

Investigation of photostationary state of chromophor/acceptor and related multistep electron relay by in situ visible absorption spectroscopy

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Abstract

In situ visible absorption spectra were measured under photoirradiated state of an aqueous solution involving Ru(bpy)₃²⁺ and methylviologen (MV²⁺). The short-lived viologen cation radical (MV^{•+}) was observed under photoirradiated conditions. In the system of ethylenediaminetetraacetic acid (EDTA)/Ru(bpy)₃²⁺/Ni-phthalocyaninesulfonate (NiPcS), the reduced species of the NiPcS was not observed, but the coexistence of MV²⁺ induced the reduction of NiPcS showing that successive electron transfers from the photoexcited Ru(bpy)₃²⁺ to MV²⁺, and then further from the MV^{•+} to NiPcS take place in the mixture. The photochemical evolution of H₂ was remarkably enhanced by the presence of the second electron acceptor (NiPcS) in the aqueous mixture of EDTA/Ru(bpy)₃²⁺/MV²⁺/Pt-black.

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1. Introduction

Photochemical reactions have been investigated either by analyzing the reaction products or by investigating the transient state after photoexcitation by a short laser pulse (laser flash photolysis). The laser flash photolysis provides the photochemists with a prominent methodology to investigate the rapid electron transfer of a photoexcited chromophor. However, this technique does not give direct information about the species present under photoirradiated conditions. For a photochemical reaction the observation of a photoirradiated state is of importance, but UV–vis absorption spectrum of a reaction mixture under photoirradiated state has scarcely been studied, especially for a system where back reaction is very rapid. An in situ investigation of a photoirradiated state of a solution by a UV–vis absorption spectroscopy is especially useful for systems where back reaction is very rapid and also where the successive reactions take place after the primary photoexcited state reaction. In photochemical energy conversion systems the research on electron relay comprising more than two electron transfer steps is especially of importance. However, these studies have been carried out almost solely by a laser flash photolysis as well as by analyzing the products [1–3].

In the present paper the in situ observation of a visible absorption spectrum under the photoirradiated state of an aqueous solution containing Ru(bpy)₃²⁺ and methylviologen (MV²⁺) was achieved for which the back electron transfer is very rapid. A successive electron transfer to a coexisting water-soluble Ni-phthalocyaninesulfonate (NiPcS) could also be investigated by the in situ visible absorption spectroscopy.

2. Experimental section

2.1. Materials

Tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) and nickel(II) phthalocyaninetetrasulfonic acid tetrasodium salt (NiPcS, **1**) were purchased from Aldrich Co. Ltd., and methyl viologen dichloride (MV²⁺) from Tokyo-Kasei Co., Ltd. Disodium ethylenediaminetetraacetic acid (EDTA) and Pt-black were obtained from Kanto Chemical Co., Inc. All the chemicals were of the purest grade, and used as received.

2.2. In situ measurement of visible absorption spectrum under photoirradiated state

A diode array spectrophotometer, Shimadzu Multispec-1500, was used for the in situ spectroscopy under photoirra-

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diated state. In this instrument the mechanical shutter speed to take in the monitoring light onto the diode array is about 0.1 s allowing the minimum time interval between the measurements to be 0.1 s. A cell box was designed and made so as to minimize the scattering excitation light. It was confirmed that the excitation light does not affect the photochemical process in sample solutions. A quartz cell with 1 cm light pass length and 5 cm height was used. A 3 ml sample solution was used and all the solution surface (1 cm \times 3 cm) was irradiated from the horizontal direction by the excitation light from a 500 W xenon lamp through a UV cutoff filter. The spot shape of the monitoring light on the solution surface was an ellipse (the line of apsides 8 mm and the minor axis 5 mm).

The sample solution was deaerated by bubbling argon gas for 10 min, and all the measurements were carried out at 25 °C. In some cases the visible absorption of a solution

before irradiation was taken as a base line, and net change of the solution by photoexcitation was monitored.

