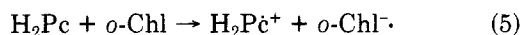
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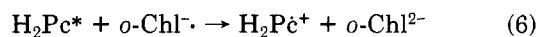
$V_{fb}$  of 0.8 V was measured for Pt/CuPc).<sup>23</sup> Besides the charge transfer resulting from the exciton-surface splitting, the electron injection can be mediated, either at the surface or even in the bulk, by intermediate states having an energy  $E_i$ .<sup>1</sup> Phthalocyanines are known to possess intermediate levels detected by differential capacitance measurements and associated with metal phthalocyanine impurities<sup>25</sup> or more probably in this case with oxygen,<sup>26</sup> with an energy of 0.45 V above the valence band for H<sub>2</sub>Pc. Mediated injection, via those levels of the bulk generated carrier, cannot be achieved in the SnO<sub>2</sub> except by tunneling (see Figure 10). Furthermore, SnO<sub>2</sub> is a very imperfect semiconductor with many surface states within the band gap; these can probably act as efficient recombination centers for those carriers. At the other interface, mediated injection into the oxidant levels can occur, and this will be even more efficient when the overlap between the  $W_{ox}$  and intermediate levels is important. This would be one of the reasons why couples more positive than 0 vs. SCE are required to obtain a very high reduction current upon excitation. There is, however, a limit in potential, since the photoreduction efficiency decreases for couples having a potential more positive than 0.37 V vs. SCE (Figure 6) where significant recombination takes place due to the accumulation of holes at the surface. This value of 0.37 V is certainly very close to the value of the flat band potential for our H<sub>2</sub>Pc samples. The behavior for ZnPc is very similar to H<sub>2</sub>Pc except that fairly large photoreduction currents are still measured with  $E_{redox}$  around 0 V; these only drop to low levels at -0.2 V, because the intermediate levels for ZnPc are divided into two sets at 0.6 and 1.0 V above the valence band edge,<sup>13</sup> both sets participating in the mediated charge transfer.

**Doping Effect.** The addition of dopant at the phthalocyanine surface improves dramatically the dark and photoconductive properties of the dyes.<sup>10,17</sup> These two effects are certainly operative in our samples but, since the doping is only achieved at the Pc/solution interface, mostly the photoreduction currents are most enhanced and this leads to complete inversion in the action spectra under the conditions of Figure 8. Because of the acceptor properties of *o*-chloranil, some spontaneous charge transfer occurs in this layer, as suggested by ESR measurements<sup>10,15</sup>



This increase in hole concentration in the dark improves the conductivity of the film and allows a better transport and a better separation of the carriers. This slows down the bimolecular recombination of charges and improves the light response of the coating. The effect is much more pronounced for very thick samples which have higher electrical resistance (Figure 9) and for strongly absorbed wavelengths where the carriers are inhomogeneously distributed in the sample.

The second effect of doping is the improvement of the photoreduction processes even for couples around 0 V (Figure 8). Here the *o*-Chl<sup>-</sup> perhaps acts as an intermediate state to trap an exciton according to<sup>10,15</sup>



The electron injection following this process originates from the hydroquinone intermediate. Although very small amounts of dopant were used in our experiments, certainly

TABLE II

A. Photooxidation Quantum Yield for SnO<sub>2</sub>/Pc  
(BS Excitation Mode; H<sub>2</sub>Q/BQ, 10 mM;  
pH 7;  $E_{redox} \sim 50$  mV)

Pc	$d$ , Å	$10^4 \phi_{ox}$
CuPc	125	3.2
H <sub>2</sub> Pc	280	4.2
InPcCl	200	28.0

B. Photoreduction Quantum Yield for Pt/Pc  
(FS Excitation Mode; H<sub>2</sub>Q/BQ, 10 mM;  
pH 2.6;  $E_{redox} \sim 300$  mV)

Pc	film absorbance at 632.8 nm	$10^3 \phi_{red}$
H <sub>2</sub> Pc	0.83	4.2
MgPc	1.65	6.0
ZnPc	1.10	9.1

C. Photoreduction Quantum Yield for SnO<sub>2</sub>/H<sub>2</sub>Pc  
(FS Excitation Mode; H<sub>2</sub>Q/BQ, 10 mM;  
pH 2.6;  $E_{redox} \sim 300$  mV)

$d$ , Å	$10^3 \phi_{red}$	
	undoped	doped <i>o</i> -chl/ toluene
650	3.6	9.6
1400	2.6	7.6
2900	1.2	9.8

less than a monolayer coverage of the rough surface of the dye, the improvement of the photoeffects was marked. This approach deserves more attention, e.g., by use of another method of doping to achieve a more homogeneous distribution of the electron acceptor in the organic layer or with other dopants.

