Photocatalysis

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Photoinduced Hydrogen Evolution from Water by a Simple Platinum(II) Terpyridine Derivative: A Z-Scheme Photosynthesis**

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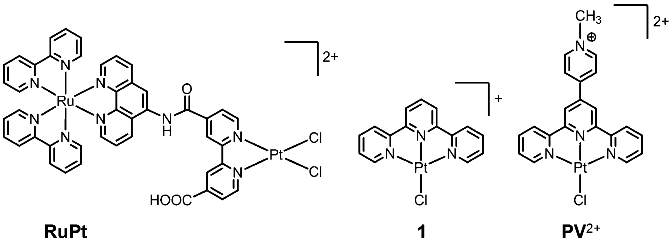
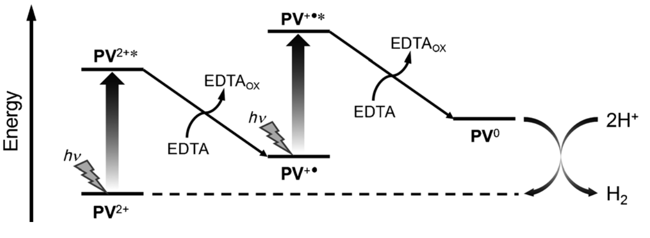
Hydrogen energy has attracted great attention as alternative energy to fossil fuels, because it does not emit greenhouse gases upon combustion. In this context, solar-light-induced water splitting into H_2 and O_2 has attracted great attention for many years.[1–4] In the last two decades, our group has made continuous efforts to better understand the chemistry of hydrogen evolution from water catalyzed by molecular catalysts having Pt^{II} centers.[4–10]

A typical example of a photosystem that is often employed for the hydrogen evolution side of a half cell is the "three-component system" made up of $[Ru(bpy)_3]^{2+}$ (sensitizer, bpy = 2,2′-bipyridine), MV^{2+} (methylviologen; electron relay), and an H_2-evolving catalyst. In earlier studies we adopted this three-component system to examine the H_2-evolving activity of Pt^{II} complexes in the reduction of water by $MV^{+\bullet}$, which can be generated in situ by the photolysis.[4a,5] Next we wanted to develop bifunctional systems having both photosensitizing centers and H_2-evolving centers, and we invented the first active model of a "photo-hydrogen-evolving (PHE) molecular device" (i.e., RuPt depicted in Scheme 1).[4,6] Such a molecular device is capable of driving photoreduction of water by a sacrificial electron donor (EDTA; ethylenediaminetetraacetic acid) into H_2 as a single-molecular photocatalyst. Moreover, a much simpler model, i.e., $[PtCl(terpyridine)]^+$ (**1**; Scheme 1), was realized to exhibit activity similar to that of RuPt.[7] To better understand and to control the PHE activity of the derivatives of **1**, we recently developed PV^{2+} (Scheme 1).[8] The study revealed that PV^{2+} exhibits a similar redox property to MV^{2+}, and the photochemical H_2 production by PV^{2+} in the presence of EDTA lasts longer owing to the higher stability of the Pt–Cl bond in PV^{2+} in comparison with **1**.[8] However, the photoproducts in the photolysis of **1** or PV^{2+} remained unknown, although it has been well-established that the intramolecular electron transfer from the ^{3}MLCT excited state (MLCT = metal-to-ligand charge transfer) of the $[Ru(bpy)_2(phen)]^{2+}$ unit (phen = 1,10-phenanthroline) to the $PtCl_2(bpy)$ moiety in RuPt is the key process leading to H_2 production from water.[4b,6]



Scheme 1. Chemical structures of PHE molecular devices.

Herein we report that the photolysis of PV^{2+} in the presence of EDTA first generates a one-electron-reduced species ($PV^{+\bullet}$) as an initial photoproduct and this further undergoes a photoinduced process leading to H_2 generation from water. As depicted in Scheme 2, this is the first demonstration of a Z-scheme photosynthesis within the family of artificial molecular systems, although these two-step reductive quenching processes do not perfectly match with the oxidative ones in natural photosynthesis. The present study also demonstrates that the PHE activity can be dramatically enhanced by the presence of a Pt^{II}-based molecular co-catalyst, such as *cis*-$[PtCl_2(NH_3)_2]$, etc.



