Photoinduced Hydrogen Production with Photosensitization of Zn Chlorophyll Analog Dimer as a Photosynthetic Special Pair Model

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Abstract

Zinc chlorophyll *a* derivatives were synthesised for use as photosensitizers. Herein, we report a system for photoinduced hydrogen production with colloidal platinum via photoreduction of methylviologen (MV^{2+}) using the photosensitization of a Zn pyropheophorbide *a* (ZnPyOH) dimer connected by lysine (ZnPy-K(ZnPy)OH) as a special pair model in the photosynthetic reaction centre in the presence of NADPH as an electron donor.

Keywords: chlorophyll derivatives, photoinduced hydrogen production, colloidal platinum

Introduction

In photosynthetic bacteria, the bacteriochlorophyll dimer, in the reaction centre (RC) protein, also called the special pair, plays an important role in the initial light reactions of photosynthesis.¹ On the other hand, photoinduced hydrogen production from water, an attractive mimetic of the photosynthetic system, has been studied extensively in the conversion of solar energy to chemical energy.^{2,3,4} Many researchers and engineers work on these research area. The construction of high efficiency hydrogen production systems will be lead the hydrogen energy society. To provide hydrogen by using renewable energy such as solar energy will incarnate the ultimate eco-friendly society. Photoinduced hydrogen production system is one of the most

attendant research area. The photoinduced hydrogen production systems composed of an electron donor, a photosensitizer, an electron mediator, and a hydrogen production catalyst have been reported.^{5,6,7,8,9} The photoinduced hydrogen production systems were studied changing four components to construct high efficiency system. Notably, colloidal platinum and hydrogenase are widely used as hydrogen production catalysts. In photoinduced hydrogen production systems, the photosensitizer molecule is important because the photo-conversion efficiency depends heavily on the absorption band and the extinction coefficient of the photosensitizer. The downpour solar energy is mainly visible region, which absorbed pigment was used as photosensitizer. Water-soluble zinc porphyrins and chlorophylls are often employed as photosensitizer molecules.^{5,6,9,10} However, photoinduced hydrogen production with photosensitization via special pairs has not been reported.

In this study, we synthesised Zn chlorophyll dimer derivatives, Zn pyropheophorbide *a* molecules (ZnPyOH) connected by lysine (ZnPy-K(ZnPy)OH), as a photosynthetic special pair (chemical structures are shown in Figure 1). Additionally, we constructed a system for visible light-induced hydrogen production using colloidal platinum and photoreduction of methylviologen (MV^{2+}) by the visible light photosensitization of the ZnPyOH dimer connected by lysine (ZnPy-K(ZnPy)OH) as a photosensitizer in the presence of NADPH as an electron donor (Scheme 1). The photosensitization of ZnPyOH or ZnPy-K(ZnPy)OH was evaluated by the photoreduction of MV^{2+} , photoinduced hydrogen production, and time-resolved fluorescence spectroscopy.

Experimental Section

General

All reactions and chromatographic separations were carried out with minimal ambient light. ZnPyOH and ZnPy-K(ZnPy)OH were prepared from chlorophyll *a* via several synthetic reaction steps including pyrolysis, hydrolysis, condensation, and metallation. These compounds were characterized by UV-vis absorption, ¹H-NMR, and MALDI-TOF mass spectroscopy. NADPH was obtained from Oriental Yeast Co. Ltd. Methylviologen dichloride and cetyltrimethylammonium bromide (CTAB) were purchased from Tokyo Kasei Co. Ltd. Hydrogen hexachloroplatinate(IV) hexahydrate and sodium citrate dihydrate were obtained from Kanto Chemical Co. Ltd. (Benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP) was obtained from Watanabe Chemical Industries Ltd. All other reagents were of the highest grade available. The silica gel used for column chromatography was silica gel, 70-230 mesh, 60 Å, obtained from Aldrich. ¹H NMR spectra were obtained using a Varian Gemini-300 NMR spectrometer, with tetramethylsilane as an internal standard

for CDCl_3 . UV-vis absorption spectra were recorded on a Multispec-1500 Shimadzu spectrophotometer. Mass spectra (MS) were obtained in R-cyano-4-hydroxycinnamic acid (CHCA) using a matrix-assisted laser desorption/ionization mode-time of flight (MALDI-TOF) mass spectrometer (PerSeptive Biosystems Voyager RN). A Shimadzu GC-14B gas chromatograph was also utilized for characterization purposes.