The in situ spectroelectrochemistry (SECV) [4] was measured for a 1 mM NiPcS aqueous solution in the presence of 0.1 M KNO₃ by using a thin layer cell composed of a platinum mesh (80 mesh) working electrode (8 mm \times 22 mm, 76 μ m thickness) sandwiched between two quartz plates; the counter electrode was a platinum wire and the reference a silver wire. The potential of the Ag wire was 0.13 V versus SHE under the present electrolyte conditions. The in situ SECV was measured with the above diode array photometer with a potentiostat/galvanostat (Hokuto Denko, HA-301), a function generator (Hokuto Denko, HB-104) and an X-Y recorder (Rikedenki RW-21). The potential sweep was from 0 to -1.2 V and then back to 0 V and further to +1.2 V and back to 0 V versus Ag wire.

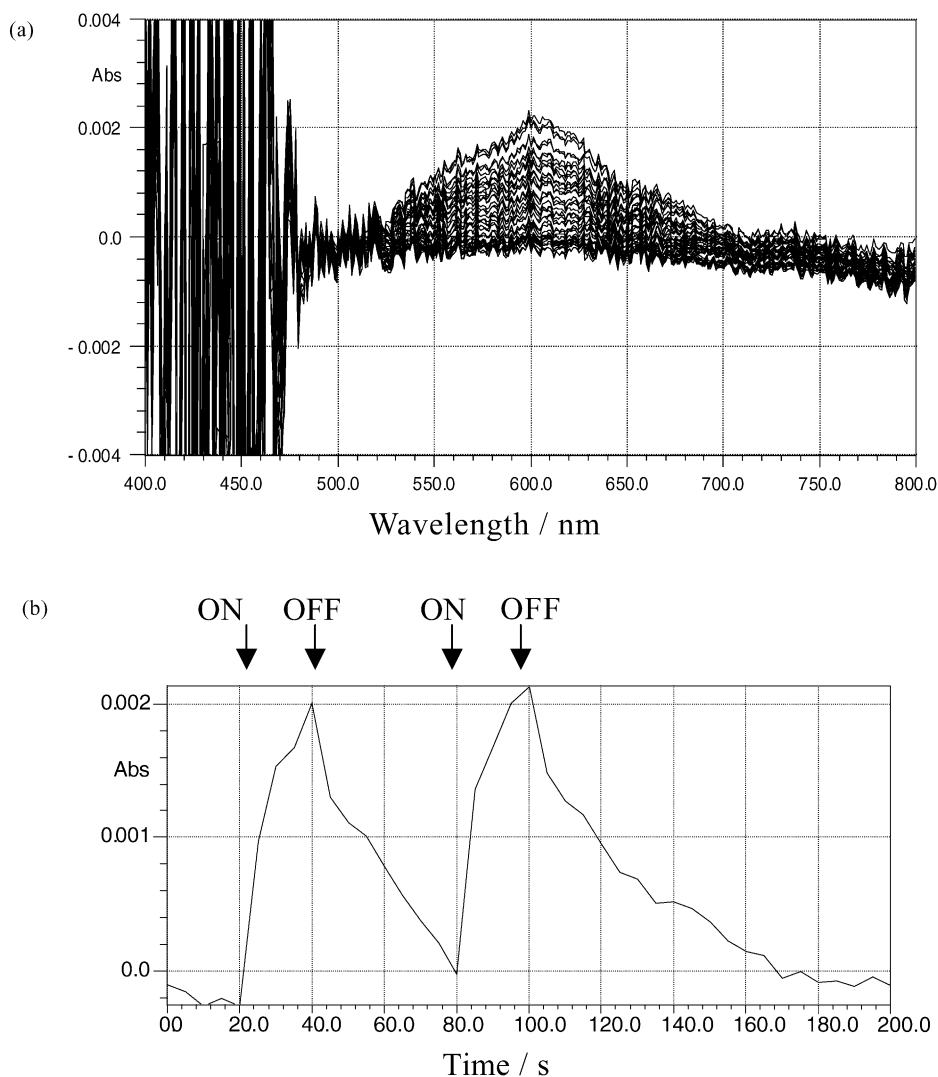


Fig. 1. In situ visible absorption spectral change of aqueous solution containing Ru(bpy)₃²⁺ (0.1 mM) and MV²⁺ (10 mM) under irradiation during 20 s (a), and the absorbance change at 602 nm (due to MV²⁺) by switching on and off of the irradiation (b).

