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Hydrogen Evolution

An Efficient Ru^{II}–Rh^{III}–Ru^{II} Polypyridyl Photocatalyst for Visible-Light-Driven Hydrogen Production in Aqueous Solution**

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Abstract: *The development of multicomponent molecular systems for the photocatalytic reduction of water to hydrogen has experienced considerable growth since the end of the 1970s. Recently, with the aim of improving the efficiency of the catalysis, single-component photocatalysts have been developed in which the photosensitizer is chemically coupled to the hydrogen-evolving catalyst in the same molecule through a bridging ligand. Until now, none of these photocatalysts has operated efficiently in pure aqueous solution: a highly desirable medium for energy-conversion applications. Herein, we introduce a new ruthenium–rhodium polypyridyl complex as the first efficient homogeneous photocatalyst for H_2 production in water with turnover numbers of several hundred. This study also demonstrates unambiguously that the catalytic performance of such systems linked through a nonconjugated bridge is significantly improved as compared to that of a mixture of the separate components.*

Solar-light-induced water splitting into hydrogen and oxygen, also referred as artificial photosynthesis, is a very attractive sustainable approach to produce the fuel H_2 as a clean and renewable energy carrier for the future.[1,2] Since the end of the 1970s, considerable effort has been devoted to the development of multicomponent homogeneous molecular systems for photocatalytic H_2 evolution that consist of a light-harvesting antenna (photosensitizer, PS), a hydrogen-evolving catalyst (HEC), and a sacrificial electron donor coupled or not to an electron mediator.[3–8] However, systems operating in pure aqueous solution—a highly desirable medium for their subsequent application in photoelectrochemical water-splitting devices[9–13]—remain only moderately developed. Among them, efficient molecular systems with a turnover number versus catalyst (denoted TON) above 100 have been obtained with catalysts based on rhodium,[14–17] platinum,[18] and cobalt complexes.[12,19–23] In some cases, TONs of 1000 or more have been reached, generally by using a low concentration of the catalyst in combination with a high PS/HEC ratio.[17,19–21,23]

Besides the development of such multicomponent systems, more recently, various single-component photocatalysts have been designed by coupling the PS and the HEC in the same molecule through a bridging ligand. These molecular photocatalysts, which operate in the presence of an electron donor, combine a Ru, Ir, Re, or Os complex, a porphyrin (Zn, Mg, or Al), or an organic dye as the PS with a Pt, Pd, Rh, Co, or Fe complex as the HEC.[3–8,24–28] However, if the objective is to improve the efficiency of the catalysis by facilitating the intramolecular electron transfer from the PS to the catalyst, the real benefit of such linked systems is often difficult to estimate. Indeed, for linked systems connected through a labile ligand, dissociation can occur, and when a conjugated link is used, it can alter the electronic properties of each component, thus making the comparison with isolated components unsuitable. A few linked systems have provided high catalyst (or photocatalyst) turnover numbers in organic or in aqueous–organic solvents.[3–8,24–26] By contrast, the most active single-component photocatalyst in pure aqueous solution, a cobaloxime catalyst described by Eisenberg and co-workers which is linked to a fluorescein organic dye and associated with triethanolamine (TEOA) as an electron donor,[29] only reached a TON value of 11. The $[\mathrm{Ru(bpy)_2(phen)–(R\text{-}bpy)PtCl_2}]^{2+}$ (bpy = bipyridyl; phen = phenanthroline; R = COOH) photocatalyst designed by Sakai and co-workers,[18,30] in which a platinum(II) catalyst is combined with ruthenium(II) as the PS, exhibited lower activity with a maximum turnover number of 4.8 in the presence of ethylenediaminetetraacetic acid. Finally, the trinuclear complexes $[\{\mathrm{L_2Ru(dpp)}\}_2\mathrm{RhX_2}]^{5+}$ (L = bpy, phen; R = H, Ph; X = Cl^-, Br^-; dpp = 2,3-di(pyridin-2-yl)pyrazine) developed by Brewer and co-workers,[31,32] in which a polypyridinyl rhodium(III) catalyst is connected to two photosensitive ruthenium(II) centers through the conjugated dpp bridging ligand, have also been studied in aqueous media. However, even if these systems are the most efficient photocatalysts in

