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ARTIFICIAL PHOTOSYNTHESIS SYSTEM OF BACTERIA TYPE

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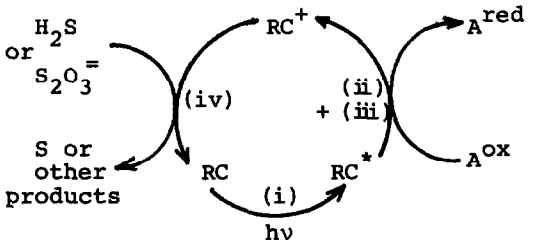
Completely artificial system was constructed to successfully mimic the photoreaction of *bacteria photosynthesis* by using a liquid membrane functionalized with n-hexylviologen. This process combined with the CO_2 fixation (see Tabushi et al., Nature, 256, 60 (1975)) may give a complete artificial photosynthesis system.

Since the solar energy conversion has absorbed special attention of chemists, many attempts have been done to construct an appropriate artificial photosynthesis system of functionalized molecules on the similar principle to plant or bacteria photosynthesis.[1,2] To mimic plant or bacteria photosynthesis, following processes should be involved:

i) Photon absorption which may be followed by the energy transfer, ii) charge separation of excited reaction centre to produce the "oxidation element" and the "reduction element" (mostly electron), iii) fixation of the "reduction element" by use of an electron acceptor (such as flavin, NAD, or finally, CO_2) at the "reduction end" after successive electron transports if necessary, iv) fixation of the "oxidation element" by use of an electron donor (such as H_2O, H_2S, $Na_2S_2O_3$, etc.) at the "oxidation end" after successive oxidation element transports if necessary.

Now the authors wish to report that the least necessary sequence of reactions involved in the bacteria photosynthesis (1) was completely reconstructed by use of appropriate artificial (not naturally occuring) compounds. So many artificial "photosynthesis models"[1,2] (often fragmental)[3] have been proposed in these years where the major problems unsolved were: a) Serious discrepancy between the model mechanism and the mechanism of the real photosynthesis, b)

difficulties of obtaining A^{red} in a directly utilizable form and in a large quantity, c) insufficient stability of a reaction centre model under the "turn-over" condition, and d) low quantum yield of A^{red}.



(1)

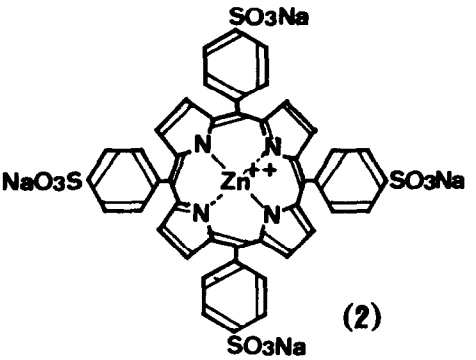
A^{ox}: electron acceptor such as NAD

RC: reaction centre

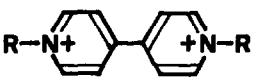
Probably because of these difficulties, the whole plant or bacteria photosynthesis process has seldom been successfully reconstructed[4] by use of totally artificial compounds except for a few examples of complex system, the function of which components are not well understood.

In our present model, the "reduction element" was successfully fixed in a utilizable form and the "oxidation element" was destroyed very effectively by reductants used in the bacteria photosynthesis (H_2S, $Na_2S_2O_3$, etc.). We have used a liquid membrane system in order to separate and insulate efficiently the "oxidation element" from the "reduction element", otherwise any nonsense "shortcut" recombination reaction between them may take place, which, markedly reduces the quantum yield. Our present liquid membrane system consists of two aqueous phases, I (6 ml) and III (5 ml) together with 25 ml of an ethylene chloride phase, II, inserted between the two aqueous phases. In aqueous phase I, following functional molecules are dissolved: $Zn^{++}T_{SO_3Na}PP$ (abbreviation of Zn^{++} complex of sodium meso-tetraphenylporphyrin-tetra-p-sulfonate) 0.36 mM (**2**), CTAB (abbreviation of cetyltrimethylammonium bromide) 10 mM, C_6V^{++} (abbreviation of N,N'-di-n-hexylviologen) 10 mM (**3a**) and an appropriate electron donor such as $Na_2S_2O_3$ (100 mM). In aqueous phase III buffered at pH 4.5 with 67 mM of KH_2PO_4, such an electron acceptor as FMN (abbreviation of flavin mononucleotide) (0.088 mM) was dissolved. This liquid membrane system was irradiated only at the agitated aqueous phase I above 410 nm by use of a glass filter. Electron was transported and fixed in a form of FMNH in aqueous phase III (FMNH 0.065 mM after the 360 min irradiation), from which FMN could be almost quanti-

tatively regenerated on treatment with oxygen, demonstrating that FMN can be used repeatedly for the electron fixation. Most of $Zn^{++}T_{SO_3Na}PP$ was kept unchanged after the irradiation, indicating that the ratio FMNH formed/$Zn^{++}T_{SO_3Na}PP$ consumed, was high. To a marked contrast to the present successful turn-over, the irradiation in the presence of EDTA, often used as an electron donor, accompanied by a considerable irreversible decomposition of $Zn^{++}T_{SO_3Na}PP$.



