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Journal of Molecular Catalysis A: Chemical 138 (1999) 107–113

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Photoinduced hydrogen evolution with viologen-linked ruthenium(II) complexes and hydrogenase

Tomohiro Hiraishi, Toshiaki Kamachi, Ichiro Okura *

Department of Bioengineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8501, Japan

Received 9 February 1998; accepted 20 April 1998

Abstract

Viologen-linked ruthenium(II) complexes with different methylene chain length between ruthenium complex and viologen, $Ru(bpy)_2(dcbpy)C_nVCH_3$ ($n = 2–3$), were synthesized and characterized by using spectroscopic techniques. From luminescence spectra, the photoexcited state of $Ru(bpy)_2(dcbpy)$ is oxidatively quenched by binding viologen, and an intramolecular electron transfer occurs. $Ru(bpy)_2(dcbpy)C_nVCH_3$ were applied for the photoinduced hydrogen evolution in the system containing nicotinamide–adenine dinucleotide phosphate (reduced form, NADPH), $Ru(bpy)_2(dcbpy)C_nVCH_3$ and hydrogenase under steady state irradiation.

Keywords: Photoinduced hydrogen evolution; Viologen-linked ruthenium(II) complexes; Hydrogenase; Intramolecular electron transfer

1. Introduction

Photoinduced hydrogen evolution from water has been studied extensively using a system composed of four components: electron donor (D), photosensitizer (P), electron carrier (C) and catalyst as shown in Scheme 1 [1–4].

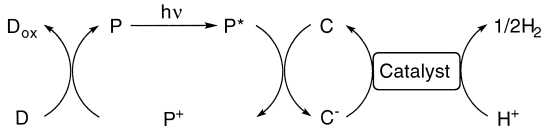
In this reaction, the reduction of electron carrier is one of the important steps. Some viologen linked photosensitizers (P–C), such as porphyrins and ruthenium complexes, have been synthesized and characterized for more effective charge separation between a photosensitizer and an electron carrier [5–9]. In the case of viologen linked ruthenium complexes, such as $Ru(dcbpy)_2(mcbpy)C_nVCH_3$, the photoexcited state of ruthenium complex site is rapidly quenched by the binding viologen. However, the complexation between ruthenium complex moiety and binding viologen may occur leading to the photoinactive species as this ruthenium complex moiety is negatively charged. To accomplish an effective photoinduced hydrogen evolution, no interaction between ruthenium complex moiety and binding viologen is desired.

In addition, as viologen linked ruthenium complexes can act as both a photosensitizer and an electron carrier in the same molecule, these compounds may be applied to photoinduced hydrogen evolution as shown in Scheme 2.

In this paper, ruthenium complexes with different methylene chain length ($n = 2–3$) between positively charged complex and violo-

* Corresponding author. Tel.: +81-924-5752; Fax: +81-924-5778; E-mail: iokura@bio.titech.ac.jp

1381-1169/99/$ - see front matter
PII: S1381-1169(98)00139-3



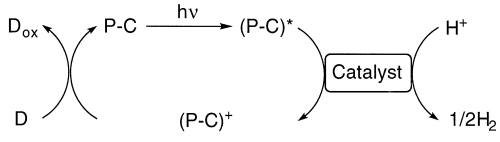
Scheme 1. Photoinduced hydrogen evolution system.

gen, $Ru(bpy)_2(dcbpy)C_nVCH_3$ (the structure is shown in Fig. 1), were synthesized and characterized by using spectroscopic techniques. As no electronic interaction between positively charged ruthenium(II) complex site and binding viologen in the ground state, $Ru(bpy)_2(dcbpy)$ was used as a photosensitizer. As the reduction of NADP to NADPH occurs with the concomitant oxygen evolution in photosynthesis, NADPH was used as an electron donor in the artificial photoinduced hydrogen evolution system. These viologen linked ruthenium(II) complexes were applied to photoinduced hydrogen evolution system containing NADPH, $Ru(bpy)_2(dcbpy)C_nVCH_3$ and hydrogenase, and photoinduced hydrogen evolution mechanism using $Ru(bpy)_2(dcbpy)C_nVCH_3$ was discussed.

2. Experimental

2.1. Materials

All reagents were of analytical or of the highest grade available. 4,4′-Dimethyl-2,2′-bipyridine (dmbpy), 4,4′-dicarboxy-2,2′-bipyridine (dcbpy) and $Ru(bpy)_2Cl_2 \cdot nH_2O$ were prepared as described previously [10–12]. The synthesis route of viologen linked ruthenium(II) complexes are shown in Scheme 3, and the structures of the compounds are shown in Fig. 1.