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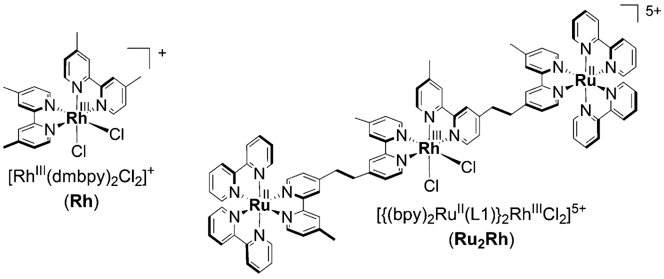
organic solvent (TONs up to 1300 observed in DMF/H_2O (0.62 M) in the presence of *N*,*N*-dimethylaniline), they are almost inactive in pure water (TON limited to 2.9).[33]

We recently reported[17] a very efficient three-component homogeneous system for visible-light-driven hydrogen production in aqueous solution. In the reported system, $[Rh^{III}(dmbpy)_2Cl_2]^+$ (**Rh**; Scheme 1) was employed as the HEC, $[Ru(bpy)_3]^{2+}$ (**Ru**) as the PS, and ascorbic acid (H_2A)/sodium ascorbate (NaHA) (1.1 M) as the sacrificial electron donor. Under optimized conditions (Ru/Rh ratio of 500:1, catalyst concentration of 1×10^{-6} M, pH 4.0), up to 1010 turnovers per catalyst molecule were possible. This finding prompted us to investigate the performance for the photocatalytic production of H_2 in water of a new single-component photocatalyst $[\{Ru(bpy)_2(L1)\}_2RhCl_2]^{5+}$ (**Ru₂Rh**) (L1 = 1,2-bis[4-(4′-methyl-2,2′-bipyridinyl)]ethane; Scheme 1), in which the $[Rh^{III}(dmbpy)_2Cl_2]^+$ catalyst is associated by a covalent link with two $[Ru(bpy)_3]^{2+}$ photoactive units. Herein, we report the synthesis and characterization of **Ru₂Rh**, and its performance in photocatalytic H_2 production. Unlike most previously reported H_2-evolving photocatalysts,[3–8,24–27,34] our photocatalyst contained nonconjugated bridges, which we introduced to maintain intact the desired photophysical and catalytic properties of each unit.[35–37] As we show herein, the **Ru₂Rh** trinuclear complex is the first efficient homogeneous molecular photocatalyst for H_2 production in pure aqueous solution: up to 430 turnovers with respect to rhodium were observed under visible-light irradiation at pH 4.0 in the presence of NaHA and H_2A. Furthermore, the performance of **Ru₂Rh** was clearly improved as compared to that of the mixture of **Ru** and **Rh** components.



Scheme 1. Catalyst and photocatalyst structures.

Ru₂Rh was synthesized in good yield by the treatment of $[Ru(bpy)_2(L1)]^{2+}$ [38] with $RhCl_3\cdot xH_2O$ (for experimental details, see the Supporting Information). The electronic absorption spectrum (see Figure S1 in the Supporting Information) and the cyclic voltammogram (CV; see Figure S2) of **Ru₂Rh** correspond to the superposition of those of the monometallic components in their respective proportions. This superposition confirms that the three metal centers are largely electronically uncoupled.

