CHEMISTRY LETTERS, pp. 307-310, 1980. © The Chemical Society of Japan 1980

EXTRINSIC PHOTOCONDUCTION IN METALLOPORPHYRIN FILMS

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The dc photoconductance in films of metalloporphyrins has been explained by a mechanism which involves singlet exciton states followed by the interaction of these excitons with aluminum and surface impurity sites. The defect model of exponential trap distribution is useful to interpret the sublinear light dependence of the photocurrent, which is difficult to understand on the basis of exciton mechanism.

It has been found that the aluminum-porphyrin interface is photoactive, *viz.* blocking contact, in the Al/porphyrin/$[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$/Pt or Al/porphyrin/Ag cell.[1,2] The interface is best described as a metal-insulator-semiconductor diode consisting of Al-Al_2O_3-porphyrin, where the porphyrin acts as a p-type semiconductor.

In order to explain the mechanism of photogeneration of charge carriers in the porphyrin films, it is advantageous to consider the following reaction processes.[3-6]

$P_o + h\nu \rightarrow P^*$,	excitation	(1)
$P^* + X \rightarrow P^+ + e^- + X$,	extrinsic charge generation	(2)
$P^* + P^* \rightarrow P^+ + e^- + P_o$,	indirect intrinsic charge generation	(3)
$P_o + h\nu \rightarrow P^+ + e^-$,	direct intrinsic charge generation	(4)

where P_o is the ground state of the porphyrin solid, P^* a singlet free-exciton state and X aluminum and/or impurity site at surface or near-surface. Fluorescence, trapping and recombination processes are then competing reactions.

For strongly absorbed light the concentration of the singlet exciton P^* at a depth x into the film can be approximately given by,

$$N_x = \varepsilon\tau I_o exp(-\varepsilon x) \qquad (5)$$

where ε is the extinction coefficient of the porphyrin, τ the singlet exciton life time and I_o is the incident photon flux.

Hence, the rate of formation of charge carriers from exciton states will be first order in the light intensity if it involves the extrinsic charge production process or second order for the indirect intrinsic process and will be proportional to the light intensity in the direct intrinsic process. Consequently, under no recombination

Table 1. Photocurrent quantum yields with light exponents of magnesium porphyrin films in Al/porphyrin/Ag sandwich cells.

Compound	λ_{max} (nm)	Quantum yield	Light exponent
MgTPP	450	0.10	0.92
MgOEP	425	0.04	0.88
Mg-Mg-7	415	0.021	0.93
Mg-H_2-7	430	0.0045	0.88
MgMPDHE	425	0.02	0.89
MgMPDOE	425	0.00044	0.89
Chl-a	445	0.0024	0.86
Chl-b	475	0.00064	0.87

Abbreviations used: TPP tetraphenylporphyrin, OEP octaethylporphyrin, Mg-Mg-7 and Mg-H_2-7 cofacial diporphyrins with 7 atoms in the covalent linking chain,[7] MPDHE mesoporphyrin dihexylester, MPDOE mesoporphyrin dioctadecylester and Chl chlorophyll. Films of porphyrins were prepared by rapid solution evaporation. Quantum yield is defined as electrons produced per photon absorbed by the porphyrin film at low light intensities (about 0.1 mW/dm^2).

limiting conditions the photocurrents vary as the first or second power of the incident light intensity for the extrinsic or indirect intrinsic processes. On the contrary, in the presence of recombination the light exponent will be 0.5 or 1.0 for the extrinsic surface production or the intrinsic bimolecular production.[4,5] The exponents obtained for some 36 metalloporphyrin films studied range between about 0.8 and 1.0 (*e.g.* see Table 1). This result shows two possibilities of the processes (2) and (3) in the absence and presence of recombination, respectively. However, the photoconduction in the porphyrin films seems to be attributed to the extrinsic process Eq. (2) as inferred from the fact that the Al-porphyrin interface is photoactive.[1] In other words, charge carriers are formed at the aluminum-porphyrin interface as a result of exciton-aluminum interactions.[8] The contribution of impurity, *e.g.* O_2, to the charge generation in the extrinsic process should be also taken into consideration. The photocurrents of porphyrin films pre-treated with I_2 vapor, which is the electron acceptor as well as O_2, become about 30 % more larger than those without the pre-treatment. Such an adsorption effect of the electron acceptors suggests that the porphyrins behave as p-type semiconductors. The sublinear differeces of light exponents from unity can be explained by a defect model.

According to Rose's theory[9] for the exponential trap distribution we obtain for the intensity dependence of the hole concentration of p-type semiconductor.

$$C_h \propto g^{\frac{T_c}{T_c + T}} \tag{6}$$

where g is the rate of generation of holes and T_c the parameter characterizing the exponential trap distribution.

In the ohmic range of dark current,[10] where $g \propto I_o$, Eq. (6) will be rewritten by,

$$i_p \propto I_o^{\frac{T_c}{T_c + T}} \tag{7}$$

where i_p is the photocurrent.

The usual condition of $T_c > T$ explains the fact that $0.8 < \gamma < 1.0$ for the metalloporphyrins, where γ is the light exponent $T_c/(T_c+T)$.

The quantum efficiencies for the charge carrier formation processes (2)-(4) with porphyrin films, which absorb all of the incident light, are given by,[5)]

$$\phi_2 \fallingdotseq k_2 \tau \varepsilon x_o C_x \cdot \tag{8}$$

$$\phi_3 = \frac{1}{2} k_3 I_o \tau^2 \varepsilon \tag{9}$$

$$\phi_4 = \frac{k_4}{\varepsilon} \tag{10}$$

where k_i is the rate constant of reactions (i), where i=2,3 or 4, x_o the effective thickness of the surface in which the exciton created will return to the surface during its life and C_x the concentration of X.