Scheme 2. Photoinduced hydrogen evolution system using an electron carrier linked photosensitizer.

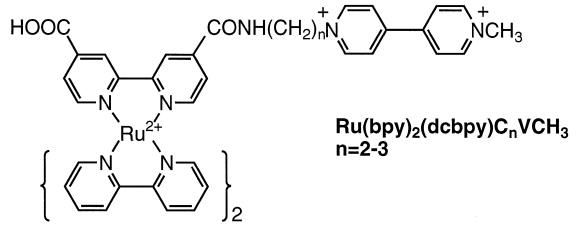


Fig. 1. Structures of $Ru(bpy)_2(dcbpy)C_nVCH_3$.

2.1.1. 1-Methyl-4,4′-bipyridinium (VCH_3)

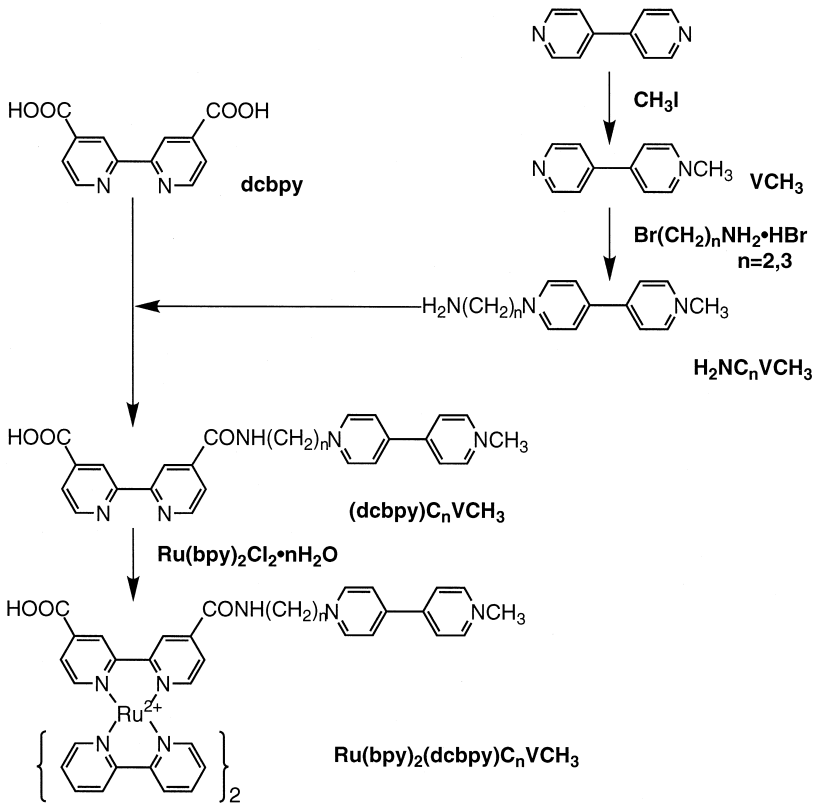
4,4′-Bipyridine (0.16 mol) and methyl iodide (0.18 mol) were dissolved in 400 ml of acetone and stirred at room temperature for 24 h. A yellow precipitate was filtered and washed with acetone. The desired product was recrystallized from ethanol (EtOH) and water and dried under vacuum overnight. ^{1}H-NMR in D_2O: δ (ppm) 4.3–4.5 (s, 3H), 7.7–7.8 (d, 2H), 8.2–8.3 (d, 2H), 8.5–8.6 (d, 2H), 8.8–8.9 (d, 2H).

2.1.2. 1-(3-Ammoniopropyl)-1′-methyl-4,4′-bipyridinium ($NH_2C_3VCH_3$)

VCH_3 (13 mmol) was refluxed with excess (3-bromopropyl)ammonium bromide in 400 ml of acetonitrile (MeCN) for 24 h. A yellow precipitate was filtered, washed with MeCN and dried under vacuum overnight. The product was recrystallized from EtOH and water, and then reprecipitated from water by the addition of ammonium hexafluorophosphate (NH_4PF_6). The white PF_6^- salt was filtered, washed with water and dried under vacuum overnight. ^{1}H-NMR in dimethylsulfoxide-d_6 (DMSO-d_6): δ (ppm) 2.2–2.4 (quintet, 2H), 2.8–3.0 (t, 2H), 4.7–4.9 (t, 2H), 8.7–8.9 (multiplet, 4H), 9.3–9.5 (multiplet, 4H).

