Photocatalysis

International Edition: DOI: 10.1002/anie.201506567
German Edition: DOI: 10.1002/ange.201506567

Increased Water Reduction Efficiency of Polyelectrolyte-Bound Trimetallic [Ru,Rh,Ru] Photocatalysts in Air-Saturated Aqueous Solutions

Theodore R. Canterbury, Shamindri M. Arachchige, Robert B. Moore, and Karen J. Brewer*†

Abstract: *The groundbreaking use of polyelectrolytes to increase the efficiency of supramolecular photocatalysts in solar H_2 production schemes under aqueous aerobic conditions is reported. Supramolecular photocatalysts of the architecture $[\{(TL)_2Ru(BL)\}_2RhX_2]^{5+}$ (BL = bridging ligand, TL = terminal ligand, X = halide) demonstrate high efficiencies in deoxygenated organic solvents but do not function in air-saturated aqueous solution because of the quenching of the metal-to-ligand charge-transfer (MLCT) excited state under these conditions. The new photocatalytic system incorporates poly(4-styrenesulfonate) (PSS) into aqueous solutions containing $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine). PSS has a profound impact on the photocatalyst efficiency, increasing H_2 production over three times that of deoxygenated aqueous solutions alone. H_2 photocatalysis proceeds even under aerobic conditions for PSS-containing solutions, an exciting consequence for solar hydrogen-production research.*

The development of stable water reduction photocatalysts that perform efficiently in aerobic aqueous solutions is a major challenge for solar energy researchers,[1] and few successful systems exist to date.[2] Early heterogeneous, multicomponent water reduction systems based on Ru chromophores and colloidal Pt were limited by diffusion and collisional quenching.[3] Homogeneous systems that couple a Ru chromophore to a reactive metal center have shown increased electron-transfer efficiency.[4] These supramolecular complexes undergo photoinitiated electron collection (PEC) to store multiple reducing equivalents to drive H_2 production from water.[5]

Supramolecular complexes, of the molecular architecture $[\{(TL)_2Ru(BL)\}_2RhX_2]^{5+}$, that couple two Ru^{II} chromophores to a Rh^{III} electron collector through dpp bridging ligands were the first reported systems to undergo PEC at Rh^{III} to form intact Rh^{I} species that function as active water reduction catalysts (dpp = 2,3-bis(2-pyridyl)pyrazine).[4e] The [Ru,Rh,Ru] photocatalysts achieve high turnover numbers (TON) in deoxygenated organic solutions but limited activity is observed in aqueous solution with activity fully suppressed under aerobic conditions.[6]

Many factors contribute to decreased efficiency in aerobic aqueous solutions, quenching of the triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state of the Ru^{II} chromophore being a primary obstacle.[6a] Efficient quenching of the excited Ru^{II} complexes in aqueous aerobic solutions is attributed to energy transfer to O_2 as well as transfer of energy to water through O−H stretching frequencies.[7]

Early studies of Ru^{II} polypyridyl complexes demonstrated that the addition of PSS to aqueous solutions increased the luminescence and excited-state lifetime in both argon-purged and air-saturated solutions.[8] PSS is a low-cost, water-soluble polymer commonly used as an ion exchange medium (Figure 1 A). The polyelectrolyte contains a hydrophobic backbone and a negatively charged hydrophilic side group that interacts strongly with positively charged photocatalysts. Herein we report groundbreaking use of PSS to increase efficiency of [Ru,Rh,Ru] supramolecular water reduction photocatalysts in aqueous solutions, including H_2 production under aerobic conditions.

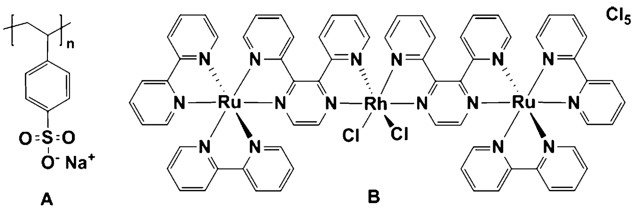

Figure 1. Structures of A) poly(styrenesulfonate) and B) $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$.

