Preparation of a Langmuir–Blodgett film of a platinized viologen-linked porphyrin and photoinduced hydrogen evolution

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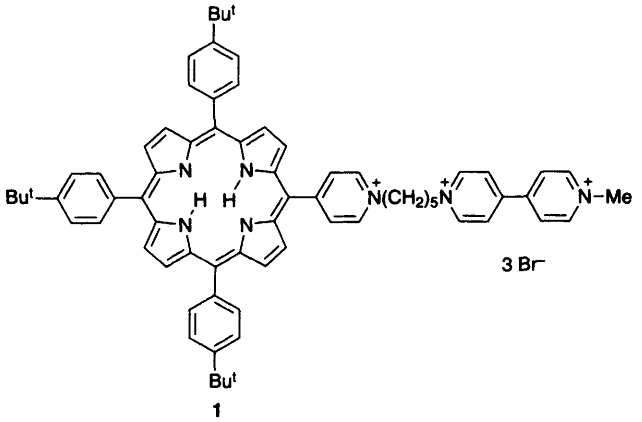
A Langmuir–Blodgett film of a platinized viologen-linked porphyrin is prepared, and steady photoinduced hydrogen evolution is observed with the porphyrin under steady-state irradiation.

Photoinduced hydrogen evolution systems comprising a porphyrin as a photosensitizer, methyl viologen as an electron carrier, the disodium salt of ethylenediaminetetraacetic acid (H_2Na_2edta) as a sacrificial electron donor and colloidal platinum as a catalyst are well known.[1] Porphyrins covalently linked to viologens have been widely used to investigate various aspects of static electron-transfer reactions,[2–4] however, few porphyrins covalently linked to viologens have been applied to photoinduced hydrogen evolution by combining with a platinum (Pt) catalyst.[5] In particular, there are no reports on platinized viologen-linked porphyrins, which would be expected to allow photoinduced static electron transfer from porphyrin to Pt *via* viologen, enabling photoinduced hydrogen evolution. Since an LB film of viologen-linked porphyrin is an oriented molecular layer and selective irradiation on the porphyrin side is possible, shielding of the irradiating light is expected to be unnecessary. In this work, an LB film of platinized viologen-linked porphyrin was prepared and the film was applied to photoinduced hydrogen evolution using H_2Na_2edta as a sacrificial electron donor.

The viologen-linked porphyrin **1** was synthesized according to the literature[4] and its structure confirmed by ^1H NMR spectroscopy. A monolayer of viologen-linked porphyrin **1** was prepared by spreading a benzene–methanol solution (9 : 1 v/v) of **1** onto a distilled water subphase. A well organized monomolecular layer of **1** was prepared on a glass plate by using the LB preparation technique under a surface pressure of 10 dyn