2.1.3. 1-(2-Ammonioethyl)-1′-methyl-4,4′-bipyridinium ($NH_2C_2VCH_3$)

$NH_2C_2VCH_3$ was prepared analogously to the procedure described above for the preparation of $NH_2C_3VCH_3$, with the substitution of (2-bromoethyl)ammonium bromide. ^{1}H-NMR in DMSO-d_6: δ (ppm) 3.5–3.7 (t, 2H), 4.4–4.5 (s, 3H), 4.9–5.0 (t, 2H), 8.7–8.9 (multiplet, 4H), 9.2–9.4 (multiplet, 4H).



Scheme 3.

2.1.4. N-(3-(1′-Methyl-4,4′-bipyridium-1-yl)propyl)-4′-carboxyl-2,2′-bipyridine-4-carboxamide ((dcbpy)C_3VCH_3)

$NH_2C_3VCH_3$ and dcbpy were stirred in the presence of 1-hydroxybenzotriazole (1.5 equivalent) and 1,3-diisopropylcarbodiimide (excess) in the dry DMF at 30°C for 5 h. The mixture was centrifuged to remove the precipitate. The solvent was removed under vacuum, dissolved in a minimum amount of MeCN and tetraethylammonium bromide ($(C_2H_5)_4NBr$) was added to obtain the white Br^- salt. The white Br–salt was dissolved in water and NH_4PF_6 was added to replace the counter-anion with PF_6^-. The white PF_6^- salt was recrystallized from water and dried under vacuum. ^{1}H-NMR in DMSO-d_6: δ (ppm) 2.3–2.5 (quintet, 2H), 3.4–3.6 (t, 3H), 4.3–4.4 (s, 3H), 4.7–4.9 (t, 2H), 7.85–8.0 (multiplet, 2H), 8.7–9.0 (multiplet, 7H), 9.1–9.2 (multiplet, 1H), 9.25–9.4 (dd, 2H), 9.45–9.55 (dd, 2H).

2.1.5. N-(2-(1′-Methyl-4,4′-bipyridium-1-yl)ethyl)-4′-carboxyl-2,2′-bipyridine-4-carboxamide ((dcbpy)C_2VCH_3)

(Dcbpy)C_2VCH_3 was prepared analogously to the procedure described above with substitution of $NH_2C_2VCH_3$. ^{1}H-NMR in DMSO-d_6: δ (ppm) 3.95–4.1 (multiplet, 2H), 4.45–4.55 (s, 3H), 4.85–5.0 (multiplet, 2H), 7.8–7.85 (dd, 1H), 7.95–8.0 (dd, 1H), 8.7–9.0 (multiplet, 7H), 9.2–9.5 (multiplet, 5H).

2.1.6. Ru(bpy)$_2$(dcbpy)C_nVCH_3 (n = 2–3)

Tris(bipyridyl)ruthenium(II) complexes were prepared by refluxing $Ru(bpy)_2Cl_2 \cdot nH_20$ with either (dcbpy)C_2VCH_3 or (dcbpy)C_3VCH_3 in 1:1 EtOH:H_2O under argon. The reaction was

monitored by UV–vis spectroscopy. The Ru(II) complexes were applied to a neutral alumina column to remove the impurity and starting material (1:1 acetone:ethanol). The desired products were eluted with methanol.

2.2. Purification of hydrogenase

Hydrogenase was purified from *Desulfovibrio vulgaris* (Miyazaki) according to the literature [13]. Protein concentration was determined using the following molar absorption coefficient: $\varepsilon = 47\ \text{mmol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$ at 400 nm.

2.3. Spectroscopic measurements

UV–vis absorption spectra were measured in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4) using a Shimadzu MultiSpec-1500 spectrometer. The absorption coefficients of $Ru(bpy)_2(dcbpy)C_n$-VCH_3 were estimated using the absorption coefficient of tris(4,4′-dimethyl-2,2′-bipyridyl)ruthenium(II) ($Ru(dmbpy)_3$) [14].

^{1}H-NMR spectra were recorded on a Varian GEMINI-200. The chemical shifts were referenced to the solvent peak calibrated against tetramethylsilane (TMS).