Synthesis of ZnPyOH and ZnPy-K(ZnPy)OH

Pheophytin *a*

Chlorophyll *a* (Chl *a*) was extracted from spinach (200 g) into acetone (500 mL) by ultrasonication, and the solution was subsequently filtered with filter paper. This procedure was repeated three times. After the solvent was removed, the resulting solid (a mixture of Chl *a*, Pheophytin *a*, Chl *b*, Pheophytin *b*, β -Carotene, Lutein, Xanthine, and Neoxanthine) was isolated by silica gel column chromatography (eluent was 2-propanol:hexane = 1:25).

The crude solid (a mixture of Chl *a*, Pheophytin *a*, Chl *b*, and Pheophytin *b*) was then dissolved in acetic acid (5 mL) to remove magnesium ions from Chl *a* and Chl *b*, and the reaction mixture was stirred for 20 min at room temperature. Next, the reaction mixture was neutralized with sodium carbonate. Dichloromethane (100 mL) was added and the reaction mixture was washed with distilled water. After the solvent was removed, the resulting solid was purified by silica gel column chromatography with a mixture of 2-propanol and hexane (1:25) as the eluent to obtain the product (102.8 mg, 118 μmol).

Characterization results: UV/vis (acetone): 408 nm (ϵ , 98.2 $\text{mM}^{-1}\text{cm}^{-1}$), 665 nm (42.6 $\text{mM}^{-1}\text{cm}^{-1}$); MS (MALDI-TOF): m/z 871.4 (MH^+); ^1H NMR(CDCl_3): δ -1.67(1H, br s, -NH), 0.48(1H, br s, -NH), 0.7~1.70(34H, m, P5~20), 1.70(3H, t, C8^1 - CH_3), 1.80(3H, d, C18- CH_3), 1.89(2H, t, P4- CH_2 -), 2.29, 2.56(2H, m, C17^1 - CH_2 -), 2.31, 2.70(2H, m, C17- CH_2 -), 3.25(3H, s, C7- CH_3), 3.41(3H, s, C2- CH_3), 3.68(3H, s, C12- CH_3), 3.70(2H, q, C8- CH_2 -), 4.30(1H, m, C17-*H*), 4.50(2H, m, P1- CH_2 -), 4.50(1H, m, C18-*H*), 5.16(1H, t, P2= CH -), 6.18(1H, q, C3^1 = CH_2 cis), 6.25(1H, s, C13^1 - CH -), 6.29(1H, d, C3^1 = CH_2 trans), 8.02(1H, q, C3- CH=), 8.56(1H, s, C20-*H*), 9.40(1H, s, C10-*H*), 9.52(1H, s, C5-*H*).

Pyropheophorbide *a* methylester, PPheide *a* ME¹¹

Pheophytin *a* (100 mg, 115 μmol) was dissolved in 2,4,6-collidine (10 mL) in a 50-mL bottle, and the reaction mixture was refluxed for 3 h under nitrogen at 130 $^\circ\text{C}$. After the solvent was removed, the resulting solid was dissolved in a solution of sulphuric acid and methanol (sulphuric acid/methanol = 1:8; 10 mL) in a 50-mL bottle, and the reaction mixture was stirred for 4 h under nitrogen at room temperature.

Dichloromethane was added, and the reaction mixture was washed with distilled water. After the solvent was evaporated by vacuum, the resulting solid was purified by silica gel column chromatography using a mixture of methanol, hexane, and chloroform (1:5:20) as the eluent to obtain the product in 50.7 % (32.0 mg) yield.

