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PHOTOELECTROCHEMICAL STUDY OF REVERSIBLE CHARGE SEPARATION IN HYDRATED MAGNESIUM PORPHYRIN AGGREGATES

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A reversible photogalvanic effect was observed with a Pt electrode coated with an aggregate of a hydrated magnesium porphyrin. Quantum efficiencies at each wavelength were obtained from the spectral dependence of the photocurrent. A charge separation responsible for the observed photocurrent was discussed comparatively with the chlorophyll system.

For the solar conversion and the fundamental understanding of photosynthesis, it is extremely important to develop chemical systems which give rise to a charge separation upon irradiation with red light. There appeared so far two possible systems which undergo charge separations with red light: One is the chlorophyll itself for in vitro solar conversion, and the other is metal porphyrins and phthalocyanine complexes for the model systems of the chlorophyll. Several groups[1-4] recently demonstrated electrochemically that chlorophyll can convert light energy into electricity. Calvin[5] was the first to use phthalocyanine complexes for the model study of chlorophyll. Wang[6] did some pioneering work on the photogalvanic effect of zinc porphyrin. In order to develop Wang's research, that is, to apply metal porphyrins for the comparative study of the chlorophyll, it seems most appropriate to use magnesium porphyrins rather than other types of porphyrins. Furthermore, it has recently been proposed[1,2] that chlorophyll-H_2O aggregates play a central role for the charge separation and the elementary process of photosynthesis.

In view of the above consideration, we have tried to use a hydrated magnesium porphyrin for the study of charge separation with red light. It will be shown that an aggregate of the hydrated magnesium porphyrin which is insoluble in water can give pronounced photovoltage and photocurrent just by putting aggregates of this compound onto platinum electrodes followed by irradiation of red light.

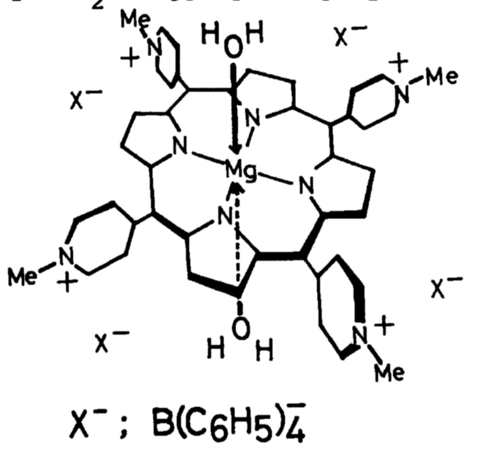

Fig. 1 Schematic structure of meso-tetrakis-(4-N-methylpyridinium)-porphine -magnesium-tetrakis-tetraphenylborate-tetrahydrates.

The compound used is meso-tetrakis-(4-N-methylpyridinium)porphine-magnesium -tetrakis-tetraphenylborate-tetrahydrates: $MgMe_4PyP(B\phi_4)_4 4H_2O$, abbreviated hereafter as MgTMePyP(see Fig. 1). The synthetic procedure of this compound is described elsewhere7). About 6.0×10^{15} MgTMePyP molecules were deposited on a Pt electrode($0.20\ cm^2$ in area) by allowing 20μl of a 5.0×10^{-4} M solution of MgTMePyP in acetonitrile to evaporate on the surface of the electrode. The Pt-MgTMePyP electrode was immersed in a 0.1 M aqueous solution of tetraethylammonium perchlorate(TEAP). The counter electrode(the other half-cell) was a silver coil which is free from MgTMePyP. Quinhydrone($Q : H_2Q = 1 : 1$)(saturated, pH 6.8) was occasionary added besides TEAP(supporting electrolyte) in solution. In this case, a platinum wire coil was used as a counter electrode instead of a silver wire. A single compartment cell was used for most of the experiments. Sample solutions were degassed by argon bubbling. Photocurrents and photovoltages were measured with electrometers Model TR-84M, vibrating-reed, and Model TR-8651 both of Takeda Riken Co. The action spectra of the observed photogalvanic effect was measured with a 750 W tungsten lamp and a Model 338607 grating monochrometer of Bansch & Lomb Co. The spectral distribution of the light source and the actual light intensities on the electrode surface were determined with a silicon photocell Model S642 from Hamamatsu TV Co.

The two types of photogalvanic cells described in the experimental section are assumed to be written as8)

$$\text{Pt, MgTMePyP} \mid \text{MgTMePyP}^{+}, \text{MgTMePyP}^{-} \mid \text{TEAP} \mid \text{AgClO}_4 \mid \text{Ag} \qquad (1)$$

$$\text{Pt, MgTMePyP} \mid \text{MgTMePyP}^{+}, \text{MgTMePyP}^{-} \mid \text{TEAP} \mid \text{H}_2\text{Q} \mid \text{Q, Pt} \qquad (2)$$

The observed photopotential(E_p) at the Pt-MgTMePyP electrode was negative of about 35 mV for the cell (1) at 450 nm with a light intensity of $140 \times 10^{-6}\ W/cm^2$ at the electrode surface. It should be noted in the case of the cell (2), the E_p decreased down to about 1 mV. The negative E_p in the present case indicates that the direction of the photocurrent(i_p) is from the counter electrode to the Pt-MgTMePyP electrode, i.e., the electron is transferred from the Pt -MgTMePyP electrode to the counter electrode. Typical tracings of the i_p are reproduced in Figs. 2AB. With the galvanic cell of (1), a simple steady state current was observed only when the light is on(Fig. 2A). The magnitude of the i_p at 450 nm is $1.73 \times 10^{-8}\ A/cm^2$ and is kept constant even standing for several hours. This i_p is increased by about 50 % with increase in the concentration of dissolved oxygen(up to saturation) or proton ions(up to pH 2). However, in the latter case, the photodecomposition of MgTMePyP starts to occur at low pH regions($<$ pH 2). With the galvanic cell of (2), an immediate increase in i_p was observed followed by the gradual decrease of it until some stationary values which are similar in magnitude to the i_p in the cell (1). When the light is turned off, a transient displacement current9) opposite in sign to i_p was observed(Fig. 2B). The i_p was found to be