The luminescence spectra were measured in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4) at room temperature using a Hitachi F-4000 spectrometer. The absorbance at the excitation wavelength was kept constant at 0.2 for all sample solutions in these experiments.

Luminescence lifetime measurements were carried out by using time-correlated single-photon-counting (Horiba NAES-500 spectrometer).

2.4. Photoinduced hydrogen evolution under steady state irradiation

For the steady state irradiation, the sample solution in a Pyrex cell was irradiated using 200 W tungsten lamp (Philips KP-8) at 30°C. Light of wavelength less than at 390 nm was removed by Toshiba L-39 cut-off filter. The sample solution containing NADPH (2.0 mmol dm^{-3}), $Ru(bpy)_2(dcbpy)C_nVCH_3$ (10 μmol dm^{-3}) and hydrogenase (0.15 μmol dm^{-3}) in 3.0 ml of 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4) was deaerated by repeated freeze–pump–thaw cycles and then incubated for 5 min under argon. Evolved hydrogen was detected by gas chromatography (Shimadzu GC-14B, detector: TCD, column: active carbon).

3. Results and discussion

3.1. Photophysical properties of $Ru(bpy)_2(dcbpy)C_nVCH_3$

The absorption maxima of $Ru(bpy)_2(dcbpy)C_nVCH_3$ and $Ru(bpy)_2(dcbpy)$ are listed in Table 1. As an example, the absorption spectrum of $Ru(bpy)_2(dcbpy)C_3VCH_3$ is shown in Fig. 2. The absorption spectra of $Ru(bpy)_2(dcbpy)C_nVCH_3$ are similar to that of $Ru(bpy)_2(dcbpy)$ with the exception of the absorbance of viologen. These results indicate that no electronic interaction between the $Ru(bpy)_2(dcbpy)$ site and the binding viologen occurs in the grand state.

The photoexcited states of $Ru(bpy)_2(dcbpy)C_nVCH_3$ were studied using the luminescence

Table 1
Wavelength of absorption maxima of $Ru(bpy)_2(dcbpy)$ and $Ru(bpy)_2(dcbpy)C_nVCH_3$

Compound	Wavelength of absorption maxima (nm)		
$Ru(bpy)_2(dcbpy)$	244 (26 750)[a]	287 (58 980)	458 (13 590)
$Ru(bpy)_2(dcbpy)C_2VCH_3$	250 (42 443)	287 (62 090)	463 (13 820)
$Ru(bpy)_2(dcbpy)C_3VCH_3$	248 (41 467)	285 (62 067)	456 (11 367)

[a]Absorption coefficient ($M^{-1}\ cm^{-1}$) given in parentheses.

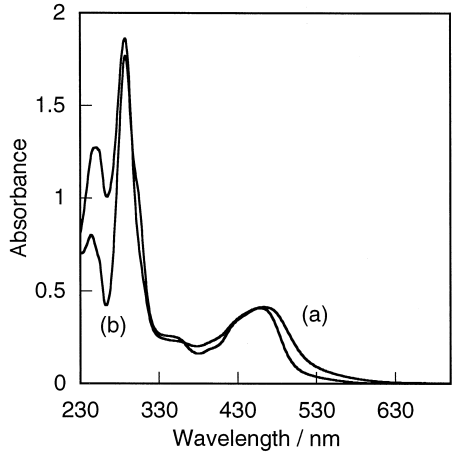


Fig. 2. Absorption spectra of $Ru(bpy)_2(dcbpy)C_3VCH_3$ (a) and $Ru(bpy)_2(dcbpy)$ (b) in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4).

emission spectra. As an example, the luminescence spectrum of $Ru(bpy)_2(dcbpy)C_3VCH_3$ is shown in Fig. 3. For $Ru(bpy)_2(dcbpy)C_3VCH_3$, the shape of the luminescence spectrum of $Ru(bpy)_2(dcbpy)C_3VCH_3$ are the same as that of $Ru(bpy)_2(dcbpy)$. However, the luminescence intensity of $Ru(bpy)_2(dcbpy)C_3VCH_3$ is lower than that of $Ru(bpy)_2(dcbpy)$. For $Ru(bpy)_2(dcbpy)C_2VCH_3$, no luminescence spectrum was observed. These results indicate that the photoexcited state of $Ru(bpy)_2(dcbpy)$ site is oxidatively quenched by the binding viologen due to an intramolecular electron transfer and no electronic interaction occurs between the $Ru(bpy)_2(dcbpy)$ site and the binding viologen in the photoexcited state.

