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Photocatalytic H_2 Production by Dirhodium(II,II) Photosensitizers with Red Light

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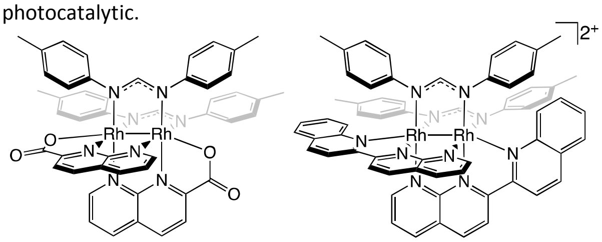
Hannah J. Sayre,[a] Agustin Millet,[b] Kim R. Dunbar,*[b] and Claudia Turro*[a]

Abstract. Photocatalytic proton reduction to generate H_2 was achieved with the photosensitizers $Rh_2(DTolF)_2(npCOO)_2$ (DTolF = *p*-ditolylformamidinate; $npCOO^-$ = 2-carboxylate-1,8-naphthyridine; **1**) and $[Rh_2(DTolF)_2(qnnp)_2][BF_4]_2$ (qnnp = 2-(quinolin-2-yl)-1,8-naphthyridine; **2**) using a relay system containing the sacrificial donor BNAH (1-benzyl-1,4-dihydronicotinamide), electron acceptor MV^{2+} (methylviologen), and Pt nanoparticles as the catalyst with 655 nm irradiation. Comparison of the H_2 evolution under similar experimental conditions show comparable activity of the Rh_2(II,II) complexes (λ_{irr} = 655 nm) to that of the prototypical $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine; **3**) with λ_{irr} = 447 nm. This work demonsrates the ability of the new panchromatic Rh_2(II,II) complexes to achive photocatalysis with red light.

Carbon-free energy sources are increasingly necessary as the human population and energy demand continue to grow.[1] Sunlight is a clean energy source able to meet global demand, but harvesting and storing solar energy remains a challenge.[2] Early reports of photocatalyzed proton reduction to generate H_2 as a solar fuel utilized multicomponent systems with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a photosensitizer.[3] This early work showed the potential of using a light absorber able to transfer electrons to an acceptor relay, which then provides reducing equivalents to a H_2-evolution catalyst. In these schemes, the oxidized sensitizer was regenerated using a sacrificial electron donor, making the system photocatalytic.



1 2

Figure 1. Schematic representation of the structures of $Rh_2(DTolF)_2(npCOO)_2$ (**1**) and $[Rh_2(DTolF)_2(qnnp)_2][BF_4]_2$ (**2**).

Photocatalytic systems for hydrogen evolution have since evolved to include new catalysts in multicomponent systems, dye sensitized solar cells, supramolecular complexes, single-component systems and metal organic frameworks, among others.[4] Although several metal-based photosensitizers have been developed, absorption of lower energy wavelengths beyond 600 nm has been limited and remains a challenge.[5] Although photons in the 600 – 900 nm range possess lower energy than those that are typically utilized in the 300 – 600 nm spectral region, they have sufficient energy for the 1.23 eV water splitting reaction at standard conditions.[6] For example, the photocatalytic proton reduction in Photosystem I is panchromatic, in which the absorption of the chlorophyll pigments extends into the near-IR, and these low-energy photons have been shown to contribute to photosynthesis.[7] Importantly, a significant fraction of the solar flux that reaches the earth is composed of photons in the 660 – 900 nm range. As such, the extension of light absorption into the near-IR in artificial photosynthesis is highly desirable.