Scheme 2. A Z-scheme photosynthesis of PV^{2+}.

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As reported,[8] UV/visible light irradiation (350 W; $\lambda >$ 350 nm) of an aqueous acetate buffer solution (pH 5.0) of PV^{2+} in the presence of EDTA results in evolution of H_2 with the turnover number (TON) being 4.1 after 12 h of photolysis (Figure 1 A a). Intriguingly, the photocatalytic performance is drastically enhanced by adding an equimolar amount of a co-catalyst, such as *cis*-$[PtCl_2(NH_3)_2]$ (**2**; Figure 1 A b). The initial rate of H_2 evolution for this "two-component" system ($d[H_2]/dt = 0.82\ \mu L\,min^{-1}$) is nearly four times higher than that of the former "one-component" system ($d[H_2]/dt = 0.21\ \mu L\,min^{-1}$). The total amount of H_2 evolved is also improved in the latter two-component system (0.41 mL, TON = 18.1 at 24 h). Other details are supplied in Table S1 in the Supporting Information.

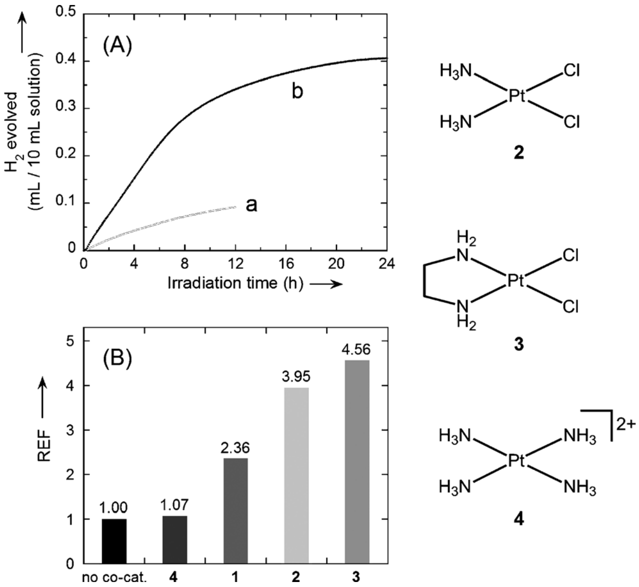

Figure 1. A) Photochemical H_2 production from an aqueous acetate buffer solution (0.1 M, pH 5.0; 10 mL) containing EDTA (30 mM) in the presence of (a) PV^{2+} (0.1 mM; data taken from Ref. [8]), (b) PV^{2+} (0.1 mM) and **2** (0.1 mM). B) Rate-enhancement factors (REFs) for Pt^{II} co-catalysts in the two-component system.

The rate-enhancement factor (REF) of **2** as a co-catalyst can be estimated as REF = 4.0 (Figure 1 B), where REF is defined as ratio of the initial H_2 evolution rate in the presence of the co-catalyst and that in the absence of the co-catalyst. Similarly, the activities of three other Pt^{II} complexes (**1**, **3**, and **4**) as co-catalysts have also been examined (Figure S1 in the Supporting Information). The highest REF value (REF = 4.6) is exhibited by $[PtCl_2(ethylenediamine)]$ (**3**; Figure 1 B). The observed order of **3** > **2** > **1** > **4** in REF values is fully consistent with the order we previously realized when these complexes were employed as major catalysts for the photochemical[5b] or thermal[9] H_2 evolution from water. The $[Pt(NH_3)_4]^{2+}$ cation (**4**) was confirmed to be inactive as an H_2-evolving catalyst; this behavior was attributed to its inability to form a stacked Pt^{II}–Pt^{III}–H intermediate owing to the electrostatic repulsion.[10] The less charged complexes like **2** and **3** seemed to more favorably form such a dimeric intermediate.