The redox properties of **Ru₂Rh** are summarized together with those of the model complexes in Table S1 of the Supporting Information. In the positive potential region, the one-electron oxidation processes for the two ruthenium units ($Ru^{II/III}$) overlap, thus resulting in a single reversible two-electron process at $E_{1/2} = +0.93$ V ($\Delta Ep = 60$ mV). In the negative region of the CV, the irreversible two-electron reduction of the central Rh unit ($Rh^{III/I}$) at $Ep_c = -1.26$ V is observed first and is followed at more negative potential by three ligand-centered reduction processes from both Ru and Rh units. A full description of all these processes is given in the Supporting Information.

Photocatalytic hydrogen-evolution experiments were carried out under visible irradiation (400–700 nm) at 298 K in water (5 mL) with **Ru₂Rh** in the concentration range of 1×10^{-6}–1×10^{-5} M in the presence of NaHA (0.55 M) and H_2A (0.55 M) at pH 4.0 (see Table S2 for a summary of the photocatalytic performance of all systems studied). This pH value corresponds to the maximum activity of the **Rh** catalyst.[17] The turnover number (TON) and initial turnover frequency (TOF = TON h^{-1}), which are always defined with respect to the Rh^{III} species, were obtained from experiments involving light irradiation between 13 and 20 h. Control experiments at pH 4.0 in the absence of **Ru₂Rh** or NaHA/H_2A produced no appreciable amount of hydrogen. The formation of rhodium colloids as possible catalytically active species in the course of the photocatalysis was ruled out on the basis of mercury-poisoning experiments (see the Supporting Information). Figure 1 shows the TON values for H_2 formation and the amount of H_2 produced as a function of the irradiation time for **Ru₂Rh** at different concentrations and for the corresponding mixture of compounds **Ru** and **Rh** at equivalent component concentrations. **Ru₂Rh** is a very active H_2-evolving photocatalyst: TONs of about 300 were observed for concentrations of 1×10^{-6} M (280), 2.5×10^{-6} M (320), and 1×10^{-5} M (310), and a TON as high as 430 when **Ru₂Rh** was used at a concentration of 5×10^{-6} M (Figure 1; see also Figure S3). Reproducible values within +/−5% were obtained in repeated experiments.

Hydrogen production thus increased almost linearly with the concentration of the photocatalyst (Figure 1b; see also Figure S3C). This result indicates that, in this range of concentrations, H_2 production is not limited by diffusion, and that efficient intramolecular electron transfer takes place. It is also clear that the photocatalytic activity of **Ru₂Rh** is much higher than that of the corresponding mixture of **Ru** and **Rh** components, whatever the concentration. As the concentration decreases, the difference in activity increases. Indeed, at 1×10^{-5} M, the trinuclear **Ru₂Rh** photocatalyst produces twice as much hydrogen (a TON of 310 versus 150), whereas at 1×10^{-6} M, hydrogen production is up to ten times higher (a TON of 280 versus 28). These observations indicate that the attachment of the PS to the catalyst offers a strong benefit in H_2 generation. A comparison of the H_2-evolving activity of **Ru₂Rh** with that of the separate **Ru** and **Rh** components is relevant in this case, since the **Ru₂Rh** photocatalyst is not prone to undergo dissociation during the course of catalysis, as previously suspected for linked systems with cobaloxime-type catalysts.[8,28] Indeed, during the catalytic cycle, the only chemical modification in the **Ru**/**Rh** systems is the release of the two chloride ligands from the reduced form of the catalyst (Rh^I).[17] The higher efficiency of the trinuclear system may be related to its higher stability, since H_2 evolution continues much longer. H_2 is produced for more