3. Results and discussion

The in situ visible absorption spectral change under photoirradiated state was measured by taking the visible absorption of the sample solution before irradiation as a base line of the spectrum. The spectral change is shown in Fig. 1(a), and the absorbance change at 602 nm due to the viologen cation radical (MV^+) induced by switching on and off the irradiation is shown in Fig. 1(b). The electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} forming viologen cation radical (MV^+) has well been established [1–3]. The absorption by the formed MV^+ centered at 602 nm increased on starting the irradiation, and decreased on switching off the irradiation showing the photoinduced formation and recombination of MV^+ . The non-smooth changes in Fig. 1(b) are not intrinsic ones, but come from the mechanical shutter speed used for switching on/off of the irradiation. In addition, some fluctuation of the absorbance was observed that should reflect real concentration fluctuation in the solution under the photoirradiated state (note that the sampling time for the diode array is 0.1 s). The saturated absorbance at 602 nm under photostationary state (after 200 s, not shown in the figure) was about 0.0046 that corresponds to 4.6×10^{-7} M MV^+ .

For a photochemical conversion system successive electron transfer is important [1–3]. The present method of the in situ spectroscopy is especially effective to study successive reactions taking place after the primary photoinduced electron transfer. The successive electron transfer after the primary electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} was investigated in the presence of various electron donor or acceptor. In the presence of EDTA as a sacrificial electron donor, the mixture solution of $Ru(bpy)_3^{2+}$ and MV^{2+} exhibited a clear change due to the accumulation of MV^+ as shown in Fig. 2(a). The in situ absorbance change at 602 nm due to MV^+ is shown in Fig. 2(b) exhibiting clear increase of MV^+ .

Reversible electron donors such as Fe^{2+} , I_3^- , and $Fe(CN)_6^{4-}$ were also tested as a donor for the photochemically formed $Ru(bpy)_3^{3+}$ instead of EDTA by adding to the $Ru(bpy)_3^{2+}/MV^{2+}$ mixture. The Fe^{2+} ion was not effective to accumulate MV^+ . The I^- and $Fe(CN)_6^{4-}$ formed a kind of complex with either $Ru(bpy)_3^{3+}$ or MV^{2+} , and the irradiation of the mixture did not induce any change of the absorption spectrum. These results indicate that these donors are not effective to accumulate MV^+ .

Water-soluble Ni-phthalocyaninetetrasulfonate (NiPcS) was investigated as an electron acceptor for the pho-

