# Photoinduced Hydrogen Evolution by Using Platinum-Loaded Langmuir-Blodgett and Cast Films of Porphyrin

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(Received February 10, 1997; CL-970096)

Platinum-loaded Langmuir-Blodgett and cast films of a porphyrin are prepared, and steady photoinduced hydrogen evolution is observed using both films under steady-state irradiation.

Photoinduced hydrogen evolution systems comprising porphyrin as a photosensitizer, methylviologen as an electron carrier, ethylenediaminetetraacetic acid disodium salt (EDTA) as a sacrificial electron donor and colloidal platinum (Pt) as a catalyst were well-known.[1] Even in the absence of an electron carrier, hydrogen was also produced in homogeneous system when 5, 10, 15, 20-tetra(N-methyl-4-pyridyl) zinc porphyrin was used as a photosensitizer.[2] However, the rate of hydrogen evolution decreased presently with reaction time in homogenous system, since colloidal Pt aggregated by degrees even at room temperature and the catalytic activity decreased. Pt-loaded film of a porphyrin would be expected to keep Pt particles from aggregating and to allow photoinduced static electron transfer from porphyrin to loaded Pt, enabling photoinduced hydrogen evolution in the absence of an electron carrier. In the present work, we prepared Pt-loaded Langmuir-Blodgett (LB) and cast films of a porphyrin and found that hydrogen was produced stably under steady state irradiation using both films.

5, 10, 15, 20-tritolyl-(N-pentyl-4-pyridyl) porphyrin (**1**) was synthesized according to the literature[3] and its structure was confirmed by $^1$H-NMR spectroscopy.[4] A monolayer of porphyrin (**1**) was prepared by spreading a benzene-methanol solution (9:1 v/v) of **1** onto a distilled water subphase. The porphyrin formed stable monolayer on a distilled water subphase according to the surface pressure versus area isotherm of the monolayer of **1** (data not shown). The limiting area per molecule of **1** was 0.70 nm$^2$, indicating that porphyrin molecules were almost vertically oriented on a water subphase. A monomolecular layer of **1** was prepared on a glass plate by using the LB preparation technique under a surface pressure of 10 mN m$^{-1}$ and the film transfer ratio of **1** onto the glass plate was 0.98 ; in this way $8.0 \times 10^{-8}$ mol of **1** was transferred onto the glass plate. The film transfer ratio is defined as $A_L/A_S$, where $A_S$ is the area of the substrate coated with a monolayer, and $A_L$ is the decrease in area occupied by that monolayer at the air/water interface at constant pressure. Since the film transfer ratio was about 1.0, porphyrin molecules were almost vertically oriented on the glass plate. A cast film of **1** was prepared as follows. 0.2 ml of the chloroform solution containing $2.0 \times 10^{-3}$ mol dm$^{-3}$ **1** was cast on the glass plate, and dried up under room temperature. The amount of **1** in the cast film is five times that in the LB film. Since the fluorescence spectra of both the LB and cast films were similar to that of the monomeric porphyrin (data not shown),[5] the electronic coupling between the porphyrin molecules in these films seemed not to be strong such as in a homogeneous solution.

Pt-loaded films were prepared by dipping the LB or cast film into argon purged aqueous solutions (5 ml) containing 0.1 mol dm$^{-3}$ EDTA and $1.0 \times 10^{-3}$ mol dm$^{-3}$ $H_2PtCl_6$, and irradiated for 72 h with visible light (720 > λ /nm >390) *via* a Toshiba L-39 filter using a 15 W fluorescence lamp as the illumination source. Negatively charged $PtCl_6^{2-}$ is assumed to be incorporated in the LB and cast films of the positively charged porphyrin (**1**) and is reduced to Pt by photoreduction.[6] The Pt particles thus produced are fixed in both films. The amount of Pt fixed in the LB and the cast films were 0.1 mg and 0.4 mg, respectively. No change of the absorption spectra of both films was observed after platinization (data not shown), so the molecular structure of **1** was maintained. Pt-loaded LB and cast films prepared was washed with distilled water prior to photoinduced hydrogen evolution experiments. The film which Pt is unloaded is defined as the metal-free LB or cast film. Pt-loaded or metal-free LB and cast films were dipped into argon purged aqueous solution (5 ml) containing 0.1 mol dm$^{-3}$ EDTA, and irradiated with visible light (720 > λ /nm >390) with a light intensity at the surface of the films of 2.8 mW cm$^{-2}$ at 25 ℃. In addition, the metal-free LB and cast films were dipped into argon purged aqueous solution (5 ml) containing 0.1 mol dm$^{-3}$ EDTA and 0.05 wt % colloidal Pt which was prepared from $H_2PtCl_6$ and sodium citrate according to the literature,[6] and irradiated with visible light. Hydrogen produced was analyzed

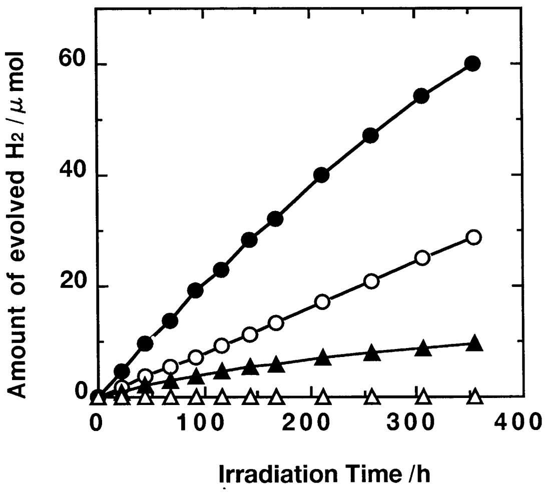

**Figure 1.** Relationship between irradiation time and the amount of evolved hydrogen when Pt - loaded LB and cast films of porphyrin (**1**) used to photoinduced hydrogen evolution in an argon purged aqueous solution containing 0.1 mol dm$^{-1}$ EDTA, or when metal-free LB and cast films used to photoinduced hydrogen evolution in an argon purged aqueous solution containing 0.1 mol dm$^{-1}$ EDTA and colloidal Pt. ○ Pt -loaded LB film: ● Pt-loaded cast film: △ metal-free LB film: ▲ metal-free cast film.

by gas chromatography.

