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PHOTO-INDUCED CHARGE SEPARATION WITH RED LIGHT IN THE HYDRATED AGGREGATES OF A SURFACE-ACTIVE MAGNESIUM PORPHYRIN

Takeshi YAMAMURA
Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A reversible charge separation induced by the red light illumination was achieved by using the hydrated powder and the hydrated reversed micellar colloid of a cationic surface-active magnesium porphyrin. The effect of the hydration was studied.

For the use of solar energy, it is important to form the system which enables the reversible charge separation accompanied with the thermal transfer of the separated charges by use of red light. According to current knowledge on the energy transfer and the electron transfer in the primary step of photosynthesis,1) hydrated aggregates of magnesium porphyrin is significant as the light harvesting system. This letter reports an example of such system, the powder and the micellar colloid of a hydrated surface-active magnesium porphyrin.

The compound used is meso-tetrakis(4-N-stearylpyridinium)porphinemagnesium tetraiodide monohydrate (abb. $MgSt_4PyPI_4 \cdot H_2O$; Fig. 1). This surfactant forms the reversed micellar colloids in some organic solvents.2) In chloroform, the B-band absorption maximum of the porphyrin shifts from 470 nm in the concentration range of $\sim 10^{-7}$ M to 410 nm above the critical micelle concentration (3.5×10^{-3} M). Since the 470 nm maximum obeys Lambert-Beer's law with the $k = 1.8 \times 10^{+5}\ M^{-1}cm^{-1}$ in the range of $\sim 10^{-7}$ M, the 470 nm species is assigned to be the monomer of the compound. From this assignment, and, from the large blue shift, it is concluded that the porphyrin chromophores in the micelle are accumulated columnarly with the layer distance of 8.2 Å, on the basis of the exciton theory of Kasha for parallel aggregates.3) (The Q-band absorption muximum shifts from 679 nm to 631 nm, and the calculation gives 8.3 Å as the layer distance.) The powder of $MgSt_4PyPI_4 \cdot H_2O$ also has the same molecular stack as the micelle, since it shows the B-band λmax at 410 nm.

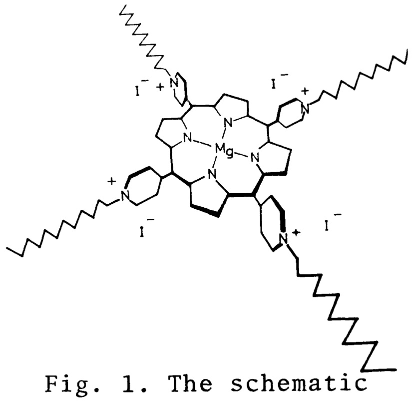

Fig. 1. The schematic structure of $MgSt_4PyPI_4$.

(Experimental): The dry compound, $MgSt_4PyPI_4 \cdot H_2O$, absorbs water under atmospheric pressure when the air is saturated with water. By using this, various compound from monohydrate to heptahydrate were prepared. The degree of hydration was determined by IR method using o-phenanthroline monohydrate as a standard in the dimethylsulfoxide-dichloromethane (1 : 20) solution. The ESR experiments were carried out both for the micellar solutions (1.3×10^{-2} M) and the powders (52 mg) of these hydrates in capillaries of 3 mm or 5 mm in dia-

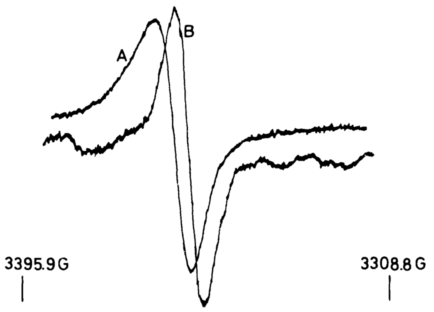

Fig. 2 The ESR signals for the micelles --- (A), and the powders --- (B).

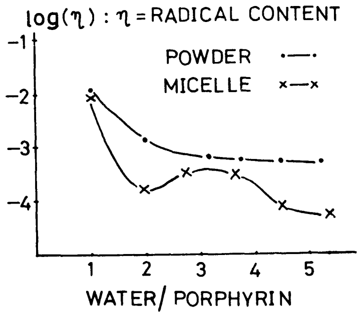

Fig. 3 The dark radical contents for the micelles and the powders with hydration number as abscissa.

meter. Light from a high pressure mercury lamp was focused on the capillaries through color filters and condensing lenses. The measurements were conducted under argon atmosphere. Pure chloroform was used as a dispersing agent for the micelles.

