Photoinduced Hydrogen Evolution with a Viologen-linked Porphyrin

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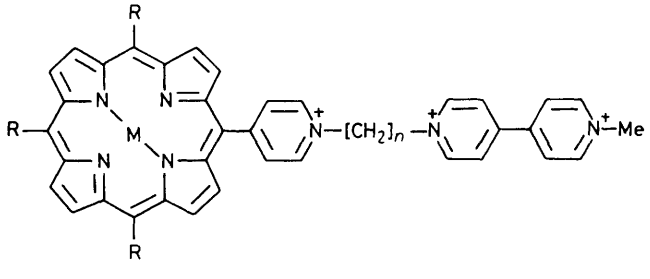
Compounds containing a viologen linked to a porphyrin *via* a number (n = 2—6) of methylene groups were used in photoinduced hydrogen evolution; hydrogen evolution was observed under steady state irradiation when n = 2.

Photoinduced hydrogen evolution systems containing an electron donor, a photosensitizer, an electron carrier, and a catalyst have been studied extensively. Porphyrins and methyl viologen were widely used as a photosensitizer and an electron carrier, respectively. In this work viologen-linked porphyrins were synthesized, since they may take part as both a photosensitizer and an electron carrier in the same molecule, and these compounds were applied to photoinduced hydrogen evolution.

The viologen linked porphyrins (**1**) and (**2**) were synthesized as follows. The starting material, 5-(4-pyridyl)-10,15,20-tritolylporphyrin (PyTP), was synthesized according to the literature.[1] PyTP was quaternized with a 200—400 fold molar excess amount of α,ω-dibromoalkane in boiling toluene. The quaternized porphyrin and a 100—200 fold molar excess amount of *N*-methyl-4,4′-bipyridyl iodide was refluxed in MeOH. For the synthesis of the zinc complexes, the following methods were used. In the first method zinc(II) 5-(4-pyridyl)10,15,20-tritolyporphyrin (ZnPyTP) was used as a starting material. In the second method (**1**) was refluxed with $ZnCl_2$ in EtOH. The final products were recrystallized from EtOH–H_2O.

Photoinduced hydrogen evolution was carried out with (**2**), n = 2—6, under steady state irradiation (200 W tungsten lamp). A sample solution containing NADPH (electron donor), (**2**) (in 10 vol% Triton X-100), and a catalyst (platinum colloid or hydrogenase)† was deaerated by freeze–pump–thaw cycles. The dependence of the amount of hydrogen evolved on the irradiation time is shown in Figure 1. In the case of (**2**), n = 2, hydrogen evolution was observed when platinum colloid or hydrogenase was used as a catalyst.

For (**2**), n = 3—6, no hydrogen evolution was observed even after 3 h irradiation. This shows that only (**2**), n = 2,



R = tolyl
n = 2—6

(**1**) M = 2H
(**2**) M = Zn

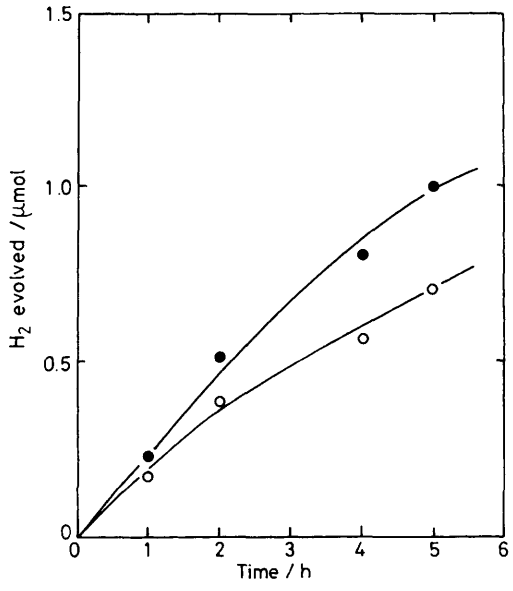


Figure 1. Photoinduced hydrogen evolution with the system containing NADPH (3.0 × 10^{-6} mol), (**2**), n = 2 (9.9 × 10^{-9} mol), and platinum colloid or hydrogenase: ● NADPH–(**2**)–platinum colloid system, ○ NADPH–(**2**)–hydrogenase system.

† Hydrogenase (obtained from *Desulfovibrio vulgaris* and purified by Yagi's method[2]) and a platinum colloid (synthesized according to the literature[3]) have the ability to release 1.32 and 1.43 μmol of hydrogen, respectively, by the reaction system: platinum colloid or hydrogenase (0.5 ml)–methyl viologen (9.9 × 10^{-7} mol)–$Na_2S_2O_4$ (2.5 × 10^{-5} mol) in 4.0 ml phosphate buffer (pH 7.0) at 30 °C for 5 min.

takes part as a photosensitizer and an electron carrier in the same molecule. Intramolecular electron transfer from porphyrin to viologen takes place in this case and the charge separated species is so stable that electron transfer can take place from reduced viologen to the catalyst.

The lifetimes of the excited triplet states of (**2**) (τ/ms $n = 2$, 1.1; $n = 3$, 2.0; $n = 4$, 1.8; $n = 5$, 1.9; $n = 6$, 1.9; ZnPyTP, 4.3) show that for $n = 2$ this state was quenched more efficiently than for $n = 3$—6. Samples were dissolved in a 10 vol. % Triton X-100 micellar solution and excited by Nd-YAG laser. The manner of determination of lifetimes is reported elsewhere.[4] Although the quenching of the excited triplet state was observed, the transient absorption of reduced viologen was not observed in all cases. For $n = 3$—6, the intramolecular electron transfer from porphyrin to viologen may not take place, or the back electron transfer is so fast that no hydrogen evolution may be observed, though the electron transfer from porphyrin to viologen takes place.

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