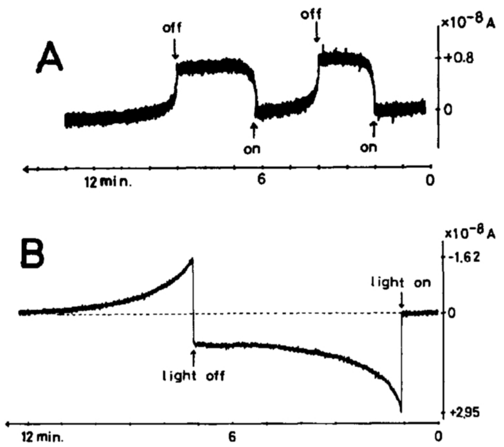

Fig. 2 Photocurrent observed at the Pt-MgTMePyP electrode(see Text).
Wavelength; 450 nm, Light intensity; 140 x 10^{-6} W/cm^2 at the electrode surface.
A and B : For the cells (1) and (2), respectively(see Text).

linear with the light intensity for both cells (1) and (2). These behaviors of the photocurrent are reproducible with the light cycle, indicating the reversible charge separation in the Pt-MgTMePyP electrode. The reason for the different i_p vs. time characteristics between cells(1) and (2) is not known at present.

The spectral dependence of the photocurrent was distinct, from which the apparent quantum efficiencies, given by the ratio of electrons released per incident photons, of the cells (1) and (2) are calculated as shown in Figs. 3AB. Also shown in Figs. 3AB is the absorption spectra of MgTMePyP aggregate deposited on a quartz plate[10)], which is quite different from its monomer spectrum[11)]. The correspondence between the absorption spectrum and the spectral dependence of the photogalvanic quantum efficiency in Fig. 3 implies that the excited molecular aggregates of MgTMePyP itself contributes to the photogalvanic effect or the charge separation in the present system.

Actual quantum efficiencies, given by the ratio of electrons released per photon absorbed, are obtained as 1.2(2.8), 1.0(3.8), and 1.5(7.3) % at 450, 575, and 625 nm, respectively for the galvanic cells (1) and (2)[12)](in parenthesis). From absorption measurements of MgTMePyP films on a transparent quartz plate, it is estimated that about 5.7, 2.0, and 1.0 % of the incident light flux at 450, 575, and 625 nm, respectively were absorbed by the MgTMePyP. It appears reasonable to expect that reflectance loss can be reduced by making more homogeneous coat of MgTMePyP on the Pt electrode.

According to Fong and Winograd[1)], a positive photopotential at the Pt-chlorophyll a electrode which they observed is accounted for in terms of the photovoltaic properties of p-type semiconductor binary compounds. Under illumination, the photoactive hydrated chlorophyll a(Chl a) aggregate is presumably excited to a charge transfer state that may be considered to be a binary compound consisting of Chl a^+ and Chl a^-. If one assumes a similar mechanism for the Pt-MgTMePyP electrode, the formation of $MgTMePyP^+$ and $MgTMePyP^-$ is suggested. The observed negative photopotential at the Pt-MgTMePyP electrode implies that the MgTMePyP aggregate in the present case behaves as an n-type semiconductor. The proposed mechanism of the formation of $MgTMePyP^+$ and $MgTMePyP^-$ is supported by the observation of an ESR signal with a g value of 2.0025 and a linewidth of 7.0 Gauss from MgTMePyP upon irradiation with red light, which is indicative of the reversible production of

Fig. 3 Action spectra of the photogalvanic effect at the Pt-MgTMePyP electrode and the absorption spectra of the MgTMePyP aggregate deposited on a quartz plate(see Text). A and B: For the cells(1) and (2), respectively(see Text).

MgTMePyP$^+$ and/or MgTMePyP$^-$ during the light cycle.

Finally, it is interesting to point out the photogalvanic effect with a platinum electrode coated with non-hydrated tetrapyridylporphine-magnesium(Pt-MgTPyP) was one order of magnitude smaller than that of the present Pt-MgTMePyP electrode$^{11)}$. In conclusion, the experimental system reported here appears to have excellent characteristics for i) the comparative study of the chlorophyll-H$_2$O aggregate from the view point of the fundamental understanding of the photosynthesis, and ii) the red light conversion under ordinary experimental conditions, because this particular compound of MgTMePyP can preserve activity against high temperatures up to 115° C, and long(e.g., 1 year) standing in air atmosphere.

Further study is in progress concerning the details of the mechanism and possible applications of the present system.

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10) The MgTMePyP was deposited on a inner wall of a quartz cuvette in the same way but twice as thick as on the Pt electrode. Then, the quartz cuvette was filled with water prior to the absorption measurement of the MgTMePyP aggregate.
11) T. Yamamura and Y. Umezawa, (unpublished work).
12) The maximum value of the transient photocurrent(see Fig. 2B) was used to calculate the quantum efficiency.

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