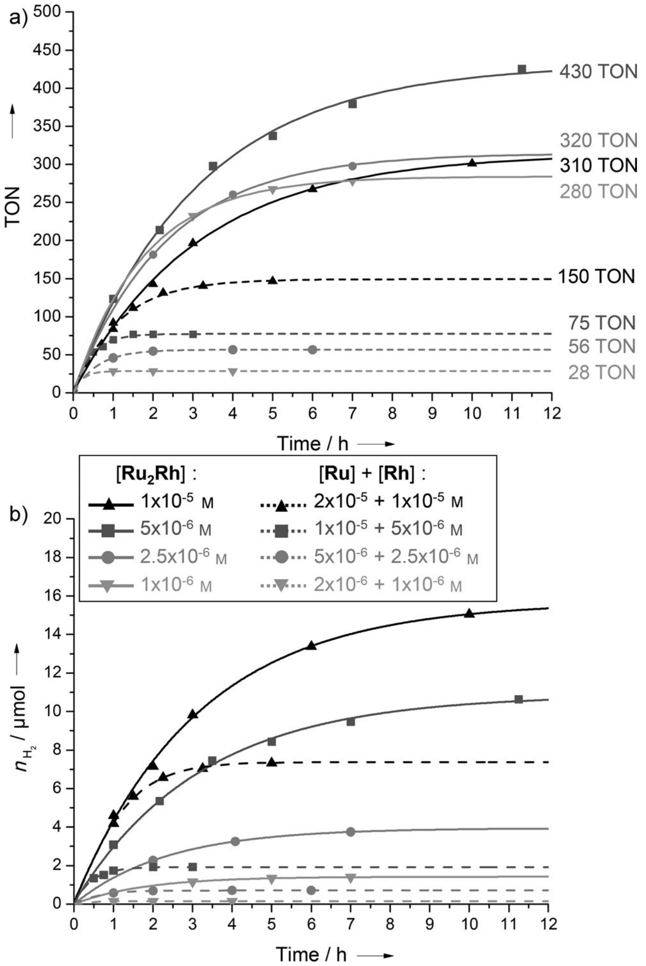


Figure 1. Photocatalytic hydrogen production as a function of time from a deaerated aqueous solution (5 mL) of NaHA (0.55 M) and H_2A (0.55 M) at pH 4.0 under irradiation at $\lambda = 400$–700 nm in the presence of **Ru_2Rh** at various concentrations (solid lines) and for the corresponding mixture of **Ru** and **Rh** compounds (2:1 ratio; dashed lines) in terms of a) TON with respect to the catalyst and b) the number of moles of H_2 produced.

than 12 h with **Ru_2Rh** at 1×10^{-5} M, as compared to 4–5 h for the equivalent mixture of compounds, and for up to 7 h at 1×10^{-6} M, as compared to less than 1 h for the separate compounds. The initial TOF for **Ru_2Rh** (between 101 and 147 h^{-1}) is similar to that of the mixture of complexes for higher concentrations of **Ru**/**Rh** ($2\times10^{-5}/1\times10^{-5}$ M and $1\times10^{-5}/5\times10^{-6}$ M, 110 and 122 h^{-1}, respectively; see Table S2). This similarity suggests that the photoinduced electron transfer from the Ru units to the Rh unit is not likely to be the rate-determining step.[39] The very low stability (less than 1 h) of the **Ru**/**Rh** system for more dilute solutions (**Ru**/**Rh**: $5\times10^{-6}/2.5\times10^{-6}$ M and $2\times10^{-6}/1\times10^{-6}$ M) does not enable a reliable estimation of the TOF. In a photocatalytic experiment combining **Rh** (1×10^{-5} M) with $[Ru(bpy)_2(dmbpy)]^{2+}$ (2×10^{-5} M) as the PS instead of **Ru**, less H_2 was produced (TON: 84) than with the equivalent mixture of **Rh** and **Ru** (TON: 150) or with **Ru_2Rh** at 1×10^{-5} M (TON: 310; see Figure S4), thus confirming that the increase in stability originates from the association of the PS and HEC through an alkyl bridge and is not due to the presence of the two alkyl substituents on one of the bpy ligands of the PS.