Photosensitizers for solar and electrosynthesis cells designed to increase red-light absorption include the N3 dye, quantum dots, and bimetallic supramolecular complexes.[5,8] For example, Hanan and Elias reported an Ir(III)-Co(III) dyad able to access photocatalytic H_2 evolution with irradiation centred at 630 nm, however, the complex exhibits an absorption maximum at 438 nm.[9] Sakai *et al.* recently reported a trimetallic ruthenium polypyridyl photosensitizer with maximum absorption at 600 nm which initiates photocatalytic H_2 production upon 730 nm irradiation.[10]

Dirhodium(II,II) complexes capable of excited-state oxidation[11] and reduction[12] upon irradiation with $\lambda_{irr} \geq 600$ nm were recently reported by us, although their ability to effect photocatalysis has not yet been demonstrated. $Rh_2(DTolF)_2(npCOO)_2$ (**1**; DTolF = *p*-ditolylformamidinate; $npCOO^-$ = 2-carboxylate-1,8-naphthyridine, Figure 1) undergoes photoinduced electron transfer to methyl viologen (MV^{2+}) with $\lambda_{irr} \geq 610$ nm.[11] This finding is important because MV^{2+} has been shown to serve as an effective electron relay between a photosensitizer and catalyst for proton reduction.[10,13] In contrast, $[Rh_2(DTolF)_2(qnnp)_2][BF_4]_2$ (**2**; qnnp = 2-(quinoline-2-yl)-1,8-naphthyridine, Figure 1) was reduced by *p*-phenylenediamine upon irradiation (λ_{irr} = 600 nm).[12] The resulting

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[a] Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210-1340, USA. E-mail: turro.1@osu.edu
[b] Department of Chemistry, Texas A&M University, College Station, Texas 77842, USA. E-mail: dunbar@mail.chem.tamu.edu

reduced complex, $\mathbf{2}^-$, is calculated to possesses sufficient driving force to transfer an electron to the MV^{2+} relay.

In the present work, we show that **1** and **2** can also serve as sensitizers in hydrogen evolution photocatalysis schemes using red light. As such, we chose a photocatalysis relay system previously used with $[Ru(bpy)_3]^{2+}$ (**3**) and conducted parallel experiments with the Rh_2(II,II) sensitizers under 447 nm and 655 nm irradiation. We chose the multicomponent photocatalytic proton reduction system reported by Kagan *et al*., in which ethylenediaminetetraacetic acid (EDTA) served as a sacrificial electron donor, **3** as the photosensitizer, MV^{2+} as the electron relay, and Pt nanoparticles as the catalyst in aqueous acetate buffer.[13] Pt nanoparticles were synthesized as previously reported,[14] and the preparation of **1** and **2** was previously published by us.[11,12]

Photocatalytic proton reduction experiments were conducted with BNAH (1-benzyl-1,4-dihydronicotinamide) as the sacrificial electron donor, either **1** – **3** as a photosensitizer, MV^{2+} as electron relay and Pt nanoparticle catalyst. The components were dissolved in a 1:1 (v:v) mixture of triethylamine acetate (TEAA) aqueous buffer and CH_3CN. Irradiation was conducted by a pair of Luxeon Rebel Star LEDs centered at 655 nm or 447 nm with the power set to 100 mW. Photocatalysis solutions were contained in a 1.5 cm diameter glass tube at a fixed 1.3 cm distance from each LED. The photon flux of the LEDs were determined by chemical actinometry according to established procedure (447 nm LED light flux = 4.9(3) × 10^{-7} mol photon s^{-1}; 655 nm LED light flux = 5.1(2) × 10^{-7} mol photon s^{-1}).[15] The amount of H_2 evolved was quantified by injection of a 200 μL sample of headspace with a Hamilton Gastight SampleLock syringe into a Shimadzu GC-2014 following 20 h irradiation of samples in a cell with 5 mL total solution volume and 5 mL headspace. Turnover numbers (TON) were calculated as moles H_2 per mole K_2PtCl_4 used in Pt nanoparticle synthesis without consideration to dissolved H_2.

