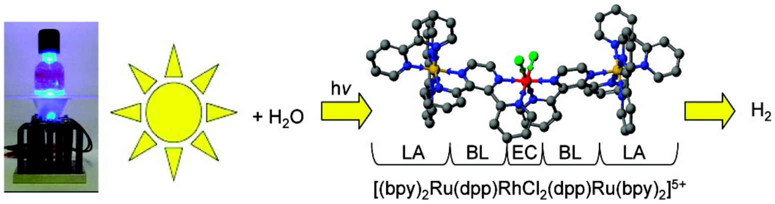
Communication

Photocatalytic Hydrogen Production from Water Employing A Ru, Rh, Ru Molecular Device for Photoinitiated Electron Collection

Mark Elvington, Jared Brown, Shamindri M. Arachchige, and Karen J. Brewer

J. Am. Chem. Soc., **2007**, 129 (35), 10644-10645• DOI: 10.1021/ja073123t • Publication Date (Web): 14 August 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Photocatalytic Hydrogen Production from Water Employing A Ru, Rh, Ru Molecular Device for Photoinitiated Electron Collection

Mark Elvington, Jared Brown, Shamindri M. Arachchige, and Karen J. Brewer*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Received May 3, 2007; E-mail: kbrewer@vt.edu

The need for an alternative energy source is the driving force for light to energy conversion research. This has motivated work towards the development of solar energy conversion schemes.[1−3] The discovery of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) led to photophysical and photochemical studies exploring the use of metal-to-ligand charge transfer (MLCT) states in light-to-energy conversion. $[Ru(bpy)_3]^{2+}$ and similar ruthenium polyazine complexes possess ^{3}MLCT excited states of sufficient energy to drive water splitting to H_2 and O_2. Much work has focused on developing complex supramolecular assemblies with light absorbing metal centers.[4−6] Recent focus on systems using light energy to collect reducing equivalents proposes such systems as potential photocatalysts for H_2 production from water. The successful design and implementation of systems capable of photochemically collecting multiple electrons has proven elusive with none leading to H_2 production from a H_2O substrate.[7−9,11] MacDonnell et al. reported a two-ruthenium bridged system capable of storing up to four reducing equivalents.[7] Trimetallic complexes reported by Bocarsly et al. containing a central platinum core can photochemically collect two electrons leading to fragmentation of the assembly.[8] Only one system, designed for multi-electron photochemistry, reported by Nocera et al., has been shown to generate hydrogen catalytically, which use HX as the substrate (X = halogen such as Cl),[9] $[(PPh)_3Rh^0\text{-}Rh^0(dfpma)_3(CO)]$ (dfpma = $CH_3N(PF_2)_2$). In the presence of a halogen trap, these complexes photocatalytically produce H_2 from HX with $\Phi \approx 0.01$.[9]

Tris(polyazine)rhodium(III) complexes are known to serve as electron acceptors in intermolecular electron-transfer schemes utilizing $[Ru(bpy)_3]^{2+}$ as the light absorber.[10] Upon MLCT excitation of $[Ru(bpy)_3]^{2+}$, bimolecular electron transfer to $[Rh(bpy)_3]^{3+}$ occurs generating $[Rh(bpy)_3]^{2+}$ which can disproportionate to $[Rh(bpy)_2]^{+}$ and $[Rh(bpy)_3]^{3+}$. In the presence of a heterogeneous platinum catalyst, this system can generate hydrogen.[10] Photoinduced H_2 production is reported for a $Ru^{II}(phen)(bpy)_2$ amide coupled to a $Pt^{II}(bpy)Cl_2$ with EDTA displaying a turnover of 4.8.[11]

A unique, homogeneous photocatalyst for H_2 production containing ruthenium light absorbers (LA) and a rhodium electron collector (EC) is reported herein that photocatalytically produces hydrogen from water. The supramolecular complex, $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine), possesses a central Rh^{III} core that serves as an electron collector for multi-electron photochemistry. We reported previously the photoinitiated electron collection by $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2]^{5+}$, resulting in conversion of Rh^{III} to the d^8 square planar Rh^{I} with loss of two chlorides to produce $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$.[12] The newly formed coordinatively unsaturated Rh^{I} is capable of interactions with substrates.