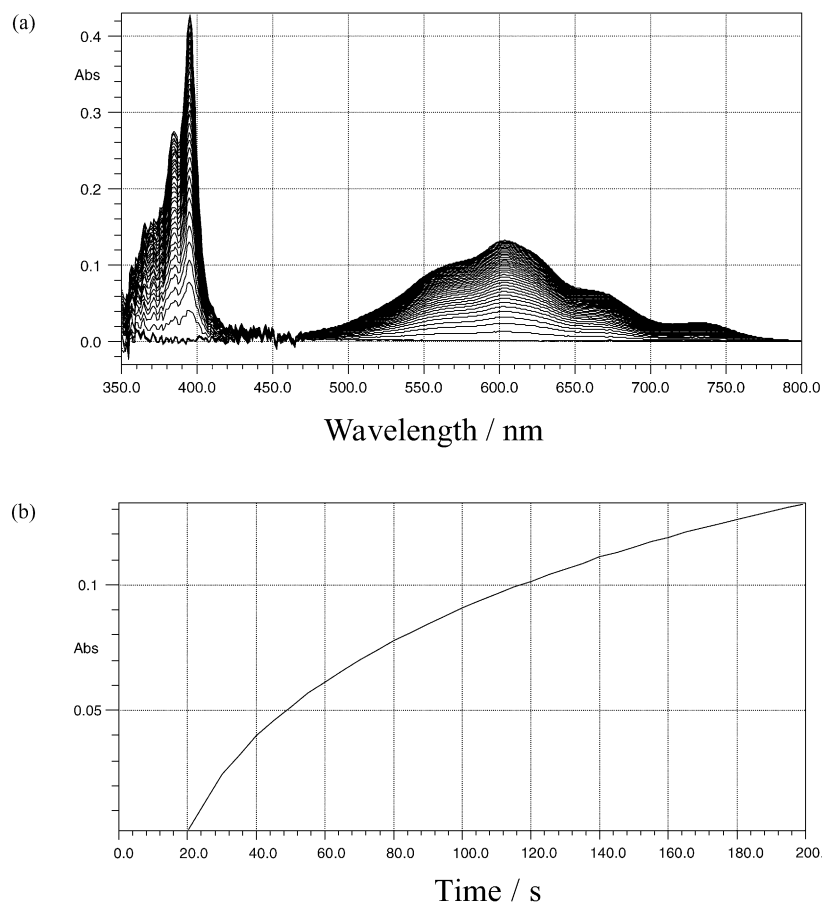


Fig. 2. In situ visible absorption spectral change of aqueous solution containing EDTA (30 mM), $Ru(bpy)_3^{2+}$ (0.1 mM) and MV^{2+} (10 mM) under irradiation (a), and the absorbance change at 602 nm (due to MV^+) by switching on the irradiation (b); the irradiation started at 20 s.

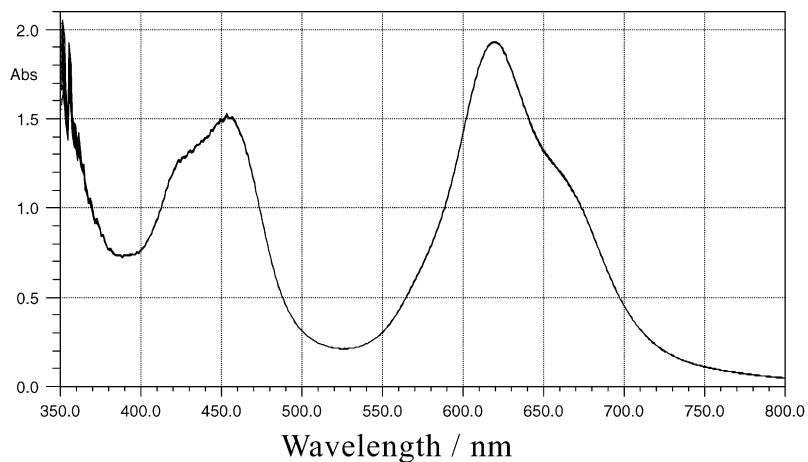


Fig. 3. In situ visible absorption spectral change of aqueous solution containing EDTA (30 mM), Ru(bpy)₃²⁺ (0.1 mM) and NiPcS (0.05 mM) under irradiation for 200 s. No change was observed.