The irradiation of the relay system containing **1** and **2** with 655 nm light resulted in the production of 0.31 and 0.54 μmol of H_2 (2.1 and 3.6 TON), respectively (Table 1). This result is comparable to the photocatalyzed H_2 evolution using $\mathbf{3}[PF_6]_2$ as the sensitizer and 447 nm irradiation under similar conditions, 0.40 μmol H_2 (2.7 TON). Electronic absorption spectra before and after irradiation are identical, consistent with the stability of the dyes under prolonged irradiation under catalytic conditions. The quantum yields for H_2 evolution, Φ_{H_2}, are 1.7 × 10^{-5}, 2.9 × 10^{-5} and 1.7 × 10^{-5} for **1**, **2** and **3**, respectively, with BNAH as the sacrificial electron donor. The presence of BNHA reduces the overall yield for all three complexes as compared to other sacrificial donors. For example, the Φ_{H_2} of **3** increases to 1.7 × 10^{-3} with Na_2EDTA, comparable to a report by Sun *et al* in which variations in the Φ_{H_2} of **3** correspond with changes in photocatalysis conditions.[16] Further optimization of conditions is expected to produce increased Φ_{H_2}. It should be noted that the system containing BNAH, MV^{2+}, and Pt nanoparticles in the absence of $\mathbf{3}[PF_6]_2$ is also able to generate a significant amount of H_2 upon λ_{irr} = 447 nm, but not with 655 nm irradiation. Component variation demonstrates that all components, including either **1** or **2**, are required for photocatalytic proton reduction using λ_{irr} = 655 nm because BNAH does not absorb red light (Table 2).

Table 1. Amount of H_2 Evolved after Photolysis.[a]

Sensitizer	⍰⍰⍰⍰⍰	λ_{irr} / nm	H_2 / μmol
1[b]	BNAH	655	0.31(6)
2 [b]	BNAH	655	0.54(8)
$\mathbf{3}[PF_6]_2$ [b]	BNAH	447	0.40(7)
$\mathbf{3}[Cl]_2$ [c]	EDTA[d]	447	40(3)
$\mathbf{3}[PF_6]_2$ [b]	BNAH	655	0

[a]Photosensitizer 150 μM; 30 mM donor, 2 mM MV^{2+}, and Pt nanoparticles from 15 μM K_2PtCl_4.; 20 h irradiation. [b]In 1:1 (v:v) CH_3CN/TEAA aqueous buffer pH 5.5. [c]In aqueous acetate buffer, pH 5.5. [d]EDTA = ethylenediamine tetraacetic acid.

Table 2. H_2 evolved upon component variation.[a]

[BNAH] / mM	[**1**] / μM	$[MV]^{2+}$ / mM	[Pt] / μM	H_2 / μmol
0	150	2	15	0.0
30	0	2	15	0.0
30	150	0	15	0.0
30	150	2	0	0.0

[a]In 1:1 (v:v) CH3CN/TEAA aqueous buffer pH 5.5, λ_{irr} = 655 nm.