Characterization results: UV/vis(acetone): 408 nm (ϵ , 99.5 $\text{mM}^{-1}\text{cm}^{-1}$), 665 nm (39.2 $\text{mM}^{-1}\text{cm}^{-1}$); MS(MALDI-TOF): m/z 549.5 (MH^+); ^1H NMR(CDCl_3): δ -1.67(1H, br s, -NH), 0.48(1H, br s, -NH), 1.70(3H, t, C8^1 - CH_3), 1.80(3H, d, C18 - CH_3), 2.29, 2.56(2H, m, C17^1 - CH_2 -), 2.31, 2.70(2H, m, C17 - CH_2 -), 3.25(3H, s, C7 - CH_3), 3.41(3H, s, C2 - CH_3), 3.61(3H, s, C17^2 - CO_2CH_3), 3.68(3H, s, C12 - CH_3), 3.70(2H, q, C8 - CH_2 -), 4.30(1H, m, C17 -H), 4.49(1H, m, C18 -H), 5.20(2H, q, C13^1 - CH_2 -), 6.18(1H, q, C3^1 = CH_2 cis), 6.29(1H, d, C3^1 = CH_2 trans), 8.02(1H, q, C3 -CH=), 8.56(1H, s, C20 -H), 9.40(1H, s, C10 -H), 9.52(1H, s, C5 -H).

Pyropheophorbide *a*, PPheide *a*

PPheide *a* ME (20 mg; 36.4 μmol) was dissolved in 5 N hydrochloric acid (150 mL) in a 300-mL bottle, and the reaction mixture was stirred for 3 h under nitrogen at room temperature. Subsequently, the reaction mixture was neutralized with sodium carbonate. Dichloromethane was added, and the reaction mixture was washed with distilled water. After the solvent was evaporated, the resulting solid was purified by silica gel column chromatography (eluent was a mixture of methanol/hexane/chloroform at a ratio of 1:5:20) to obtain the product in 50.0% (9.6 mg) yield.

Characterization results: UV/vis(acetone): 408 nm (ϵ , 134 $\text{mM}^{-1}\text{cm}^{-1}$), 665 nm (60.0 $\text{mM}^{-1}\text{cm}^{-1}$); MS(MALDI-TOF): m/z 534.9 (MH^+); ^1H NMR(CDCl_3): δ -1.90(1H, br s, -NH), 0.87(1H, br s, -NH), 1.60(3H, t, C8^1 - CH_3), 1.80(3H, d, C18 - CH_3), 2.20, 2.60(2H, m, C17^1 - CH_2 -), 2.40, 2.65(2H, m, C17 - CH_2 -), 3.14(3H, s, C7 - CH_3), 3.35(3H, s, C2 - CH_3), 3.58(3H, s, C12 - CH_3), 3.58(2H, q, C8 - CH_2 -), 4.23(1H, m, C17 -H), 4.45(1H, m, C18 -H), 5.19(2H, q, C13^1 - CH_2 -), 6.10(1H, q, C3^1 = CH_2 cis), 6.23(1H, d, C3^1 = CH_2 trans), 7.87(1H, q, C3 -CH=), 8.45(1H, s, C20 -H), 9.20(1H, s, C10 -H), 9.35(1H, s, C5 -H).

Pyropheophorbide *a*-L-Lysine (Pyropheophorbide *a*)-Methylester, PPheide *a*-K(PPheide *a*)-OMe

PPheide *a* (18.8 mg, 35.2 μmol), H-L-Lys(Boc)-OMe (16 mg, 61.5 μmol), and (Benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP) (60 mg, 136 μmol) were dissolved in THF (10 mL) in a 50-mL bottle. Triethylamine (1 mL, 7.21 mmol) was added to the solution, and the reaction mixture was stirred for 1 h under nitrogen at room temperature. After the solvent was evaporated, dichloromethane was added and the reaction mixture was washed with distilled water. The solvent was

removed, and the resulting solid was purified by silica gel column chromatography (eluent was acetonitrile/chloroform = 1:9).

