

A Photo-Hydrogen-Evolving Molecular Device Driving Visible-Light-Induced EDTA-Reduction of Water into Molecular Hydrogen

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Molecular hydrogen is known as a clean-burning fuel free of CO₂ emission and is now considered as a promising candidate to solve the current energy problems.¹ The tris(2,2'-bipyridine)-ruthenium(II) (Ru(bpy)₃²⁺, bpy = 2,2'-bipyridine) has attracted considerable attention for many years due to its potential application as a photosensitizer which promotes the visible-light-induced splitting of H₂O into H₂ and 1/2O₂.² The fundamental concepts on the application of this photosensitizer has been well demonstrated by the observation that the photochemical hydrogen production is effectively promoted upon the visible-light irradiation of an aqueous solution containing three key components shown in Figure 1 (top),

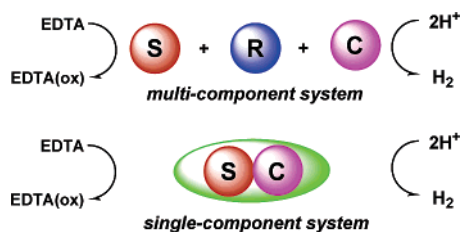


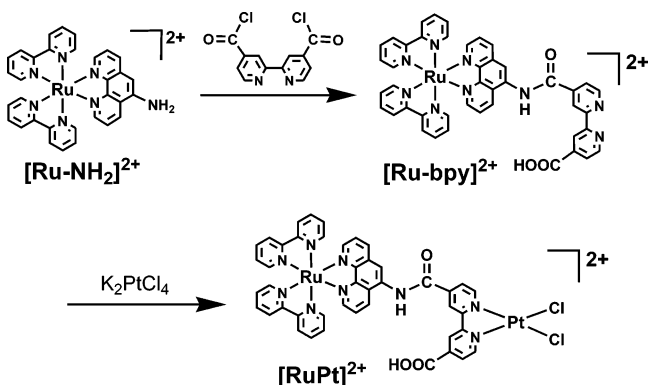
Figure 1. Definition of multicomponent and single-component systems. S denotes a photosensitizer, such as Ru(bpy)₃²⁺. R is an electron relay such as methyl viologen (*N,N'*-dimethyl-4,4'-bipyridinium, abbreviated as MV²⁺). C corresponds to a H₂-evolving catalyst, such as colloidal Pt, Pt(II), or Rh-(I) complexes, etc.

in the presence of a sacrificial electron donor, such as EDTA (ethylenediaminetetraacetic acid disodium salt).³ Some related multicomponent systems revealing the usefulness of Ru(bpy)₃²⁺ have also been reported to date.⁴ On the other hand, we previously demonstrated that certain mononuclear and dinuclear platinum(II) complexes serve as efficient H₂-evolving catalysts in a multicomponent system consisting of EDTA, Ru(bpy)₃²⁺, MV²⁺, and a Pt-(II) complex.^{3c-e} In view of achieving compact and functional artificial photosynthetic devices, we have postulated so far that it is important to study on a single-component system consisting of a Ru(bpy)₃²⁺ derivative and a Pt(II) complex (Figure 1, bottom). We now succeeded for the first time in observing the reduction of water into molecular hydrogen which is photochemically driven by a "photo-hydrogen-evolving molecular device" developed in our group ([RuPt]²⁺ in Scheme 1).

As shown in Scheme 1, [RuPt]²⁺ was prepared as follows. A 1:1 condensation of [Ru-NH₂]²⁺ ([Ru(bpy)₂(5-amino-phen)]²⁺; phen = 1,10-phenanthroline) and 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine afforded a complex ligand [Ru-bpy]²⁺ (yield: 25%).⁶ The chloride salt of this complex was reacted with K₂PtCl₄ in water to give [RuPt]²⁺ (yield: quantitative).^{7,8}

The maximum absorption wavelengths and the molar absorption coefficients at the MLCT bands of [Ru-NH₂]²⁺, [Ru-bpy]²⁺, and

Scheme 1



[RuPt]²⁺ are similar to one another^{6,8} (Figure S3). The luminescence intensity at 610 nm observed for an aqueous solution of [Ru-bpy]²⁺ (under air-equilibrated conditions) is similar to that of [Ru-NH₂]²⁺ but is about 3 times larger than that of [RuPt]²⁺ (Figure S4), implying that a certain intramolecular quenching process, such as an electron-transfer process, is enhanced in [RuPt]²⁺.