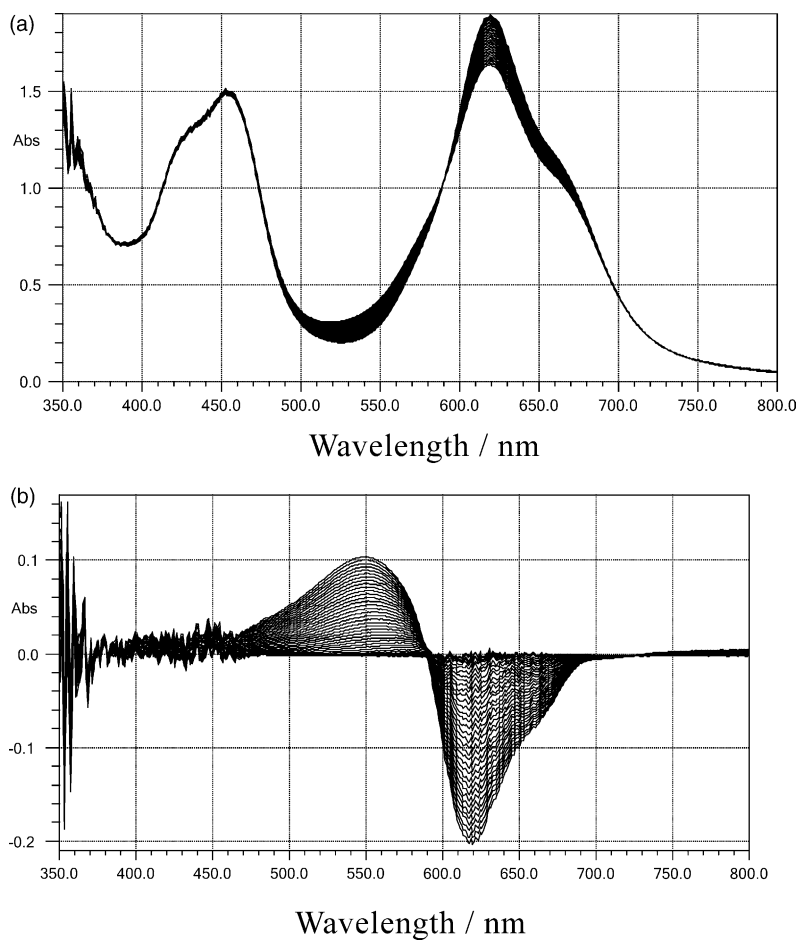


Fig. 4. In situ visible absorption spectral change under photoirradiated state of an aqueous solution containing EDTA (30 mM), Ru(bpy)₃²⁺ (0.1 mM), MV²⁺ (0.05 mM) and NiPcS (0.05 mM) during 180 s irradiation (a), and the change by taking the absorption of the solution before irradiation as the base line (b).

toexcited $\text{Ru}(\text{bpy})_3^{2+}$. The irradiation of the mixture, $\text{EDTA}/\text{Ru}(\text{bpy})_3^{3+}/\text{NiPcS}$, did not induce any change in the in situ visible absorption spectrum (Fig. 3) showing that NiPcS can not be used instead of MV^{2+} as an electron acceptor from the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$. The in situ spectral change of the mixture, $\text{EDTA}/\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}/\text{NiPcS}$, under irradiation is shown in Fig. 4(a) by taking pure water as a base line, and in Fig. 4(b) by taking the absorption of the $\text{EDTA}/\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}/\text{NiPcS}$ mixture before irradiation as a base line: Fig. 4(b) shows therefore the net absorption change of the mixture by irradiation. As shown in Fig. 2(b) for the $\text{EDTA}/\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ mixture, the change due to the MV^+ formation was not observed in Fig. 4(b) indicating that the MV^+ formed by the photoexcited Ru complex reduced NiPcS by working as an electron mediator from the photoexcited Ru complex to the NiPcS .

The spectral change due to the reduction of NiPcS was studied by a thin layer cyclic voltammogram (SCV) to confirm the above reduction of the NiPcS . In order to study both for the reduction and oxidation of the compound, the in situ visible absorption spectral change was investigated

during the cyclic potential sweep from 0 to -1.2 V and then to $+1.2\text{ V}$, and finally back to 0 V versus Ag (corresponds to $0.13 \rightarrow -1.07 \rightarrow +1.07 \rightarrow 0.13\text{ V}$ versus SHE) at a thin layer of a NiPcS aqueous solution in the presence of 0.1 M KNO_3 . The cyclic voltammogram (CV), and its absorption spectral change by taking the absorption of the solution before starting CV as a base line are shown in Fig. 5(a and b), respectively. Although the starting potential for the reduction of the NiPcS was not very clear in the CV (a), a small redox couple was recognized at the potential centered at around -0.5 V versus Ag. The in situ spectral change (b) showed evidently that the reduction starts at around -0.2 V versus Ag (-0.07 V versus SHE) with the simultaneous decrease of the absorption at around 610 nm and the increase of that at 556 nm . These spectral changes following the reduction are identical to those shown in Fig. 4 indicating that the change in Fig. 4 is due to the reduction of the NiPcS . The slight difference of the peak wavelength of the change in Figs. 4 and 5 would be due to the different solute conditions; the former was in the presence of cationic Ru complex and viologen, so that the electrostatic