The purified solid was subsequently dissolved in a solution of HCl (12 N HCl_{aq}/dichloromethane/methanol = 4:10:15; 1 mL), and the reaction mixture was stirred for 12 h at room temperature. Next, the reaction mixture was neutralized with sodium carbonate and the resulting solution was washed with distilled water, and the solvent was removed under reduced pressure. The resulting solid, PPheide *a* (20.0 mg, 37.4 μ mol), and BOP (60 mg, 136 μ mol) were dissolved in THF (20 mL) in a 50-mL bottle. Triethylamine (2 mL, 14.4 mmol) was added to the solution, and the reaction mixture was stirred for 2 h under nitrogen at room temperature. After the solvent was evaporated by vacuum, dichloromethane was added, and the reaction mixture was washed with distilled water. After the solvent removed, the resulting solid was purified by silica gel column chromatography (eluent was acetonitrile/chloroform = 1:1) to obtain the product in a yield of 33.0% (14.7 mg).

Characterization results: UV/vis(acetone): 427 nm (ϵ , 141 mM⁻¹cm⁻¹), 653 nm (80.0 mM⁻¹cm⁻¹); MS(MALDI-TOF): *m/z* 1194.5 (MH⁺); ¹H NMR(CDCl₃): δ -1.68, -1.90(2H, 2br s, -NH), 0.13(2H, br s, -NH), 1.35, 1.25(6H, 2t, C8¹-CH₃), 1.48(2H, m, C22 -CH₂-), 1.80(2H, m, C23 -CH₂-), 1.85(6H, 2d, C18 -CH₃), 2.05~2.40(8H, 8m, C17, C17¹-CH₂-), 2.85 (2H, q, C24 -CH₂-), 3.08(4H, 2q, C8 -CH₂-), 3.18, 2.97(6H, 2s, C7 -CH₃), 3.30, 3.20(6H, 2s, C2 -CH₃), 3.45(2H, t, C21 -CH₂-), 3.70(6H, 2s, C12 -CH₃), 4.08, 3.85(2H, 2m, C17 -H), 4.61, 4.23(2H, 2m, C18 -H), 4.92, 4.62(4H, 2q, C13¹-CH₂-), 5.28(3H, q, C21 -CO₂CH₃), 6.15, 6.00(4H, 2d, C3 =CH₂), 6.98(1H, t, CONH2 -NH-), 7.18(1H, d, CONH1 -NH-), 7.82, 7.60(2H, 2q, C3 -CH=), 8.19, 8.00(2H, 2s, C10 -H), 8.38(2H, 2s, C20 -H), 9.18, 8.93(2H, 2s, C5 -H).

Pyropheophorbide *a*-L-Lysine(Pyropheophorbide *a*)-OH, PPheide *a*-K(PPheide *a*)-OH

PPheide *a*-K(PPheide *a*)-OMe (10.4 mg, 8.71 μ mol) was dissolved in 5 N hydrochloric acid (20 mL) in a 50-mL bottle, and the mixture was stirred for 8 h under nitrogen at room temperature. Next, the reaction mixture was neutralized with sodium carbonate. Dichloromethane was added, and the mixture was washed with distilled water. After the solvent was removed, the resulting solid was purified by silica gel column chromatography (eluent was acetonitrile/chloroform = 1:1) to obtain PPheide *a*-K(PPheide *a*)-OH in 81.7% (8.4 mg) yield.

Characterization results: UV/vis (acetone): 397 nm (ϵ , 126 mM⁻¹cm⁻¹), 666 nm (70.6 mM⁻¹cm⁻¹); MS(MALDI-TOF): *m/z* 1180.8 (MH⁺).