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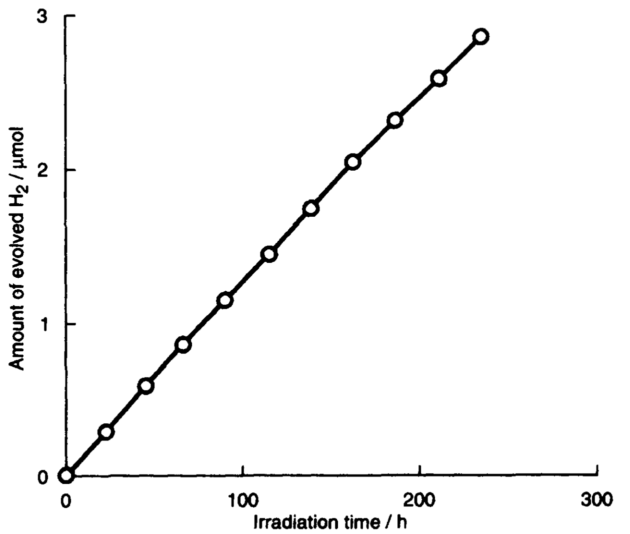
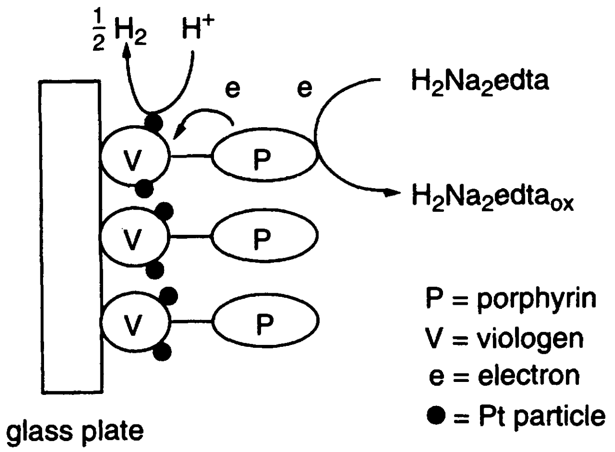
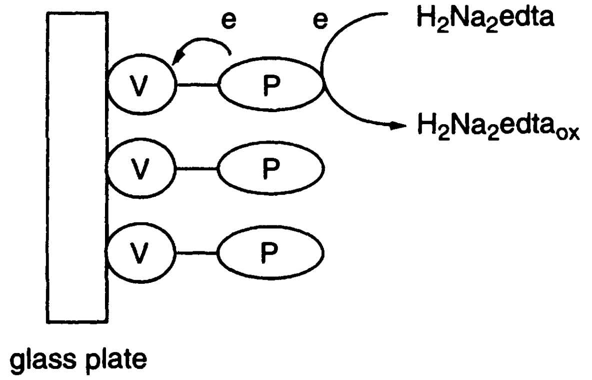


Fig. 1 Relationship between irradiation time and the amount of evolved hydrogen when a platinized viologen-linked porphyrin LB film was used to photoinduce hydrogen evolution in an argon purged aqueous solution containing 0.1 mol dm^{-3} H_2Na_2edta



Scheme 1



Scheme 2

cm^{-2}; in this way 2.2×10^{-8} mol of **1** was transferred onto the glass plate.

Platinization was carried out by dipping the prepared LB film into an argon purged aqueous solution containing 1.0×10^{-1} mol dm^{-3} H_2Na_2edta and 1.0×10^{-3} mol dm^{-3} H_2PtCl_6, and irradiating for 72 h with visible light ($720 > \lambda/nm > 390$) *via* a Toshiba LH-39 filter using a 15 W fluorescence lamp (Mitsubishi Electric Osram Ltd., N color) as the illumination source. Negatively charged $PtCl_6^{2-}$ is assumed to be incorporated in the vicinity of the positively charged viologen moiety and is reduced to Pt by hydrogen produced by electron transfer from reduced viologen species formed upon irradiation.[6] The Pt particles thus produced are fixed in the LB film in close vicinity to the viologen. The fixed Pt LB film catalyst thus prepared was washed with distilled water prior to photoinduced hydrogen evolution experiments. The fixed or non-fixed Pt LB films were dipped into argon purged aqueous solution containing 1.0×10^{-1} mol dm^{-3} H_2Na_2edta, and irradiated with visible light ($720 > \lambda/nm > 390$) with a light intensity at the surface of the LB film of 2.8 mW cm^{-2} (irradiated area = 165 cm^2). Hydrogen produced was analysed by gas chromatography.

Fig. 1 shows the relationship between irradiation time and the amount of evolved hydrogen when the fixed Pt catalyst LB film was used for photoinduced hydrogen evolution. The stability of the fixed Pt catalyst was evident from the constant rate of hydrogen evolution, and the turnover number of viologen-linked porphyrin reached 265 after 240 h irradiation. Under irradiation, the colour of the fixed Pt LB film catalyst remained brown, indicating that Pt particles were fixed near the viologen moiety and played a role as catalyst in transferring electrons from the reduced viologen forms, which are produced by intramolecular electron transfer from the photo excited porphyrins to the bonded viologens, to protons. As a result, hydrogen is evolved (Scheme 1). On the other hand, the colour of the non-fixed LB film catalyst turned from brown to blue due to reduced viologen formation and no hydrogen was observed even after 120 h irradiation. This shows that the reduced viologen form cannot reduce protons in the absence of Pt. Rather they accumulate as according to Scheme 2.

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