If recombination and trapping effects are small, the spectral dependence of extrinsic or indirect intrinsic photocurrents should closely follow the optical absorption curve, while the direct intrinsic process should vary inversely. However, slight shifts of the absorbed peaks to longer wavelength have been often observed in the action spectra (Fig. 1). Action spectra were corrected for both the variation of photon flux with wavelength of the incident light source and the transmission of the aluminum film. In a typical case, in which the surface recombination process is dominant compared with the volume recombination, carriers produced with strong absorption of light, where ε is large, in a thin layer recombine rapidly and contribute but little to the conductivity. Only for carriers produced by weakly absorbed light with small ε at greater distance from its surface the slower volume recombination becomes effective.[11,12)] Thus, the shifts of the absorption peaks to longer wavelength may be due to a little surface recombination of charge carriers.[13)] The adsorbed electron acceptors such as O_2 and I_2 sometimes result in such an anticorrelation attributed to an increased surface recombination.

The dependence of photocurrent for the Al/porphyrin/Ag cell on the polarity of

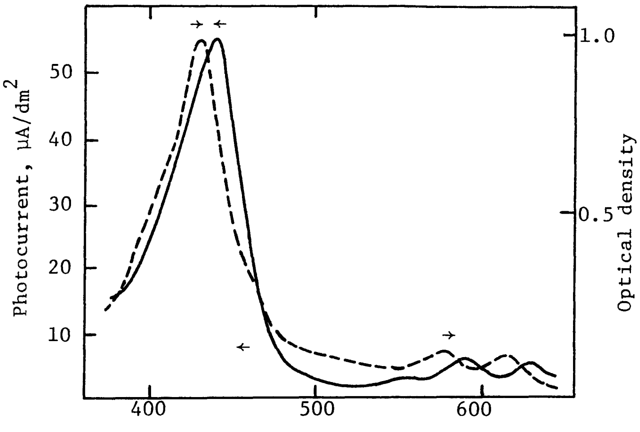

Fig. 1 Absorption and action spectra of the film of magnesiumtetra(*n*-propyl)porphyrin produced by sublimation.

The illumination was done through the aluminum in the Al/porphyrin/Ag sandwich cell. The thickness of the porphyrin film was *ca.* 100 nm and films of Al and Ag were *ca.* 30 nm thick.

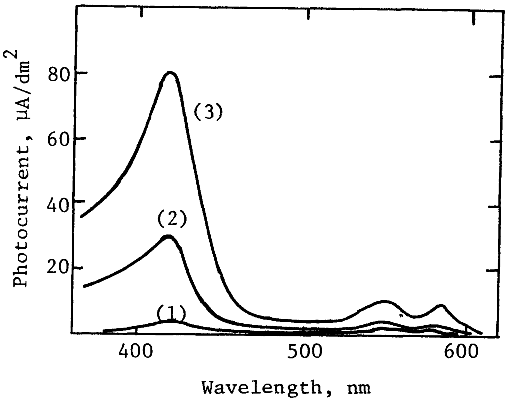

Fig. 2 Voltage dependences of action spectra for the Al/magnesium mesoporphyrin dihexylester/Ag cell.

The film of MgMPDHE was prepared by rapid solution evaporation. Curve (1) with a negative voltage (-0.7 V) applied to the Al electrode, (2) zero voltage, and (3) positive voltage (+0.7 V).

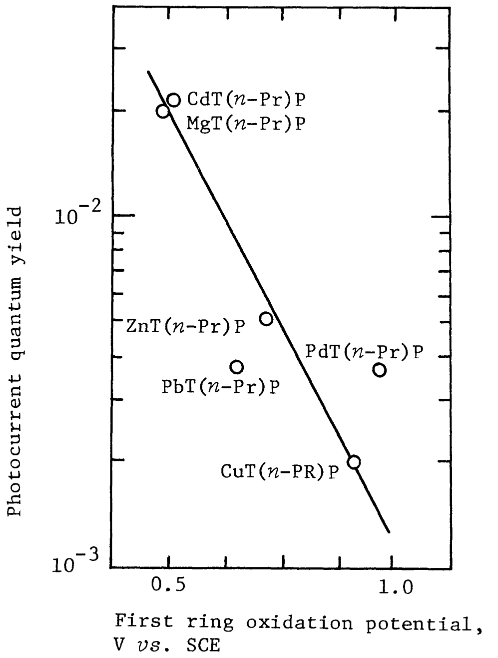

Fig. 3 Semilogarithmic plots of photocurrent quantum yields *vs.* first ring oxidation potentials of tetra(n-propyl)porphyrins. Al/porphyrin/$[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$/Pt cells were used, where the porphyrin films were prepared by sublimation and *ca.* 100 nm thick. Films of Al and Ag were *ca.* 30 nm thick.

the illuminated electrode coincides with that of a p-type semiconductor sandwiched between metals such as Al and Ag. Therefore, the voltage dependence observed can be attributed to that electrons which are generated near the surface are more deeply trapped than are the surface-generated holes.

We have found that for a given ligand quantum yields of the photocurrents paralelled the first ring oxidation potentials of the porphyrins[1,2] (Fig. 3). Namely, the more easily oxidized porphyrins exhibted the higher quantum yields. At this time it is difficult to understand completely the relation between the quantum yield and oxidation potential. According to Eq. (8), ϕ_2 will be in direct proportion to the product of k_2 and τ because of $x_o = \varepsilon^{-1}$ for large ε, as C_x is assumed to be almost constant. The value of k_2 probably correlates exponentially with the oxidation potential of P^* and with that of P, either. Hence, the photocurrent quantum yields may be varied exponentially with oxidation potentials of the porphyrins, if the variation in τ are small.

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(Received December 17, 1979)