(2)

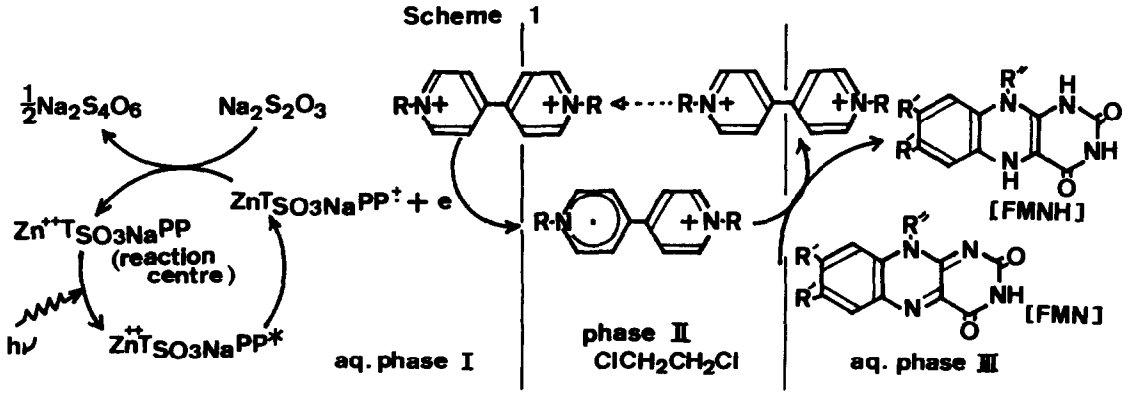


(3) a; R= n-C6H13
b; R= n-C18H37

In the present bacteria photosynthesis model, following electron donors and acceptors were successfully used —— donor; $Na_2S_2O_3$, H_2S and ascorbic acid, acceptor; FMN and anthraquinonedisulfonate.

The present reaction pathway was concluded to be (i) the photon absorption followed by the charge separation of the reaction centre, $Zn^{++}T_{SO_3Na}PP$ (ii) the electron transport from the reaction centre to the electron transporter, C_6V^{++}, which is present both in organic and in aqueous phase to form viologen radical, $C_6V^{+\cdot}$, the one electron reduced state of viologen in the aqueous phase I (iii) the one-sided phase transfer of $C_6V^{+\cdot}$, which is less hydrophilic than C_6V^{++}, from aqueous phase I to the organic phase II. (iv) The reduction of the oxidation element, $ZnT_{SO_3Na}PP^{+\cdot}$, with an electron donor (v) the electron transport from $C_6V^{+\cdot}$ to an electron acceptor. The whole reaction scheme is shown in Scheme 1.

Scheme 1



To ascertain the elementary processes described above to take place, separate two phase systems were investigated. When the two phase system, I + II was irradiated for 1/2 hr the formation of $C_6V^{+\cdot}$ up to 0.12 mM was observed by electronic spectrum and $C_6V^{+\cdot}$ was rapidly and completely destroyed by bubbling air to regenerate C_6V^{++} almost quantitatively within 1 min. In the other two phase system, II + III $C_6V^{+\cdot}$ readily reduced FMN to give FMNH quantitatively. Therefore, the electron transporting role of C_6V^{++} is evident. According to our preliminary results, the liquid membrane can also be replaced by the bilayer membrane functionalized by electron transporting detergent $C_{18}V^{++}$ (**3b**).[5]

The significant characteristics of the present bacteria model system are as follows; (1) successful accumulation of readily utilizable reduced material, (2) efficient catalytic cycle, (3) clear function (and mechanism) of every component and its close similarity to real bacteria photosynthesis (4) wide applicability of the system by appropriate choice of an electron donor, an electron acceptor, a surfactant or a phase transfer reagent, an electron transporting material, a reaction centre and their possible combination.

REFERENCES AND NOTES

1. See review, for example, M. Calvin, Acc. Chem. Res., **11**, 369 (1978).
2. (a) G. M. Brown, B. S. Brunschwig, C. Creutz, J. F. Endicott, and N. Sutin, J. Am. Chem. Soc., **101**, 1298 (1979); (b) J.-M. Lehn and J.-P. Sauvage, Nouv. J. Chim., 1, 449 (1977); and references therein.
3. (a) CO_2 fixation model of the bacteria type: T. Nakajima, Y. Yabushita, and I. Tabushi, Nature, **256**, 60 (1975); (b) oxidation end model of the plant type: I. Tabushi and S. Kojo, Tetrahedron Letters, 1577 (1974); (c) I. Tabushi and S. Kojo, ibid., 305 (1977).
4. See the following paper as a typical successful example, J. J. Grimaldi, S. Boileau, and J.-M. Lehn, Nature, 265, 229 (1977); J.-M. Lehn, J.-P. Sauvage, and R. Ziessel, Nouv. J. Chim., 3, 423 (1979).
5. See bilayer membrane functionalized with porphyrin-Mn^{IV}, I. Tabushi and M. Funakura, J. Am. Chem. Soc., **98**, 4684 (1976).

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