**Quantum Yield.** A major goal of this research is to understand the mechanism governing charge carrier generation and electron transfer in organic semiconductors to optimize various parameters for a solar cell. The efficiency of power conversion is obviously a very important parameter. However, since intermediate states are involved in the photoprocesses and the porosity of the phthalocyanine coatings allows the direct dark discharge through the film, the magnitude of the photopotential remains relatively small. Comparison of the efficiency of the dye layers is presented in terms of the photocurrent quantum yield defined as the ratio of photocurrent measured vs. the photocurrent expected for the light effectively absorbed at a given potential. The quantum yields for photocurrent production presented in Table II were measured under equivalent short circuit conditions for which the potential of the Pc electrode was solely determined by the equilibrium potential of the redox solution. As far as photooxidation is concerned, the  $\phi$  values are rather low and in the range of  $1 \times 10^{-4}$  (Table IIA); however, InPcCl yields a better photocurrent because of some stacking order in the film.<sup>4d</sup>

The photoreduction quantum yield can reach higher values, especially with fairly positive couples. This emphasizes the p-type character of layers. Very little difference was seen between H<sub>2</sub>Pc, MgPc, and ZnPc; their behavior was very similar even when the potential of the couple was changed, although their work functions and resistivities are different. However, the latter is strongly modified when the organic layer is in contact with a solution compared to vacuum. Most of our experiments dealt with H<sub>2</sub>Pc in the  $\alpha$ -form. The photoreduction currents measured with Pt as a substrate were usually larger than with SnO<sub>2</sub> and this was even more pronounced as the

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TABLE III: Efficiency of a Very Porous Pt/H<sub>2</sub>Pc Film (980 Å)<sup>a</sup>

	undoped	<i>o</i> -chloranil doped
$V_{oc}$ , mV	29.8	49.5
$I_{sc}$ , $\mu$ A	4.6	28.0
$\phi_{red}$ , %	0.76	4.6
$\eta_{red}$ , %	0.60	3.6
ff	0.37	0.33
$\eta_E$ , %	$4.3 \times 10^{-3}$	0.04

<sup>a</sup> FS excitation mode: H<sub>2</sub>Q/BQ, 10 mM; pH 1.3;  $E_{redox} \sim 380$  mV.  $V_{oc}$  is the open circuit photovoltage,  $I_{sc}$  the short circuit photocurrent;  $\phi_{red}$  the photoreduction quantum yield,  $\eta_{red}$  the photoreduction efficiency, ff the fill factor, and  $\eta_E$  the power conversion efficiency.

potential of the couple became more negative, perhaps because the contact with Pt is ohmic while the work function of SnO<sub>2</sub> is such that a barrier may occur at this contact. Furthermore, there is no spectral sensitization on platinum, since a metal electrode leads to quenching of the excited states<sup>4a</sup> and no photooxidation current competes with the photoreduction component.

Table IIC presents the influence of doping on the photoreduction quantum yield for three electrodes. These coatings were sublimed at the same rate and there was probably very similar porosity for the different layers. The strongest effect was observed for the thickest sample, which was also the least efficient one. This sample showed a rather small light exponent (cf. Figure 7) and was the most electrically resistant. The sample was particularly sensitive to doping, which improved all these character-

istics. Usually the thicker samples were more affected by doping than the thinner ones. However, the porosity of the layer also played an important role (Table III). The 980-Å Pt/H<sub>2</sub>Pc sample was found to be very porous and actual holes in the layer could be observed; the thickness given, measured by absorption spectrophotometry, is certainly not very accurate. As a result of the porosity, large dark oxidation currents were measured and an unusually low photopotential developed upon FS illumination.

Although the  $\phi_{red}$  for the undoped film was already large compared to some other electrodes, a remarkable doping effect was achieved upon *o*-chloranil treatment, and a photoreduction yield of 4.6% was the best obtained so far with our electrodes. A somewhat porous electrode appears favorable for this method of doping, since it allows penetration of the dopant solution into the film structure and probably a more uniform doping by diffusion of dopant along the grain boundaries.

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**Registry No.** ZnPc, 14320-04-8; MgPc, 1661-03-6; CuPc, 147-14-8; InPcCl, 19631-19-7; Co(bpy)<sub>3</sub><sup>2+</sup>, 15878-95-2; Co(bpy)<sub>3</sub><sup>3+</sup>, 19052-39-2; Co(*o*-phen)<sub>3</sub><sup>2+</sup>, 16788-34-4; Co(*o*-phen)<sub>3</sub><sup>3+</sup>, 18581-79-8; Co(5-nitro-*o*-phen)<sub>3</sub><sup>2+</sup>, 47882-05-3; Co(5-nitro-*o*-phen)<sub>3</sub><sup>3+</sup>, 80711-15-5; Pt, 7440-06-4; Fe, 7439-89-6; H<sub>2</sub>Pc, 574-93-6; SnO<sub>2</sub>, 18282-10-5; H<sub>2</sub>Q, 123-31-9; BQ, 106-51-4; *o*-Chl, 2435-53-2.