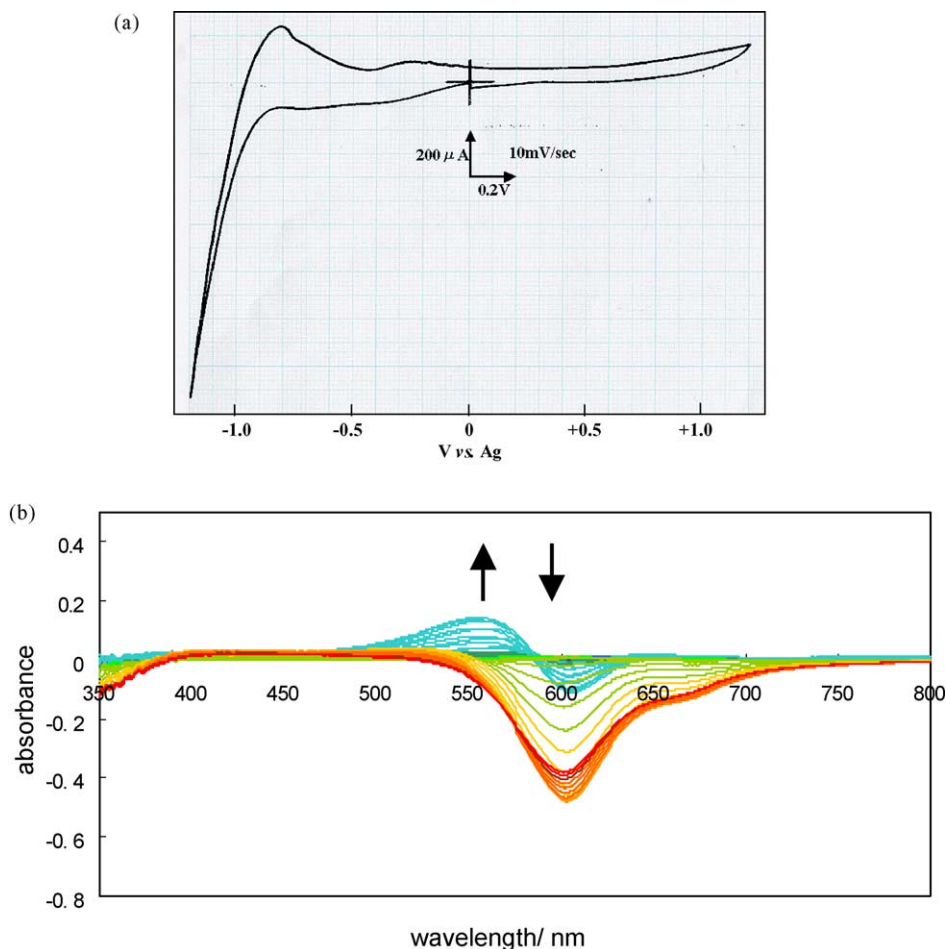
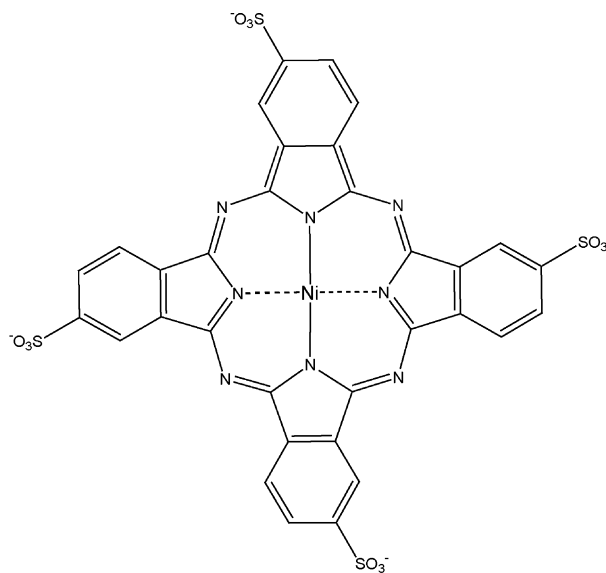
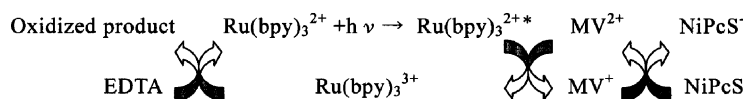


Fig. 5. In situ cyclic voltammogram of a thin layer NiPcS aqueous solution (1 mM) in the presence of 0.1 M KNO_3 with Pt mesh thin layer working, Pt wire counter and Ag wire reference electrodes in the potential sweep, $0 \rightarrow -1.2 \rightarrow +1.2 \rightarrow 0\text{ V}$ vs. Ag (a), and the in situ visible absorption spectral change by taking the absorption of the solution before starting the measurement as the base line (b).