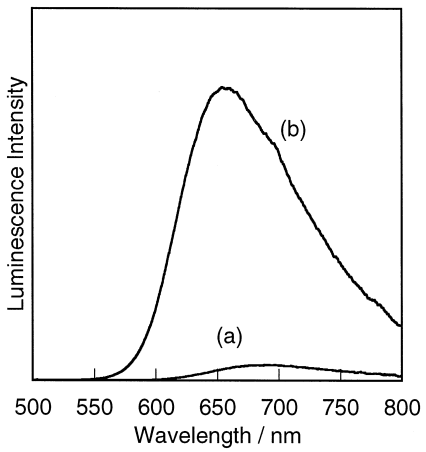


Fig. 3. Luminescence spectra of $Ru(bpy)_2(dcbpy)C_3VCH_3$ (a) and $Ru(bpy)_2(dcbpy)$ (b) in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4). The excitation wavelength was 287 nm.

The excited-state lifetime of $Ru(bpy)_2(dcbpy)C_nVCH_3$ was measured by time-correlated single photon counting. For $Ru(bpy)_2(dcbpy)$, the excited lifetime was determined as 370 ns. However, no luminescence decay of $Ru(bpy)_2(dcbpy)C_nVCH_3$ was observed. This result also indicates that the oxidative quenching of photoexcited state of $Ru(bpy)_2(dcbpy)$ site is the major deactivation pathway of the photoexcited state.

3.2. Photoreduction of binding viologen in $Ru(bpy)_2(dcbpy)C_nVCH_3$

When the solution containing NADPH and $Ru(bpy)_2(dcbpy)C_nVCH_3$ was irradiated, the absorbance at 605 nm increased as shown in Fig. 4. In the case of an individual component system containing NADPH, $Ru(bpy)_2(dcbpy)$ and methylviologen, no reduced methylviologen was observed. In the both cases, the absorbance

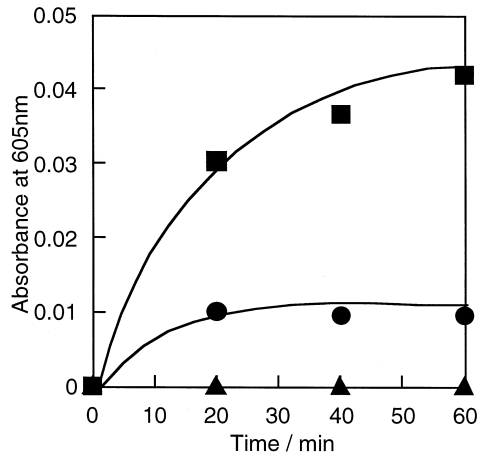


Fig. 4. Time dependence of the absorption change of $Ru(bpy)_2(dcbpy)C_nVCH_3$ under steady state irradiation monitored at 605 nm. The solution contains 2.0 mmol dm^{-3} of NADPH and 10 μmol dm^{-3} of $Ru(bpy)_2(dcbpy)C_nVCH_3$ in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4) (■: $n=2$, ●: $n=3$). For the individual system, the solution contains 2.0 mmol dm^{-3} of NADPH, 10 μmol dm^{-3} of $Ru(bpy)_2(dcbpy)$ and 10 μmol dm^{-3} of methylviologen (▲).

at 450 nm due to the MLCT band of $Ru(bpy)_2$-(dcbpy) decreased by the irradiation. On the other hand, when the above solution with the substitution of triethanolamine as an electron donor was irradiated, no viologen reduction was observed, indicating the photoreduction of binding viologen via reductive quenching of photoexcited state of ruthenium complex moiety by electron donor. These results suggest that the binding viologen in $Ru(bpy)_2(dcbpy)C_nVCH_3$ molecule is more easily reduced than that of individual system and the reduced form of ruthenium complex may be formed by the reductive quenching of the photoexcited state of the ruthenium complex by NADPH.