Zinc Pyrochlorophyllide *a* (ZnPyOH), Zn Pyrochlorophyllide *a*-L-Lysine(Zinc Pyrochlorophyllide *a*)-OH (ZnPy-K(ZnPy)OH)

The syntheses of ZnPyOH and ZnPy-K(Py)OH were carried out using similar methods. For example, ZnPyOH was prepared as follows:

Pyropheophorbide *a*, PPheide *a* (10.0 mg, 18.7 μmol), was dissolved in dichloromethane (20 mL) in a 50-mL bottle. Zinc acetate dihydrate (20.5 mg, 93.5 μmol) was added to the solution, and the reaction mixture was stirred for 1 h at room temperature. Next, the reaction mixture was washed with distilled water to remove excess zinc acetate, and the product was obtained in 90.2% (10.1 mg) yield, after the solvent was evaporated.

Characterization results: UV/vis (acetone): 425 nm (ϵ , 57.8 $\text{mM}^{-1}\text{cm}^{-1}$), 654 nm ($38.5 \text{ mM}^{-1}\text{cm}^{-1}$); MS(MALDI-TOF): m/z 597.082 (MH^+).

Zinc Pyrochlorophyllide *a*-L-Lysine(Zinc Pyrochlorophyllide *a*)-OH, ZnPy-K(ZnPy)-OH

The yield was 82.1 %. Characterization results: UV/vis (acetone): 427 nm (ϵ , 159 $\text{mM}^{-1}\text{cm}^{-1}$), 657 nm ($96.0 \text{ mM}^{-1}\text{cm}^{-1}$); MS(MALDI-TOF): m/z 1309.81 (MH^+).

Preparation of Colloidal Platinum

Colloidal platinum was prepared by refluxing a mixture of hydrogen hexachloroplatinate (IV) hexahydrate and sodium citrate as previously described.¹² The prepared colloidal platinum had the ability to release 0.7 μmol of hydrogen in the reaction system of 10 μL colloidal platinum solution, 1.2×10^{-5} mmol MV^{2+} , and 7.7×10^{-5} mmol sodium dithionite in 4 mL of 50 mmol dm^{-3} Tris-HCl buffer (pH 7.4) at 30 °C for 10 min. One unit of colloidal platinum activity was defined as the release of 1.0 μmol of hydrogen per min.

Photoreduction of MV^{2+}

The photoreduction of MV^{2+} was evaluated in a reaction mixture of ZnPyOH (10 $\mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)OH (5.0 $\mu\text{mol dm}^{-3}$), MV^{2+} (2.0 mmol dm^{-3}), and NADPH (2.0 mmol dm^{-3}) in 3.0 mL of 10 mmol dm^{-3} potassium phosphate buffer (pH 7.0). ZnPyOH and ZnPy-K(ZnPy)OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} micellar cetyltrimethylammonium bromide (CTAB). The solution was deaerated by freeze-pump-thaw cycles, which were repeated 6 times. The solution was irradiated with a 200 W halogen lamp (Philips) at a distance of 3.0 cm with a Sigma Koki short wave cutoff filter 60R at 30 °C. The reduced MV^{2+} , MV cation radical ($\text{MV}^{•+}$) concentration was determined by a spectrophotometer set at 605 nm using the molar coefficient $13\,000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.¹³

Photoinduced Hydrogen Production

The photoinduced hydrogen production was determined using a reaction mixture of ZnPyOH ($10 \mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)OH ($5.0 \mu\text{mol dm}^{-3}$), MV²⁺ (2.0 mmol dm^{-3}), NADPH (2.0 mmol dm^{-3}), and colloidal platinum (0.5 units) in 3.0 mL of 10 mmol dm^{-3} potassium phosphate buffer (pH = 7.0). ZnPyOH and ZnPy-K(ZnPy)OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} CTAB. The solution was deaerated by 6 freeze-pump-thaw cycles, and was substituted by argon gas. The photoreaction conditions were the same as for photoreduction of MV²⁺. The hydrogen evolution was detected by gas chromatography (detector: TCD, column: active carbon, carrier gas: nitrogen).