1 (NiPcS)



Scheme 1.

interaction with the anionic NiPcS would cause red-shift of the peak.

By scanning the potential from -1.2 V back to 0 V versus Ag, the negative peak at 610 nm disappeared, and then in the scan from 0 to $+1.2$ V the negative peak at 605 nm increased by oxidation which diminished by scanning back to 0 V versus Ag. About the change around 556 nm in Fig. 5(b), the peak appeared in the reduction towards -1.2 V, disappeared in the scan back to 0 V, and then a slight decrease (small negative peak) was observed in the scan to $+1.2$ V. These results including oxidation again indicates evidently that the photochemical change in Fig. 4 is ascribed to the reduction of the NiPcS and not due to oxidation.

The formal redox potential of the NiPcS/NiPcS $^-$ redox couple was -0.41 V versus SHE, and that of MV $^{2+}$ /MV $^+$ -0.45 V, so that the NiPcS can work as the second electron acceptor for the MV $^+$. The photochemical electron relay in the EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /NiPcS mixture is then represented by the Scheme 1.

The effect of the added NiPcS for the H $_2$ evolution by the EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /NiPcS mixture in the presence of Pt-black was investigated. Fig. 6 shows the time course of the H $_2$ evolution either in the (◆) EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /NiPcS/Pt-black or (■) EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /Pt-black mixture. Although the initial rate of H $_2$ evolution was much more rapid in the latter system, the H $_2$ evolved

was saturated at a low level. The reason for the saturation of the H $_2$ evolution under the present conditions in the EDTA/Ru(bpy) $_3^{2+}$ /MV $^{2+}$ /Pt-black system is not clear yet, but it might be ascribable to a disproportionation of two MV $^+$ molecules to MV $^{2+}$ and two-electron reduced MV that should be stable and unable to reduce H $^+$. Although

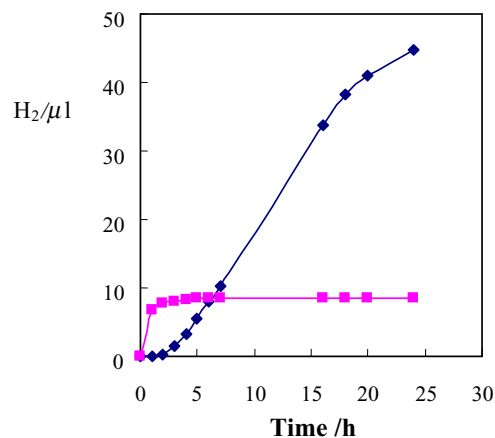


Fig. 6. Photosensitized H $_2$ evolution by the system, EDTA(30 mM)/Ru(bpy) $_3^{2+}$ (01 mM)/MV $^{2+}$ (0.05 mM)/NiPcS (0.2 mM)/Pt-black (2 mM) (◆), and by EDTA(30 mM)/Ru(bpy) $_3^{2+}$ (01 mM)/MV $^{2+}$ (0.05 mM)/Pt-black (2 mM) (■).

the rate of H₂ evolution is slow in the initial stage in the presence of NiPcS, the H₂ evolved increased steadily to much higher H₂ amount. The initial slow increase of the H₂ evolution for the NiPcS system might be ascribable to the slightly higher redox potential of the NiPcS (−0.41 V versus SHE) than that of the MV²⁺ (−0.45 V versus SHE). Anyway, the presence of the second electron acceptor, NiPcS, thus enhanced the H₂ evolution in the later stage of the photochemical reaction.

To conclude, the in situ visible absorption spectroscopy was very useful to investigate the electron transfer reactions under photoirradiated conditions of a chromophor/electron acceptor mixture including the successive electron relay composed of more than two electron transfer steps. This method was successfully applied to study the photoinduced electron transfer involving Ru(bpy)₃³⁺, MV²⁺ and the second electron acceptor.

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