The previously reported trimetallic complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ [Ru,Rh,Ru] (Figure 1 B) was synthesized using a building block approach.[4c,e] Electrochemical analyses (see Figure S1 in the Supporting Information) for the photocatalyst give evidence for a Ru-based highest occupied molecular orbital (HOMO) and Rh-based lowest unoccupied molecular orbital (LUMO).[4e] The Rh^{III} undergoes two overlapping one-electron reductions to generate a Rh^{I} species that functions as the water reduction catalyst.[4e]

The [Ru,Rh,Ru] complex is an efficient light absorber in the UV and visible regions (Figure S2). Electronic absorption transitions in the UV are assigned to dpp($\pi\rightarrow\pi^*$) and bpy($\pi\rightarrow\pi^*$) intraligand (IL) transitions with Ru(dπ)→dpp(π^*) and Ru(dπ)→bpy(π^*) MLCT transitions dominating

---

[*] T. R. Canterbury, Dr. S. M. Arachchige, Prof. R. B. Moore, Prof. K. J. Brewer
Department of Chemistry, Virginia Tech
Blacksburg, VA 24061-0212 (USA)
E-mail: rbmoore3@vt.edu

[†] Deceased, October 24, 2014

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201506567.

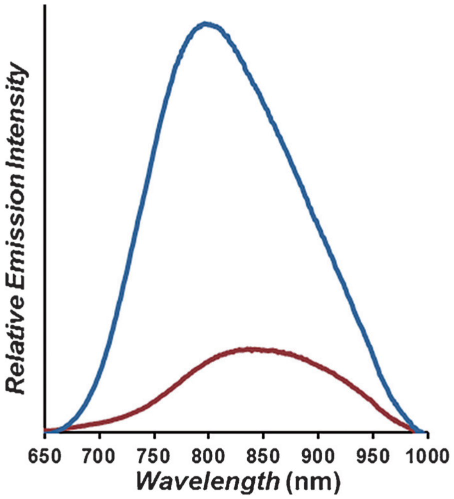

Figure 2. Emission profile of [Ru,Rh,Ru] (10 μM) in (red) aqueous solution and (blue) 2.5 mM poly(4-styrenesulfonate). Spectra corrected for PMT response (PMT = photomultiplier tube). Measured in pH 7 deoxygenated aqueous solutions at 23 °C.

in the visible. These spectral transitions are unperturbed in the presence of PSS.

Steady-state emission spectroscopy (Figure 2) provides insight into the excited-state dynamics of the complex in the presence and absence of polyelectrolytes. In organic solvent, CH_3CN, emission from the ^{3}MLCT excited state of [Ru,Rh,Ru] ($\lambda_{em} = 780$ nm, quantum yield of emission, $\Phi^{em} = 2.8 \times 10^{-4}$) is greatly quenched compared to the $[\{(bpy)_2Ru\}_2(dpp)]^{4+}$ model complex ($\Phi^{em} = 1.4 \times 10^{-3}$) due to the presence of low-lying Rh(dσ)-based acceptor orbitals in [Ru,Rh,Ru] that allow for electron collection on the catalytic center through a metal-to-metal charge transfer (MMCT) excited state (Figure 3).[4e] In deoxygenated aqueous solution the ^{3}MLCT excited state is further quenched ($\Phi^{em} = 1.4 \times 10^{-5}$; Table 1).

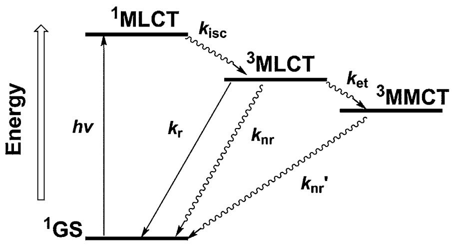

Figure 3. Simplified Jablonski-type state diagram for [Ru,Rh,Ru].

Table 1: Photophysical properties of [Ru,Rh,Ru].