Results and Discussion

Photoreduction of MV²⁺

Photoreduction of MV²⁺ is the most important step in photoinduced hydrogen production. When a sample solution containing ZnPyOH or ZnPy-K(ZnPy)OH, MV²⁺, NADPH, and CTAB in 3.0 mL of potassium phosphate buffer (pH 7.0) was irradiated, the accumulation of MV^{•+} was observed, as shown in Figure 2. For the system containing ZnPyOH, the conversion ratio of MV²⁺ to MV^{•+} was estimated to be 9.0 % after 60 min irradiation. In contrast, the conversion ratio was estimated to be 6.5 % for the system using ZnPy-K(ZnPy)OH. In both systems, the concentration of Zn pyrochlorophyllide was nearly the same. However, the accumulation rate of MV^{•+} in the system using ZnPy-K(ZnPy)OH was lower than that of ZnPyOH system. These results indicated that the MV²⁺ photoreduction rate of ZnPy-K(ZnPy)OH was faster than that of ZnPyOH.

Photoinduced Hydrogen Production

After the MV²⁺ photoreduction system using ZnPyOH or ZnPy-K(ZnPy)OH was achieved, the development of a photoinduced hydrogen production system was attempted. Photoinduced hydrogen production with ZnPyOH or ZnPy-K(ZnPy)OH was evaluated using a sample solution that contained ZnPyOH or ZnPy-K(ZnPy)OH, MV²⁺, NADPH, and colloidal platinum in 3.0 mL of phosphate buffer (pH = 7.0). When the sample solution was irradiated, hydrogen production was observed, as shown in Figure 3. It was found that hydrogen was not evolved even in the missing of one of the above four components, NADPH, ZnPyOH or ZnPy-K(ZnPy)OH, methylviologen and colloidal platinum. With irradiation, hydrogen evolved continuously for more than 120 min. After 120 min of irradiation, the hydrogen production in the ZnPyOH- and ZnPy-K(ZnPy)OH-based systems was estimated to be *c.a.* 0.3 and 0.2 μmol , respectively. The turnover number of ZnPyOH and ZnPy-K(ZnPy)OH was calculated

20 and 13 times in 120 min respectively. With the system using ZnPy-K(ZnPy)OH, the MV^{2+} photoreduction rate and photoinduced hydrogen production rate were faster than that observed with the ZnPyOH system. Sabatini et al. reported ultrafast electron transfer under the conditions for dye-sensitized solar cells (DSSC) and a slow electron transfer under conditions for photoinduced hydrogen production, making a chromophore's triplet yield an important parameter.¹⁴ In a previous study, Sakai et al. reported the fluorescence decay-curve of ZnPyOH and ZnPy-K(ZnPy)OH.¹⁵ The fluorescence decay-curve of ZnPyOH showed a single exponential decay with a fluorescence life time of 3.8 ns. The fluorescence decay-curve of ZnPy-K(ZnPy)OH showed a multiexponential decay. ZnPy-K(ZnPy)OH tended to form intramolecular π - π stacking via the ZnPy moieties in acetonitrile. The multiexponential decay curve-fitting analysis displayed a double exponential decay; one was estimated at 1.6 ns and the other at 0.17 ns. The former lifetime at 1.6 ns might be the natural lifetime of the ZnPy-K(ZnPy)OH, which is a little shorter than that of ZnPyOH. By contrast, the shorter lifetime at 0.17 ns might result from the acceleration of fluorescence quenching, reflecting a contiguous alignment of two ZnPyOHs. The fast electron transfer of ZnPy-K(ZnPy)OH advantageously works in photoelectric conversion systems such as DSSC, but not photoinduced hydrogen evolution systems. In fact, the activity of the photoinduced hydrogen production using ZnPy-K(ZnPy)OH was faster than that of the ZnPyOH system. Thus, we conclude that the photosensitization activity of ZnPy-K(ZnPy)OH was lower than that of ZnPyOH in the photoinduced hydrogen production.