The $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ photoinitiated electron collector displays properties advantageous for the application to photocatalytically produce H_2 from H_2O. The electronic absorption spectroscopy of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ displays bpy and dpp based $\pi \rightarrow \pi^*$ transitions in the UV and Ru → bpy and Ru → dpp CT transitions in the visible. The lowest energy transition is a Ru → dpp CT transition at 520 nm. The lowest unoccupied molecular orbital (LUMO) in this complex is $Rh(d\sigma^*)$ providing a lowest lying ^{3}MMCT state. The optically populated ^{3}MLCT state is weakly emissive $\Phi^{em} = 7.3 \times 10^{-5}$ in CH_3CN solution with no impact on emission intensity with addition of 0.62 M H_2O indicating k_{et} to populate the ^{3}MMCT state is not changed. The cyclic voltammogram shows overlapping $Ru^{II/III}$ oxidations at 1.63 V (vs Ag/AgCl), an irreversible $Rh^{III/II/I}$ couple at −0.37 V, followed by two reversible $dpp^{0/-}$ couples at −0.76 and −1.00 V.[12] The addition of 0.62 M H_2O to CH_3CN (Supporting Information) results in no change in the potentials of the redox couples but an increase in reductive current for the second reduction at −0.76 V which could be indicative of electrocatalysis of H_2O reduction to produce H_2.

Table 1. Photocatalysis of H_2 Production Using a Supramolecular Catalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$

[complex] (μM)	[DMA] (M)	[H_2O] (M)[a]	Photolysis time (hr)	H_2 (μmol)
65	1.5	0.62	1	2.4
65	1.5	0.62	2	4.7
65	1.5	0.62	3	6.3
65	1.5	0.62	4	8.2
65	0	0.62	2	<0.02
0	1.5	0.62	2	<0.02
65	1.5	0.62	0	<0.02
55	1.5	0.62	2	4.8
70	1.5	0.62	2	4.7
65	1.5	0.62 (HCl)[b]	2	3.4
61	0.35	0.62	2	0.3
61	0.73	0.62	2	1.2
61	2.2	0.62	2	8.1
61	1.5	6.2 (pH3)[c]	2	4.7
mono[d]	1.5	0.62	2	0.5

[a] M of H_2O in final photolysis solution; pH of H_2O added was adjusted to 2.0 with CF_3SO_3. [b] pH of H_2O adjusted to 2.0 with HCl. [c] pH of H_2O added was adjusted to 3.0 with CF_3SO_3. [d] A 2:1 ratio of $[(bpy)_2Ru(dpp)\}(PF_6)_2$: $[Rh(dpp)_2Cl_2](PF_6)_2$, 122 and 61 μM, respectively.

The complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ produces hydrogen catalytically when excited with visible light (470 nm) in an acetonitrile/water solution in the presence of dimethylaniline (DMA) with $\Phi \approx 0.01$, assuming two photons are used to produce H_2. Photolyses were conducted using an LED array.[13] Hydrogen was quantified by gas chromatography using a molecular sieves column with Ar as the carrier gas. Detailed experimental procedure is provided as Supporting Information. Upon photolysis of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ in the presence of DMA and H_2O, a color change is observed that is a result of the shift of the Ru → dpp CT band from 520 to 460 nm, Supporting Information. This shift in the Ru → dpp CT band is consistent with Rh reduction from Rh^{III} to Rh^{I}.[12] The spectroscopy along with the above-discussed electrochemistry suggests that $[(bpy)_2Ru(dpp^-)Rh^{I}(dpp)Ru(bpy)_2]^{4+}$ is the active catalyst.