Figure 1 shows the time dependence of evolved hydrogen when Pt-loaded LB and cast films were used for photoinduced hydrogen evolution. In both cases, hydrogen was evolved. The stability of Pt-loaded LB and cast films catalyst was evident from the constant rate of hydrogen evolution, and the turnover number of porphyrin in Pt-loaded LB and cast films reached 360 and 151, respectively, after 354 h irradiation. No change of the shapes of the absorption spectra of both films was observed after photoinduced hydrogen evolution (data not shown), so the molecular structure of **1** was maintained. Although the cast film contained porphyrin molecules per area five times as many as the LB film, the rate of hydrogen evolution of Pt-loaded cast film was about twice that of Pt-loaded LB film. This result indicates that the thickness of the porphyrin film affects the hydrogen evolution which seems to take place efficiently at the interface between the film and water. Since all of porphyrin molecules in the LB film were considered to contact with water, the reaction between porphyrin molecules and EDTA seemed to take place efficiently. As a result, the turnover number of porphyrin in the LB film became larger than the case of the cast film. In the presence of colloidal Pt, hydrogen was evolved using the metal-free cast film, however, no hydrogen was observed using the metal-free LB film (Figure 1). The rate of hydrogen evolution by the metal-free cast film was small and unstably compared to that by Pt-loaded cast film. Since the aggregation of colloidal Pt seems to take place and make the particle size of Pt larger, it becomes difficult to install colloidal Pt into the cast film. In paticular, the particle size of colloidal Pt seemed too large to be installed into the LB film.

On the other hand, no hydrogen was observed using both the metal-free LB and cast films in the absence of colloidal Pt catalyst. Under irradiation, the color of both the metal-free LB and cast films turned green from brown, however, that of the Pt-loaded LB and cast films remained brown. The green colored porphyrin may belong to the reduced form of **1** which is produced due to the reductive quenching of **1** by EDTA, and Pt played a role as a catalyst which transfered electrons from the reduced forms of **1** to protons. As a result, hydrogen was produced. In the case of the metal-free films, electron transfer from the reduced form of **1** to proton did not occur due to the absence of Pt. To get some informations about the green colored porphyrin, the change of the absorption spectrum of **1** was measured. Figure 2 shows the absorption spectra of the metal-free LB film of **1** before (Figure 2a) and after (Figure 2b) 12 h irradiation in the presence of 0.1 mol dm$^{-3}$ EDTA. When oxygen was purged after 12 h irradiation, the absorption spectrum was almost recovered (Figure 2c). This shows that the green colored porphyrin does not belong to the degradation of porphyrin (**1**). Moreover, the spectrum (Figure 2b) was obviously different from that of chlorin which was produced by decreasing pH of aqueous solution using HCl (data not shown). In the case of using 2-mercaptoethanol and ascorbic acid as electron donors, the same changes of the absorption spectra were observed. The absorption spectra of the metal-free LB and cast films were not changed after 120 h irradiation in the absence of electron donors. The absorption spectrum (Figure 2b) is seemed to belong to the reduced form of **1** which is produced due to the reductive quenching of **1** by electron donors.

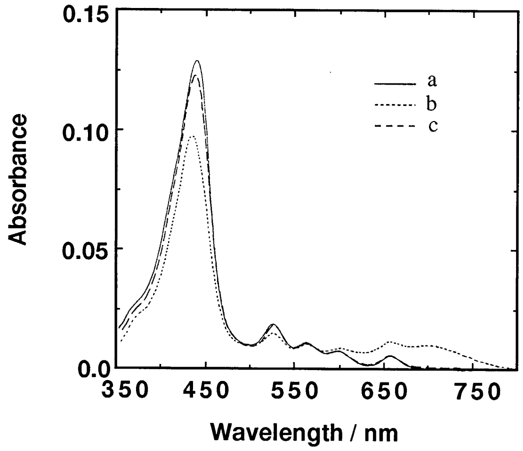

**Figure 2.** The changes of the UV-visible absorption spectra of the metal-free LB film of porphyrin (**1**) on the glass plate before (a), after (b) 12 h irradiation in an argon purged aqueous solution containing 0.1 mol dm$^{-3}$ EDTA and oxygen was purged after 12 h irradiation (c).

Since no accumulation of green colored porphyrin was observed under steady-state irradiation in case of Pt-loaded LB and cast films in the presence of EDTA, the reaction between the porphyrin molecules of these films and EDTA seemed the rate-limiting step. The dynamics of the reaction between the porphyrin molecules of these films and EDTA is currently investigated in detail.

## References and Notes

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4 For **1**: $^1$H-NMR (270 MHz, DMSO-$d_6$) $\delta$ (ppm) -2.9(s, 2H), 1.2 (t, 3H), 1.6-1.8 (m, 4H), 2.4-2.5 (m, 2H), 2.7 (s, 9H), 5.0 (t, 2H), 7.7 (d, 6H), 8.1 (d, 6H), 8.8 (dd, 4H), 8.9 (dd, 4H), 9.0 (d, 2H), 9.5 (d, 2H).

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