Examination of the visible spectrum at the end of photocatalysis with **Ru_2Rh** shows the typical change corresponding to the release of one bpy ligand in the MLCT band of the Ru units (see Figure S5; for experimental details, see the Supporting Information).[17] This phenomenon is known as a cause of the deactivation of photocatalytic systems with $[Ru(bpy)_3]^{2+}$ derivatives in aqueous solution.[40,41] However, this degradation process is undoubtedly slower when the PS is covalently linked to the catalyst, thus resulting in higher TON values as compared to those of the nonconnected system. Therefore, significant savings PS was expected as a result of the use of covalently attached components. This hypothesis was confirmed by the following experiment: For the activity of **Ru_2Rh** at 1×10^{-5} M (i.e., a TON of 310) to be reproduced with an equivalent concentration of the **Rh** catalyst, a **Ru** concentration of 1×10^{-4} M was required (instead of 2×10^{-5} M for **Ru_2Rh**); thus, about five times more of the PS was required (see Figure S6).

In this line, the better stability of the **Ru_2Rh** photocatalytic system under these high-dilution conditions could be the result of a fast intramolecular electron-transfer process between the reduced form of the PS (photogenerated Ru^I) and the Rh^{III} catalyst. This premise was confirmed by photophysical experiments. As mentioned in our previous report on the photogeneration of H_2 from a **Ru**/**Rh** mixture,[17] the PS excited state (denoted Ru*) can undergo 1) reductive quenching by electron transfer from HA^-, whereupon the Ru^I species formed transfers an electron to the Rh unit, and/or 2) oxidative quenching by electron transfer to the Rh unit. Since the Ru* lifetime in **Ru_2Rh** in the absence of HA^- is only moderately decreased (22.5 %) as compared to that in the regular **Ru** complex (see Figure S7), we infer that the oxidative quenching of Ru* is not efficient in the trinuclear photocatalyst, and consequently, that the initial photoinduced electron-transfer process mainly occurs by reductive quenching with HA^-. Scandola and co-workers[42,43] reported several RuL_3–RhL_3 polypyridyl-dyad analogues in which the two units are linked by a conjugated or nonconjugated bridge. For these complexes, the oxidative quenching of the Ru excited state by the Rh unit, with rates ranging from 1.1×10^6 to $3\times10^9\ s^{-1}$, is faster than in **Ru_2Rh** ($4.9\times10^5\ s^{-1}$; see the Supporting Information). This faster oxidative quenching can be ascribed to a larger electron-transfer driving force in the dyads as compared to that in **Ru_2Rh** owing to a less negative reduction potential of the Rh–trisdiimine unit as compared to that of $[Rh(dmbpy)_2Cl_2]^+$.[17]

Nanosecond transient absorption spectroscopy revealed that the rate of disappearance of the Ru excited state, as monitored at 450 nm, is faster ($k = 1.4\times10^7\ s^{-1}$) in **$Ru_2Rh$** than in the bimolecular photocatalytic system ($k = 8.6\times10^6\ s^{-1}$; Figure 2; see also Figure S8).[17] Furthermore, owing to the very fast reduction of Rh^{III} by Ru^I in **Ru_2Rh** by a subnanosecond electron shift, no strong transient absorption typical of the Ru^I species was detected at 510 nm[44] in the 100–500 ns time range (Figure 2 a), in contrast to observations with the bimolecular photocatalytic system (Figure 2 b). The fast consumption of Ru^I in **Ru_2Rh** can limit its degradation by