10.1021/ja073123t CCC: $37.00 © 2007 American Chemical Society

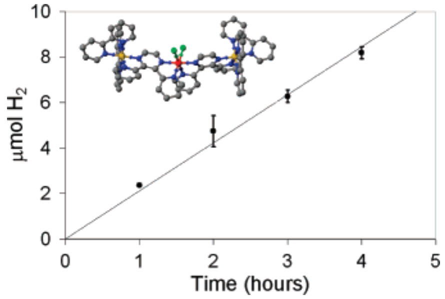


Figure 1. Photocatalytic H_2 production by $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ in CH_3CN/H_2O solution using dimethylaniline (DMA) as an electron donor, excited at 470 nm using a 5 W LED. Photolysis of 65 μM $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ with 0.62 M H_2O and 1.5 M DMA results in H_2 production that varies linearly with photolysis time.

The production of hydrogen by the photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ is impacted by a variety of factors. The catalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, H_2O, and an electron donor (DMA) are all necessary for H_2 production, Table 1. Photolysis of 65 μM $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ in CH_3CN/H_2O with 1.5 M DMA at 470 nm results in the production of H_2 that varies linearly with photolysis time (Figure 1). The presence of large amounts of DMA makes the reaction conditions basic. Assuming the pK_a of DMA is not greatly perturbed relative to aqueous conditions, the effective pH can be estimated as ca. 9.1 under the conditions used in Figure 1. Following photolysis of the $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, DMA and acidified water mixture for 4 h, 8.2 μmol of H_2 are produced representing 30 turnovers of the catalytic system with no reduction in the rate of H_2 production. Continued photolysis for 6 h results in continued increase in the pressure in the head space with a concurrent reduction of ca. 30% in H_2 production efficiency.

Hydrogen generation by the photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ is impaired by chloride addition. Photolysis of 65 μM $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ in CH_3CN/H_2O for 2 h produces 3.4 μmol H_2 with 7×10^{-4} M added HCl versus 4.7 μmol H_2 using HCF_3SO_3 as the proton source. The inhibition of catalysis by Cl^- addition is consistent with Rh^{III} to Rh^I reduction with Cl^- loss being photocatalytically important. The H_2 production efficiency increases with increasing [DMA], consistent with the known electron-transfer quenching of the ^{3}MLCT state by DMA.[12] The addition of large amounts of H_2O does not change catalyst functioning indicating that, at these concentration ranges, H_2O is in sufficient excess to not limit H_2 production. Increasing photocatalyst concentration does not impact H_2 production in the 45−90 μM range where the photocatalyst absorbs all the light from the LED source. The photolysis of a mixture of the monometallic components of this system, $[(bpy)_2Ru(dpp)](PF_6)_2$ and $[Rh(dpp)_2Cl_2](PF_6)$, does lead to H_2 production with a much lower yield indicating the advantage of trimetallic assembly. The speciation of the related $[Rh^I(bpy)_2]^+$ complex in aqueous solution has been studied in detail.[14] In the basic pH region under which our photocatalytic experiments are carried out, the bpy analogue exists as $[Rh^I(bpy)_2]^+$ in equilibrium with a dimer $[Rh^I(bpy)_2]_2^{2+}$ and a protonated dimer $[Rh^I(bpy)_2]_2H^{3+}$. The presence of the large $(bpy)_2Ru^{II}(dpp)$ subunits on the reduced trimetallic $[\{(bpy)_2Ru(dpp)\}_2Rh^I]^{5+}$ will likely prohibit dimerization of this Rh^I complex. The nature of the Rh^I complex and the catalytic cycle are the subject of ongoing studies.