As discussed below, we must note here that the major part of the H_2 evolution event does not proceed through a simple dark reaction, i.e., $2H^+ + 2PV^{+\bullet} \rightarrow H_2 + 2PV^{2+}$, which is simply accelerated by the additional Pt^{II} complex as a major catalyst for H_2 formation. In other words, it is not likely that $PV^{+\bullet}$ simply serves as a reductive equivalent that replaces the $MV^{+\bullet}$ in our previous investigations, since H_2 evolution ceases upon light-off treatment (Figure 2). After the initiation of either the light-on or light-off event, it takes approximately ten minutes until the rate of H_2 evolution (gray plots in Figure 2) reaches its pseudo-stationary condition, which is clearly attributable to the fact that the photolysis solution is continuously bubbled with Ar ($10\ mL\,min^{-1}$) for collecting the H_2 evolved during the photolysis.

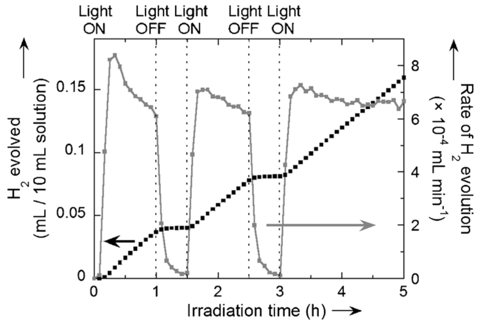

Figure 2. Photoresponse property in the H_2 production by the EDTA/PV^{2+}/**2** system. Black and gray squares correspond to the amount of H_2 evolved and the rate of H_2 evolution, respectively. The experimental conditions are the same as in Figure 1 A b.

In contrast, the evidence for the formation of $PV^{+\bullet}$ during the photolysis is afforded spectrophotometrically. The time-course of spectral changes when a solution of PV^{2+} and EDTA was photolyzed (Figure 3 A) shows the formation of a new species that possesses broad absorption in the visible to near infrared region, where the band is centered at 892 nm, and two isobestic points are seen at 352 and 363 nm (Figure S2 in the Supporting Information). This reaction completes within four minutes (Figure 3 B), and the major photoproduct has been reasonably assigned as $PV^{+\bullet}$ based on the time-dependent density functional theory (DFT) calculation and chemical reduction method using $Na_2S_2O_4$ as a reducing agent (Figures S3 and S4 in the Supporting Information).[8] The same behavior was observed for the EDTA/PV^{2+}/**2** system (Figure S5 in the Supporting Information). The electrochemical reduction of PV^{2+} in aqueous media resulted in electrodeposition of the one- and two-electron reduced species over the glassy carbon electrode (Figure S6 in the Supporting Information). Although the absorption features of $PV^{+\bullet}$ in aqueous media cannot be determined electrochemically, those determined in anhydrous dimethylformamide (DMF) (see Figure S7 in the Supporting Information) qualitatively match the spectral features of the major photoproducts in Figure 3 A,C,D. Based on these results, we conclude that the saturation seen in Figure 3 B corresponds to a quantitative conversion of PV^{2+} into $PV^{+\bullet}$, as a result of reductive quenching of PV^{2+} as depicted in Scheme 2. If this one-