Conclusion

The synthesised chlorophyll compounds, ZnPyOH and ZnPy-K(ZnPy)OH, exhibited photosensitization activities on MV^{2+} photoreduction and photoinduced hydrogen production. In these photoreaction systems, the activity of ZnPy-K(ZnPy)OH was lower than that of ZnPyOH, potentially owing to the intramolecular aggregation of ZnPyOH within CTAB micelles. To construct an effective photoinduced hydrogen production system using a dimer-based photosensitizer, a molecular design that is not susceptible to intramolecular aggregation and higher triplet yield are needed.

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Figure Caption

Figure 1. Chemical structures of ZnPyOH and ZnPy-K(ZnPy)-OH.

Scheme 1. Photoinduced hydrogen production with colloidal platinum via photoreduction of methylviologen (MV^{2+}) using the sensitization of ZnPyOH or Zn-K(Py)OH in the presence of NADPH.

Figure 2. Time dependence of $MV^{•+}$ production in the systems composed of ZnPyOH ($10 \mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)-OH ($5.0 \mu\text{mol dm}^{-3}$), MV^{2+} (2.0 mmol dm^{-3}), and NADPH (2.0 mmol dm^{-3}) in 3.0 mL of 10 mmol dm^{-3} potassium phosphate buffer (pH 7) under steady state irradiation at 30°C . ZnPyOH and ZnPy-K(ZnPy)-OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} micellar cetyltrimethylammonium bromide (CTAB). Squares: ZnPyOH, circles: ZnPy-K(ZnPy)-OH.

Figure 3. Time dependence of hydrogen production in the systems composed of ZnPyOH ($10 \mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)-OH ($5.0 \mu\text{mol dm}^{-3}$), MV^{2+} (2.0 mmol dm^{-3}), NADPH (2.0 mmol dm^{-3}), and colloidal platinum (0.5 units) in 3.0 mL of 10 mmol dm^{-3} phosphate buffer (pH=7.0) under steady state irradiation at 30°C . ZnPyOH and ZnPy-K(ZnPy)-OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} CTAB. Squares: ZnPyOH, circles: ZnPy-K(ZnPy)-OH.

Figure 1. Chemical structures of ZnPyOH and ZnPy-K(ZnPy)-OH.

Scheme 1. Photoinduced hydrogen production with colloidal platinum via photoreduction of methylviologen (MV^{2+}) using the sensitization of ZnPyOH or Zn-K(Py)OH in the presence of NADPH .

Figure 2. Time dependence of $MV^{\bullet+}$ production in the systems composed of ZnPyOH ($10 \mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)-OH ($5.0 \mu\text{mol dm}^{-3}$), MV^{2+} (2.0 mmol dm^{-3}), and NADPH (2.0 mmol dm^{-3}) in 3.0 mL of 10 mmol dm^{-3} potassium phosphate buffer (pH 7) under steady state irradiation at 30°C . ZnPyOH and ZnPy-K(ZnPy)-OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} micellar cetyltrimethylammonium bromide (CTAB). Squares: ZnPyOH, circles: ZnPy-K(ZnPy)-OH.

Figure 3. Time dependence of hydrogen production in the systems composed of ZnPyOH ($10 \mu\text{mol dm}^{-3}$) or ZnPy-K(ZnPy)-OH ($5.0 \mu\text{mol dm}^{-3}$), MV^{2+} (2.0 mmol dm^{-3}), NADPH (2.0 mmol dm^{-3}), and colloidal platinum (0.5 units) in 3.0 mL of 10 mmol dm^{-3} phosphate buffer (pH=7.0) under steady state irradiation at 30°C . ZnPyOH and ZnPy-K(ZnPy)-OH were dissolved in an aqueous solution containing 0.1 mmol dm^{-3} CTAB. Squares: ZnPyOH, circles: ZnPy-K(ZnPy)-OH.