The complex $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2](PF_6)_5$ undergoes photoinitated electron collection in CH_3CN solution in the presence of DMA with maintenance of the Ru, Rh, Ru supramolecular assembly $[\{(bpy)_2Ru(dpp)\}_2Rh^I]^{5+}$ allowing the reported use of this system for multi-electron chemistry. Addition of water to the photochemical system results in the photocatalytic production of hydrogen. This represents a unique structural motif whereby photoinitiated electron collection occurs at a metal enabling multi-electron reduction of water to H_2. The rate of hydrogen production is decreased by chloride addition and increased by increasing electron donor concentration. The photocatalytic production of hydrogen from water using a homogeneous supramolecular assembly will allow for more detailed analysis of system functioning and enhancement of functioning by component modification. Studies are underway to explore this and related systems in more detail.

Acknowledgment. Acknowledgement is made to the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy for their generous support of this research.

Supporting Information Available: Materials and methods, LED array schematic, statistical analysis, electrochemistry of CH_3CN/H_2O, and spectroscopy during catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Campagna, S.; Serroni, S.; Puntoriero, F.; Di Pietro, C.; Ricevuto, V. In *Electron Transfer in Chemistry;* Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 168 and references therein. (b) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. A. *Coord. Chem. Rev.* **1975**, *15*, 321.
(2) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1576.
(3) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(4) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; NATO ASI Series 214, Reidel: Dordrecht, The Netherlands, 1987; p 1 and references therein.
(5) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759 and references therein.
(6) Serroni, S.; Campagna, S.; Puntoriero, F.; Loiseau, F.; Ricevuto, V.; Passsalacqua, R.; Galletta, M. *C. R. Acad. Sci., Ser. IIc: Chim.* **2003**, *6*, 883.
(7) (a) Konduri, R.; Ye, H.; MacDonnell, F. M.; Serroni, S.; Campagna, S.; Rajeshwar, K. *Angew. Chem., Int. Ed.* **2002**, *41* (17), 3185. (b) Chiorboli, C.; Fracasso, S.; Scandola, F.; Campagna, S.; Serroni, S.; Konduri, R.; MacDonnell, F. M. *Chem. Commun.* **2003**, 1658. (c) Chiorboli, C.; Fracasso, S.; Ravaglia, M.; Scandola, F.; Campagna, S.; Wouters, K.; Konduri, R.; MacDonnell, F. *Inorg. Chem.* **2005**, *44* (23), 8368.
(8) (a) Chang, C. C.; Pfennig, B.; Bocarsly, A. B. *Coord. Chem. Rev.* **2000**, *208*, 33. (b) Watson, D. F.; Tan, H. S.; Schreiber, E.; Mordas, C., J.; Bocarsly, A. B. *J. Phys. Chem. A* **2004**, *108*, 3261. (c) Mordas, C.; Pfennig, B.; Schreiber, E.; Bocarsly, A. B. *Springer Ser. Chem. Phys.* **2003**, *71*, 453.
(9) (a) Heyduk, A. F.; Nocera, D. G. *Science* **2001**, *293*, 1639. (b) Nocera, D.; Heyduk, A. *PCT Int. Appl.* **2003**, 157. (c) Gray, T.; Nocera, D. *Chem. Commun*. **2005**, *12*, 1540. (d) Esswein, A.; Veige, A.; Nocera, D. *J. Am. Chem. Soc.* **2005**, *127* (47), 16641.
(10) (a) Brown, G. M.; Chan, S. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc*. **1979**, *101*, 7638. (b) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.
(11) Ozawai, H.; Haga, M.; Sakai, K. *J. Am. Chem. Soc.* **2006**, *128*, 4926.
(12) Elvington, M.; Brewer, K. J. *Inorg. Chem.* **2006**, *45*, 5242.
(13) Brown, J. R.; Elvington, M.; Mongelli, M. T.; Zigler, D. F.; Brewer, K. *Proc. SPIE-Opt. Photo. Sol. Hydrogen Nanotechnol.* **2006**, *6340*, 634007W1-13.
(14) Chou, M.; Creutz, C.; Mahajan, D.; Sutin, N.; Zipp, A. R. *Inorg. Chem.* **1982**, *21*, 3989.

JA073123T