The most important finding is that the visible-light-induced EDTA-reduction of water into molecular hydrogen is promoted by [RuPt]Cl₂·3H₂O (Φ(¹/₂H₂) = ca. 1%) (Figure 2a, entry 6 in Table 1), even though a relatively low number of turnovers (4.8) is estimated on the basis of the total amount of H₂ evolved after 10 h (2.4 μmol) and the amount of [RuPt]²⁺ (1 μmol). The photolysis experiments have been repeatedly carried out to confirm the reproducibility of the results. It has also been confirmed that the H₂ formation is not retarded and is rather higher in its rate when ultraviolet lights are eliminated by use of a suitable interference filter (Figure 2b), presumably due to the decrease in the degree of photodegradation of the system.

Several additional experiments have been carried out to ascertain that there is no intervention of any photodecomposition products (entry 1–5 in Table 1). As shown in Table 1, PtCl₂(dcbpy)·H₂O (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) is more or less effective as a hydrogen-evolving catalyst in a multicomponent system (entry 1). However, the H₂ production is completely retarded in the absence of MV²⁺ (entry 3), showing that MV²⁺ plays a crucial role in a multicomponent system. Furthermore, the H₂ production does not occur when a set of [Ru-NH₂]²⁺ and PtCl₂(dcbpy)·H₂O was employed instead of [RuPt]²⁺ (entry 4). Similarly, a set of [Ru-bpy]²⁺ and K₂PtCl₄ in place of [RuPt]²⁺ does not lead to the H₂ formation (entry 5). These results clearly indicate that the covalent bond connecting the Ru(II) sensitizer and the Pt(II) catalyst is essential for the observed "photo-hydrogen-evolving activity" of [RuPt]Cl₂·3H₂O (entry 6).

The wavelength dependence of the rate of H₂ formation (action spectrum) agrees with the absorption spectrum of [RuPt]²⁺ (Figure

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Table 1. Photochemical Hydrogen Production under Various Conditions^a

entry	sensitizer	electron relay	catalyst	$\Phi(^{1/2}\text{H}_2)^b$
1	[Ru(bpy) ₃](NO ₃) ₂ ·3H ₂ O (0.04)	MV(NO ₃) ₂ ·c(2.0)	PtCl ₂ (dcbpy)·H ₂ O (0.1)	0.02
2	[Ru(bpy) ₃](NO ₃) ₂ ·3H ₂ O (0.04)	—	K ₂ PtCl ₄ (0.4)	—
3	[Ru(bpy) ₃](NO ₃) ₂ ·3H ₂ O (0.04)	—	PtCl ₂ (dcbpy)·H ₂ O (0.1)	—
4	[Ru-NH ₂](PF ₆) ₂ ·H ₂ O (0.1)	—	PtCl ₂ (dcbpy)·H ₂ O (0.1)	—
5	[Ru-bpy](PF ₆) ₂ ·3H ₂ O (0.1)	—	K ₂ PtCl ₄ (0.1)	—
6	← [RuPt]Cl ₂ ·3H ₂ O (0.1) →			ca. 0.01

^a Hydrogen production from an aqueous solution (10 mL) containing 30 mM EDTA, 0.03 M CH₃CO₂H, and 0.07 M CH₃CO₂Na (pH = 5.0), in the presence of additional components listed in this table. Other details are given in Figure 2. Values in parentheses are concentrations in mM. ^b The quantum yield was estimated on the basis of the initial rate of H₂ production, as previously described.^{3c-e} ^c Reported in ref 3d.