(Results and discussion) : The micelles and the powders have dark radicals, which are formed thermally in the dark. These radicals are also produced when the aggregates are exposed to red light.

Dark radicals $MgSt_4PyPI_4 \cdot nH_2O$ (n = 1~ 7) gives no ESR signals both in the dark and under illumination in a polar solvent such as dimethylformamide, in which the porphyrin is monomeric (^{1}H-NMR spectrum). In the aggregated states, however, the compounds indicate the presence of some unpaired spins. The signals of the micellar colloids are an unsymmetric singlet having g(apparent) = 2.0013 and ΔH(peak-to-peak linewidth) = 9 G (Fig. 2-A). The powders give a more complicated signal, in which a strong Gaussian singlet (g = 2.0032, ΔH = 6.5 G) is accompanied by a satellite having 17~ 19 hyperfine structure (Fig. 2-B). Both singlets of the micelles and the powders are influenced by hydration (Fig. 3).

Photoradicals The micelles and the powders of the wet samples ($MgSt_4PyPI_4 \cdot nH_2O$, where n = 2~ 7) are sensitive to red light ($\lambda \gtrsim 550$ nm), although those of the dry compound ($MgSt_4PyPI_4 \cdot H_2O$) are insensitive to the light. The ESR absorptions of the wet micelles and the wet powders increase under red light without changing their g-values, linewidths and lineshapes. Then, they recover the intrinsic dark levels in the dark. Therefore, the micelles and the powders generate reversibly the respective photoradicals, which are the same species as the dark ones. The responses of the micelles to red light are rapid ($\lesssim$ 20 sec.), compared with those of the powders ($\gtrsim$ several min.). These light induced charge separations depend on the degree of hydration (Fig. 4). In the powder samples, the trihydrate is the best charge separator under illumination (4-a). As for the micelles, the di- or trihydrate is the best one after 1 or 7 days' equilibration time (4-d and 4-c respectively), although the pentahydrate is the best soon after the preparation of the micelle (4-b). The curve 4-a for the powders seems to be composed of the three curves for the micelles. In view of this, the mechanism of the photo-induced charge separation in the micelles and that in the powders are almost identical.

Signal species The ESR signals originate from separated charges. Both singlets from the powders and the micelles are temperature dependent in the dark. The relative ESR absorption (I) as a function of temperature (T) obeys the equation: $\ln(I \cdot T) = C - \Delta Ep/RT$, where $\Delta Ep = 0.065$ eV for the powder of trihydrate in argon (T = 183 ~ 300 K). This result leads to the conclusion that there exists the magnetic singlet-triplet excitation[4)] in the tightly bound radical ion pairs which are effectively trapped in the array of the neutral molecules with the help of the water, or exists the thermal excitation of the non-bound radical anion and cation whose doublets are accidentally overlapped having almost the same g values, lineshapes and linewidths. The validities of the two mechanisms are judged by the photo-excitation at low temperature (Fig. 5). At liq. N_2 temperature, the signal intensity of the wet micelles increases strongly upon irradiation with red light. However, it can not recover to the original dark level at that temperature when the light is cut off. The dark level is recovered by the annealing at room temperature. This result is explained by the second mechanism which involves the charge separation accompanied by the thermal transfer of the hopping electrons and holes. The lineshapes of the micellar samples are not symmetric and the g values of them slightly shift from that of free radicals. These are accounted for by the weak magnetic interaction between the anion radicals and the cation radicals which are confined in the colloids. Since the radicals lie on the stack of the porphyrin ring-water system as is shown below, they should be the anion and the cation radicals of the magnesium porphyrin. Considering that the primary electron donor (P-700) of the photosynthetic membrane of green plants is recognized to be the dimer of hydrated chlorophyll-a,[1), 5)] it is interesting to know whether the cation radical in our system is dimer or not. Further investigations on the radical species are continued now.