It is also evident from the data presented in Table 1 that $\mathbf{3}[PF_6]$ is not able to sensitize the production of H_2 with 655 nm irradiation, as expected from its lack of absorption at this wavelength. To ensure that **3** was indeed an active photosensitizer, the reaction was conducted in aqueous buffer with EDTA as the sacrificial donor, which resulted in good yield of H_2. Attempts to use EDTA and the aqueous buffer for photocatalysis with **1** and **2** were not successful due to the poor solubility of the photosensitizers in water. In addition, EDTA was not soluble in the 1:1 CH_3CN/buffer mixture. While both **1** and **2** sensitize the production of H_2 with red light, their excited state redox potentials dictate that the reaction must proceed via different mechanisms (Table 3). Both complexes possess triplet metal/ligand-to-ligand charge transfer, ^{3}ML-LCT, excited state lifetimes (τ) that are sufficiently long-lived to afford bimolecular charge transfer, τ = 25 ns for **1** and 7 ns for **2**.[11,12] The ^{3}ML-LCT state of **1**, with oxidation potential of –0.49 V *vs* Ag/AgCl, is able to reduce MV^{2+}, $E_{1/2}(MV^{2+/+\bullet})$ = –0.40 V *vs*. Ag/AgCl,[15] as previously shown by us.[11] In contrast, the ^{3}ML-LCT excited state of **2** is not able to reduce MV^{2+}, but has sufficient energy to oxidize the sacrificial donor, $E_{1/2}(BNAH^{+\bullet/0})$ = +0.41 V *vs* Ag/AgCl,[17] such that the reduction of MV^{2+} occurs from the reduced ground state, $\mathbf{2}^-$, following electron transfer from BNAH. Direct electron transfer from the ^{3}ML-LCT excited state of **2** to Pt nanoparticles is not operative, since no H_2 is observed in the absence of MV^{2+} in solution. The rate of H_2 production in the related system described by Kagan *et al*. was shown to be limited by the rate of electron transfer from $MV^{+\bullet}$ to colloidal Pt and by the competitive hydrogenation of MV^{2+} also catalysed by the Pt nanoparticles.[18] The two different pathways for **1** and **2** are depicted in Figures 2a and 2b, respectively.

Several electron donors frequently utilized with other sensitizers are too difficult to oxidize to be used with **1** and **2** (Table 3).[19] BNAH was selected as the electron donor because of its oxidation potential and solubility in a broad range of solvents.[20] While other sacrificial electron donors, such as EDTA ($E_{1/2}$ = +0.62 V *vs*. Ag/AgCl) and ascorbic acid ($E_{1/2}$ = +0.50 V *vs*. Ag/AgCl),[21] satisfy electronic requirements for participation in this photocatalysis system, their use was precluded by insolubility in organic solvents.

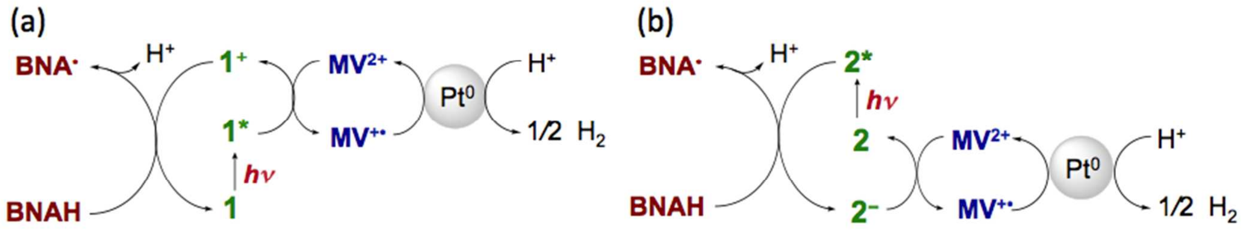

Figure 2. Schematic representation of the distinct mechanisms for photocatalytic H^+ reduction with photosensitizers (a) **1** and (b) **2**.

Table 3. Ground and Excited State Electrochemical Potentials of **1** and **2** in CH_3CN.[a]

Complex	$E_{1/2}$ / V	$E_{1/2}[Rh_2]^{+/*}$ / V[d]	$E_{1/2}[Rh_2]^{*/-}$ / V[d]
1[b]	+0.61, −1.07	−0.49	+0.03
2[c]	+0.99, −0.62	−0.11	+0.48

[a] *vs* Ag/AgCl. [b] From ref. 10. [c] Estimated from ref. 11. [d] E_{00} ~ 1.1 eV from refs. 10 and 11.

The photocatalytic H_2 generation upon 655 nm irradiation was demonstrated with two red-light absorbing photosensitizers. The photocatalysis discussed herein demonstrates that this recently developed class of photosensitizers does in fact initiate photocatalytic reactions. The ground state and excited state redox properties of these dirhodium(II,II) dyes are tunable and can be modified to investigate mechanisms of photocatalytic processes.

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Conflicts of interest

There are no conflicts to declare.

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