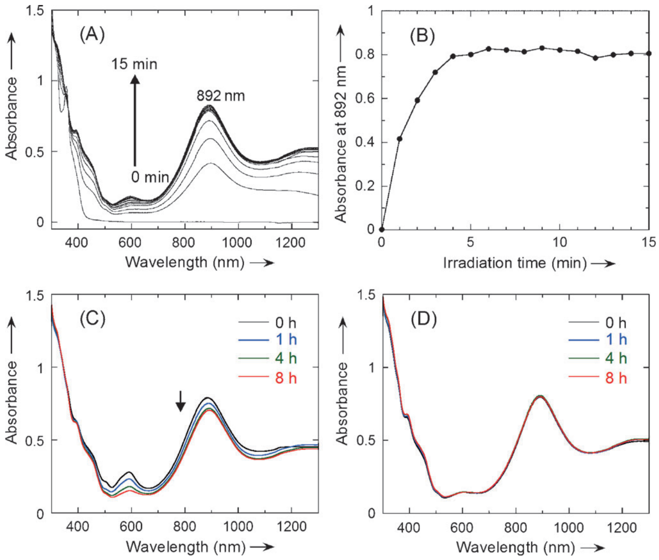

Figure 3. A) Spectral changes during the photolysis of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing EDTA (30 mM) and PV^{2+} (0.1 mM). B) Change of absorbance at 892 nm depending on irradiation time. C, D) Time courses of spectral changes in the dark after 15 min of photolysis in C) the absence and D) the presence of **2** (0.1 mM).

electron-reduced species merely serves as a reductive equivalent for the thermal reduction of $2H^+$ into H_2, $PV^{+\bullet}$ must be rapidly consumed in the H_2 production. However, this species remains unreacted after stopping the light irradiation. $PV^{+\bullet}$ almost remains unreacted overnight in the dark (Figure 3C), thereby revealing that the dark reaction of $2PV^{+\bullet} + 2H^+ \rightarrow 2PV^{2+} + H_2$ is extremely slow even in the presence of a co-catalyst (see Figure 3D), thus indicating that preliminary reduction of the co-catalyst, such as reduction at Pt^{II} to Pt^{I}, does not take place.[11]

Another important feature deduced from the comparison of the dark processes after the formation of $PV^{+\bullet}$ in the absence and presence of **2** is that a minor species that has an absorption maximum at 591 nm only appears in the absence of **2**, and this species gradually decays over eight hours (Figure 3C). Since this behavior was unaffected even when NaCl was added as a chloride source (Figure S8 in the Supporting Information), **2** does not play a role as a simple chloride source. It is reasonable to consider that this species corresponds to doubly reduced species PV^0, which immediately decays in the presence of **2** because of the catalytic enhancement by **2** (Figures 1Ab and 3D; no 591 nm band is observable).[11] Indeed, PV^0, electrochemically generated in DMF, shows a strong 523 nm band assignable to the MLCT band (Figure S7 in the Supporting Information). Such large solvatochromic shifts have been well-documented in literature.[12] Thus we assign the 591 nm absorption band to the doubly reduced species PV^0.

Furthermore, the rate of H_2 formation for the one-component system (EDTA/PV^{2+}) was observed to saturate at higher EDTA concentrations. The rate of H_2 formation, estimated from the initial slope of the H_2 formation curve, saturates at EDTA concentrations above 15 mM (Figure S9 and Table S1 in the Supporting Information). Thus, the reaction rate appears to obey the so-called enzymatic kinetics (i.e., Michaelis–Menten kinetics), suggesting that there is a pre-equilibrium that affords an ion-pair adduct of monoradical $PV^{+\bullet}$ and the anionic forms of EDTA. Under the present experimental conditions [EDTA(2Na) (0.03 M), CH_3CO_2H (0.03 M), and CH_3CO_2Na (0.07 M); pH 5.0], the dianionic form of EDTA (i.e., H_2Y^{2-}, where the fully protonated form is defined as H_4Y) is the major form of EDTA (93 % in relative abundance).[13] Therefore, the adduct formation between $PV^{+\bullet}$ and H_2Y^{2-} (i.e., $[PV^{+\bullet}\cdots H_2Y^{2-}]$) must be regarded as a major form of ion-pair adducts. Very similar enzymatic kinetics were observed for the photochemical H_2 production catalyzed by the first active model of a PHE molecular device[4b,6c] and $[PtCl(terpyridine)]^+$.[7] It is also likely that the first photoreduction step goes via the formation of such an ion-pair adduct ($[PV^{2+}\cdots H_2Y^{2-}]$), as confirmed spectrophotometrically (Figure S11 in the Supporting Information).