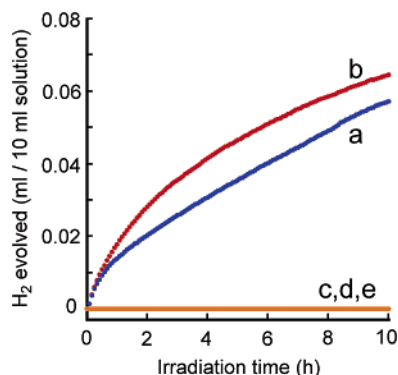


Figure 2. Photochemical H₂ production from aqueous acetate buffer solutions (0.03 M CH₃CO₂H and 0.07 M CH₃CO₂Na; pH 5.0, 10 mL) containing 30 mM EDTA in the presence of additional photocatalysts: (a) 0.1 mM [RuPt]Cl₂·3H₂O (entry 6 in Table 1), (b) 0.1 mM [RuPt]Cl₂·3H₂O (a HOYA L39 interference filter was used to eliminate the lights having wavelengths below 390 nm), (c) 0.04 mM [Ru(bpy)₃](NO₃)₂·3H₂O^{3d} and 0.1 mM PtCl₂(dcbpy)·H₂O (entry 3), (d) 0.1 mM [Ru-NH₂](PF₆)₂·H₂O and 0.1 mM PtCl₂(dcbpy)·H₂O (entry 4), (e) 0.1 mM [Ru-bpy](PF₆)₂·3H₂O and 0.1 mM K₂PtCl₄ (entry 5). The irradiation was carried out using 350 W Xe lamp with a Pyrex-glass filter ($\lambda > \text{ca. } 350 \text{ nm}$), under the continuous flow of Ar (10.0 mL/min), where the vent gas was automatically analyzed by gas chromatography every 5 min. The photolysis solutions were immersed in a water bath thermostated at 20 °C.

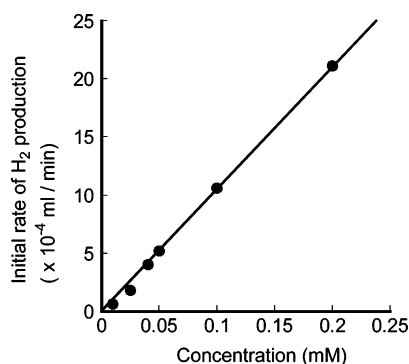


Figure 3. Initial rate of H₂ production as a function of the concentration of [RuPt]Cl₂·3H₂O. Other experimental conditions are same to those described in Figure 2, where the L39 filter was not used in this experiment (additional data in Figure S8).

S6). Moreover, the rate of H₂ formation is confirmed to be linear to the photon flux (Figure S7), revealing that one-photon excitation of a molecule operates. In addition to these results, the rate of H₂ formation is found to be linear to the [RuPt]²⁺ concentration (Figure 3), where the plots at the higher concentration region (0.1–0.2 mM) nearly satisfy a condition required for the complete absorption of

incident photons (see also Figures S5 and S8). A possible interpretation is that the H₂ formation takes place through the reaction of [RuPt]²⁺ and {[RuPt]²⁺}* (the excited state of [RuPt]²⁺). The ultrafast spectroscopic studies must be carried out to settle down the detailed reaction mechanism for the present system.

In summary, we have succeeded in the development of the first example of a photo-hydrogen-evolving molecular device made up of a Ru(bpy)₃²⁺ derivative and a Pt(II)-based H₂-evolving catalyst. We think this is important progress toward the achievement of molecule-based solar energy conversion systems. The extended studies are now in progress in our laboratory.

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Supporting Information Available: All experimental procedures, ESI-TOF MS, absorption, and luminescence spectra. This material is available free of charge via the Internet at <http://pub.acs.org>.

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- (6) Anal. Calcd for [Ru-bpy](PF₆)₂·3H₂O: C, 44.83; H, 3.16; N, 10.69. Found: C, 44.97; H, 3.12; N, 10.63. ESI-TOF mass: *m/z* 417.55 for [Ru-bpy]²⁺ (Figure S1). UV-vis spectrum in H₂O [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 235 (41000), 285 (64600), 450 (15700) (Figure S3).
- (7) Anal. Calcd for [RuPt](PF₆)₂: C, 38.00; H, 2.25; N, 9.06. Found: C, 37.92; H, 2.28; N, 9.11. ESI-TOF mass: *m/z* 550.67 for [RuPt]²⁺ (Figure S2).
- (8) Anal. Calcd for [RuPt]Cl₂·3H₂O: C, 43.11; H, 3.04; N, 10.28. Found: C, 43.39; H, 3.17; N, 10.03. UV-vis spectrum in H₂O [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 285 (61800), 450 (14300) (Figure S3).

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