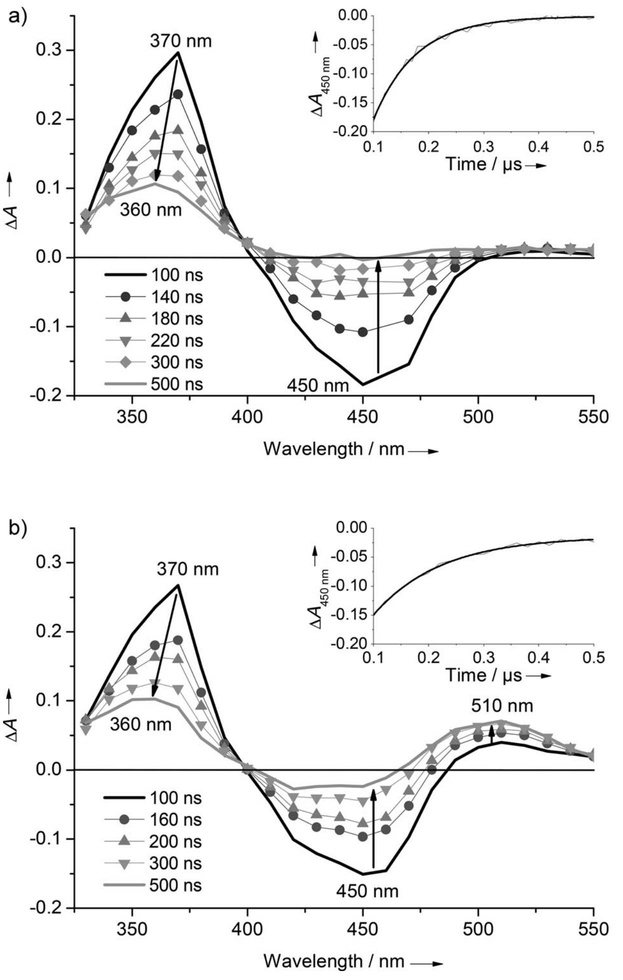


Figure 2. Nanosecond transient absorption spectra (time range: 100–500 ns after laser excitation at 460 nm) of a deaerated aqueous solution containing a) **Ru_2Rh** (5×10^{-5} M) or b) **Ru** (1×10^{-4} M) and **Rh** (2×10^{-4} M), in the presence of H_2A (0.55 M) and NaHA (0.55 M) at pH 4.0 (path length: 1 cm). The insets in (a) and (b) are the respective decay–time profiles of the absorbance at 450 nm as result of the repopulation of the PS ground state.

the loss of one bpy ligand and thus, as mentioned above, improves the global stability of the **Ru_2Rh** photocatalytic system as compared to that of the **Ru**/**Rh** mixture. Several species contribute to the positive transient absorption band at approximately 370 nm (Figure 2): 1) the excited and reduced states of the PS (Ru*, Ru^I species) and 2) the species resulting from the oxidation of ascorbic acid (the ascorbate radicals $HA^{\bullet}$ and $A^{\bullet-}$).[16,45] When the disappearance of the bleach at 450 nm with the **Ru_2Rh**/HA^-/H_2A mixture is complete (Figure 2a), the substantial absorption band remaining at 360 nm is only ascribed to $HA^{\bullet}$ and $A^{\bullet-}$ species.

In summary, the **Ru_2Rh** compound reported herein is the first efficient single-component molecular photocatalyst for H_2 production in pure aqueous solution: Several hundred turnovers were observed at all investigated concentrations (from 1×10^{-5} to 1×10^{-6} M), whereas previously reported homogeneous systems based on a molecular photocatalyst did not exceed a TON of 11 in this solvent.[18,30,33] This study also demonstrates unambiguously the beneficial effects for H_2 production of the use of such a photocatalyst in which the active units are connected by covalent bridges. This arrangement stabilizes the system and enables faster electron transfer from the PS to the HEC. Since the links are nonconjugated, the electronic properties of the active units remain intact, and the benefits observed can only be attributed to their covalent attachment, which maintains them close to each other and thus promotes photoinduced electron transfer by avoiding the need for diffusional contact.

In the future, we plan to synthesize and study similar bimetallic Ru–Rh photocatalysts in which both units are coupled through various conjugated bridging ligands to evaluate the effect of the electronic coupling on photocatalytic performance. Finally, the strategy reported herein can certainly be successfully applied to noble-metal-free systems and systems grafted on semiconductor surfaces.

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