The initial H_2 evolution rate was also examined as a function of PV^{2+}. The H_2 evolution rate gradually increases at lower concentrations of PV^{2+} and saturates above 0.1 mM (Figure S12 and Table S1 in the Supporting Information). If the enzymatic kinetics discussed above are simply adopted, the H_2 evolution rate must be proportional to the catalyst concentration according to Equations (1–3):

$$PV^{+\bullet} + H_2Y^{2-} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} [PV^{+\bullet}\cdots H_2Y^{2-}] \xrightarrow{k_{+2}} \tag{1}$$

$$K_S = \frac{[PV^{+\bullet}][H_2Y^{2-}]}{[PV^{+\bullet}\cdots H_2Y^{2-}]} \tag{2}$$

$$v_{H_2} = \frac{k_{+2}[PV^{+\bullet}][H_2Y^{2-}]}{K_S + [H_2Y^{2-}]} \tag{3}$$

where K_s is the dissociation constant, k_{+2} is the H_2 evolution rate constant, and v_{H2} is the rate of H_2 production.

However, the H_2 evolution rate (v_{H2}) clearly saturates at a higher PV^{2+} concentration (Figure S12 in the Supporting Information), thus implying that there is a maximum allowed concentration of $PV^{+\bullet}$ during the photolysis as further discussed below. Since this is a photochemical reaction, the overall reaction rate is basically controlled by the flux of photons absorbed by the photocatalyst. The relative intensity of the photon flux absorbed by each photolysis solution at several sampling wavelengths can be estimated from the absorption spectra for the solutions of PV^{2+} employed in these photolysis experiments (Figure S14 in the Supporting Information). Since the photolysis experiments were carried out by eliminating the wavelengths below 350 nm by the Pyrex glass used in the reaction vessel, light of wavelengths around approximately 370 nm must have a major contribution to the photochemical processes in these experiments. Indeed, the flux of photons absorbed by PV^{2+} gradually saturates at PV^{2+} concentrations above 0.1 mM (Figure S14B in the Supporting Information). Thus, the saturation observed in Figure S11 in the Supporting Information can be partly explained by the saturation in photon absorption.

Finally, we must reconsider a possibility of forming a heteroleptic intermediate in the H_2 formation. The abovementioned higher stability of $PV^{+\bullet}$ in the presence of co-catalyst **2** (Figure 3D) is an indirect evidence implying an interaction between $PV^{+\bullet}$ and **2**. To further understand the association between $PV^{+\bullet}$ and each co-catalyst, the H_2 evolution rate was also examined as a function of the co-catalyst concentration in the two-component system (EDTA/PV^{2+}/**2**; Figure S15 in the Supporting Information). At lower concentrations of **2** (i.e., $[\mathbf{2}] < 0.1$ mM) the initial rate of H_2 formation linearly increases as the concentration of **2** is increased, whereas at higher concentrations (i.e., $[\mathbf{2}] > 0.1$ mM) the H_2 evolution rate saturates. This implies that the H_2 evolution undergoes via the formation of a heteroleptic intermediate, i.e., $[PV^{+\bullet}\cdots\mathbf{2}]$. However, this kind of pre-adduct cannot be the major species, if any, in solution, for the difference in the spectral features of $PV^{+\bullet}$ in the absence and presence of **2** (Figure 3C,D) is almost negligible. Nevertheless, we still cannot rule out the formation of a possible heteroleptic Pt^{II}–Pt^{III}–H intermediate, as discussed elsewhere.[10]

In conclusion, we realized that the overall photocatalytic efficiency in H_2 evolution from water is remarkably improved by adding an extra Pt^{II}-based molecular catalyst to the EDTA/PV^{2+} system. Important findings are that 1) the $PV^{+\bullet}$ generated is stable in solution in the dark, 2) a simple dark reaction of $PV^{+\bullet}$ and a Pt^{II}-based co-catalyst leading to H_2 formation does not proceed, and 3) the H_2-evolving reaction in both one- and two-component system proceeds via the photoexcited state of $PV^{+\bullet}$. This is the first example of molecule-based two-step photoexcitation leading to hydrogen evolution from water, which is reminiscent of the "Z-scheme photosynthesis" in green plants.

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