3.3. Photoinduced hydrogen evolution with hydrogenase

When the solution containing NADPH, $Ru(bpy)_2(dcbpy)C_nVCH_3$ and hydrogenase was irradiated, the efficient photoinduced hydrogen evolution was observed. Fig. 5 shows the time dependence of the photoinduced hydrogen evolution. On the other hand, when an individual component system consisting of NADPH, $Ru(bpy)_2(dcbpy)$, methylviologen and hydrogenase was irradiated, no hydrogen evolution was observed. The photoinduced hydrogen evolution rate in the case of $Ru(bpy)_2(dcbpy)C_2VCH_3$ was more effective than that of $Ru(bpy)_2$-$(dcbpy)C_3VCH_3$. For $Ru(bpy)_2(dcbpy)C_2VCH_3$, $Ru(bpy)_2(dcbpy)$ site was more close to viologen than for $Ru(bpy)_2(dcbpy)C_3VCH_3$, so that the electron may transfer rapidly from $Ru(bpy)_2(dcbpy)$ site to binding viologen. By using the system containing NADPH, $Ru(bpy)_2$-$(dcbpy)C_nVCH_3$ and hydrogenase, the effective photoinduced hydrogen evolution was accomplished compared with the individual system.

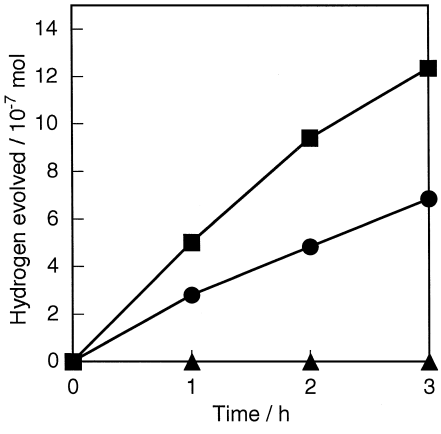
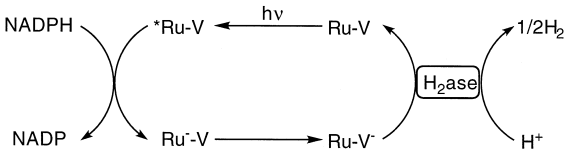


Fig. 5. Time dependence of photoinduced hydrogen evolution under steady state irradiation. The solution contains 2.0 mmol dm^{-3} of NADPH, 10 μmol dm^{-3} of $Ru(bpy)_2(dcbpy)C_nVCH_3$ and 0.15 μmol dm^{-3} of hydrogenase in 25 mmol dm^{-3} Tris–HCl buffer (pH 7.4) (■: $n=2$, ●: $n=3$). For the individual system, the solution contains 2.0 mmol dm^{-3} of NADPH, 10 μmol dm^{-3} of $Ru(bpy)_2(dcbpy)$, 10 μmol dm^{-3} of methylviologen and 0.15 μmol dm^{-3} of hydrogenase (▲).

3.4. Mechanism of photoinduced hydrogen evolution

When $Ru(bpy)_2(dcbpy)C_nVCH_3$ was irradiated in the presence of NADPH, the absorbance at 605 nm due to reduced form of viologen increased and the binding viologen was not directly reduced by NADPH. When the above solution with the substitution of triethanolamine as electron donor was irradiated, no viologen reduction was observed. These results indicate that the photoreduction of binding viologen proceeds via the reductive quenching of photoexcited state of ruthenium complex moiety by electron donor. Kelly and Rodgers [9] reported previously that viologen linked ruthenium(II) complex was reductively quenched by *N*-phenylglycine as an electron donor. In addition, when the solution containing $Ru(bpy)_2(dcbpy)C_n$-VCH_3, hydrogenase and NADPH was irradiated, the effective hydrogen evolution was observed. Hence, these results suggest that the photoinduced hydrogen evolution proceed via the reductive quenching of the photoexcited state of ruthenium(II) complex moiety by NADPH. The proposed mechanism is shown in Scheme 4.

In the first step, the photoexcited state of $Ru(bpy)_2(dcbpy)C_nVCH_3$ is formed by the irra-



Scheme 4. Proposed mechanism of photoinduced hydrogen evoluiton with viologen-linked ruthenium(II) complex (Ru-V) and hydrogenase (H_2ase).

diation. Then the photoexcited state of ruthenium(II) complex moiety is reductively quenched by NADPH in the second step. In the final step, the electron transfer from reduced ruthenium(II) complex moiety to binding viologen occurs and hydrogen evolve due to the electron transfer from reduced viologen to hydrogenase.

Acknowledgements

The present work is partly defrayed by the Grant-in-Aid on Priory-Areas-Research from the Ministry of Education, Science, Sports and Culture of Japan (No. 08231226).

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