Active structure The iodide ion I^- does not participate directly in the charge separation, since the similar photo-induced charge separations are observed for the hydrated powders of the anion substituted compounds (for example, the perchlorate). The pyridinium moiety also is independent of the charge separation, because the hydrated reversed micelle and the powder of stearylpyridinium iodide does not show neither dark nor light signals even when fairly large quantity of the surface-active porphyrin is dissolved monomerically in the aggregate as the sensitizer. Therefore, the $(\text{magnesiumporphyrin-water}_n)_m$ array, where n is the hydration number and m the association number, is essential for the appearance of the dark radicals and the photoradicals. The dark radical content in the hydrated powders seems to be too large (especially for the monohydrate), considering that the array is fundamentally a neutral π-layer system. This anomaly is perhaps due to that the direct contact interaction between the two waters of the $(\text{porphyrin-water})_2$ unit in

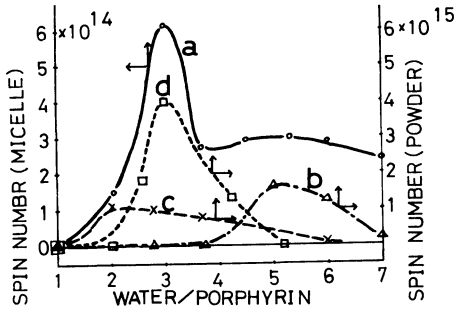

Fig. 4 The amount of the photoradicals with hydration number n: a -- for the powders; b, c, d, -- for the micelles.

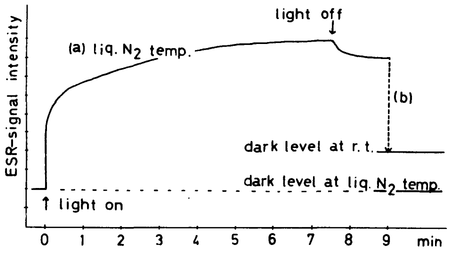

Fig. 5 The rise and decay curve at liq. N_2 temperature -- (A), the annealing at room temperature -- (B).

the columnar layer triggers the thermal electron transfer. On the other hand, the content in the equilibrated micelles is not so large as that in the powders. The discrepancy is accounted for by the difference of the molecular stack between in the powders and the micelles. In the former, the vertical stratum of the porphyrin is kept, since the B-band absorption maxima are all positioned at 410 nm. In the latter, however, the maximum shifts from 410 nm of the monohydrate to 470 nm of the hexahydrate. Therefore, in the equilibrated micelles, the stack is displaced from the vertical one to other ones with the increase of hydration. The porphyrin of the equilibrated micelle is sometimes demetalated rapidly to the metal free base in the dark. This reaction proceeds particularly in the trihydrate. Since the demetalation means the acidic environment around the porphyrin, the (porphyrin-water$_3$)$_m$ array is liable to yield H^+ near the magnesium atom. Therefore, in view of the fact that the metal free base is inactive to red light, three possible mechanisms can be postulated for the prominent charge separation in the trihydrate under light. (1) The H^+ near the porphyrin might promote the charge separation under light with its electric field. (2) The metal free base itself contributes to the photo-induced charge separation. For example, as one of the conjugated heterocycles, the metal free base might adiabatically produce the local electric field near the neighboring magnesium porphyrin by attracting H^+ from the intercalated water when it is exposed to light.6) Or, the metal free porphyrin might become the primary acceptor of the electron from the adjacent excited magnesium porphyrin. (3) The separation under light is promoted by the local electric field due to the proton transfer resonance between the ligand water and the water ligated to the anion I^-. As for the non-equilibrated micelles (see curve 4-b), they still keep the vertical stratum having the absorption maxima at 410 nm, and are not demetalated yet. Therefore, another mechanism is proposed for their photo-behavior. In general, the waters intercalated into the layer are perhaps operative to the stabilization and the activation of the thermal and the photo-induced CT state by changing their orientation and hydrogenbonds. This idea based on the "conformon" theory7) seems to be supported by the result that the photo-response of the powders becomes rapid with the increase of the hydration.

Triplet From exciton theory, the columnar stack of the porphyrin is effective for the trap of triplet energy.3) In practice, the fluorescence of the compound in dilute chloroform solution ($\sim 10^{-5}$M) is quenched, when the micelle is formed by adding hexane to the solution. Furthermore, the efficiency of the charge separation in air is lower than 1/3 of that in argon. Thus, in view of the excellent quantum efficiency, the photo-induced charge separation takes place via triplet.

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