Solvent	λ_{max}^{abs} [nm][a]	λ_{max}^{em} [nm][a]	Φ^{em} [$\times 10^4$][a,b]	τ [ns][a]	α[c]
CH_3CN	516	780	2.8	38	–
H_2O	518	845	0.14	14	–
H_2O (2.5 mM PSS)	518	798	1.7	35[d]	0.74

[a] Measured in deoxygenated H_2O at RT using a 1 cm quartz cuvette. [b] Referenced to $Os(bpy)_3^{2+}$. [c] α = pre-exponential factor. [d] Additional decay component of 63 ns ($\alpha = 0.26$) was observed.

Addition of PSS ($M_w = 68300$, PDI = 1.18) to aqueous solutions of [Ru,Rh,Ru] dramatically increases the emission intensity from the ^{3}MLCT excited state ($\Phi^{em} = 1.7 \times 10^{-4}$). Consistent with previous studies on Ru chromophores, addition of poly(vinyl sulfonate) (PVS), without a hydrophobic side group, does not alter the excited-state dynamics of the [Ru,Rh,Ru] motif (Figure S3)[9] attributing the increased Φ^{em} in the presence of PSS to strong interaction of the chromophore with the hydrophobic polymer backbone which decreases the vibrational non-radiative decay (k_{nr}) thus increasing the radiative decay (k_r).[8e,f,c] The emission energy ($\lambda_{max}{}^{em}$) for the [Ru,Rh,Ru] photocatalyst shows a hypsochromic shift in PSS ($\lambda_{em} = 798$ nm) consistent with decreased solvent reorganization following excitation.[7b] The lifetime (τ) of the ^{3}MLCT excited state for the photocatalyst in aqueous solution is short-lived ($\tau = 14$ ns) which increases (35 ns) and becomes bi-exponential in the presence of 2.5 mM PSS, suggesting the complex resides in multiple microenvironments in PSS solutions (Figure S5).[8e] The increased ^{3}MLCT excited-state lifetime for the photocatalyst in the presence of PSS is a promising result as the lifetime of the excited state plays a major role in electron transfer to the reactive metal center and photocatalytic efficiency.[6b]

Stern–Volmer analysis of [Ru,Rh,Ru] using ascorbate (HA^-) as electron donor (Figure S4) shows decreased quenching rates in the presence of PSS ($k_q = 3.4 \times 10^8$ M^{-1} s^{-1}) relative to its absence ($k_q = 2.4 \times 10^{11}$ M^{-1} s^{-1}). The higher k_q in the absence of PSS is likely the result of preassociation of the quencher with the photocatalyst in solution.[4e] When PSS is present, coulombic repulsion of the quencher by the negatively charged polymer along with decreased mobility of the complex upon binding to the polyanion most likely leads to the lower k_q.[8d]

Addition of PSS to deoxygenated aqueous solutions of [Ru,Rh,Ru] results in the formation of aggregates, which are not observed for the individual components. Morphology of the aggregates was investigated using cryogenic transmission electron microscopy (Cryo-TEM).[10] The findings indicate that globules of approximately 20 nm in diameter aggregate to form larger structures on the order of 1–2 microns (Figure 4), similar to porphyrin:PSS assemblies.[10] Dynamic light scattering experiments were used to confirm aggregate dimensions (Figure S6). Aggregate size and structure have been shown to play an important role in electron-transfer efficiency and could greatly impact quenching of the photocatalyst in solution.[11]

Photolysis of [Ru,Rh,Ru] solutions using ascorbate buffer (H_2A/HA^-) as sacrificial electron donor affords $[\{(bpy)_2Ru(dpp)\}_2Rh^I]^{5+}$, consistent with previous studies.[4e] A hypsochromic shift of the low-energy Ru(dπ)→dpp(π*) transition is observed, consistent with photoreduction of the reactive metal center from Rh^{III}-Rh^I (Figure 5).

Interestingly, in deoxygenated solutions, complete photoreduction to the active Rh^I species in the absence of PSS requires 4.5 h but decreases to only 2 h in the presence of 2.5 mM PSS. Photolysis in air-saturated aqueous solutions greatly increases the photoreduction time to 20 h in the absence of the

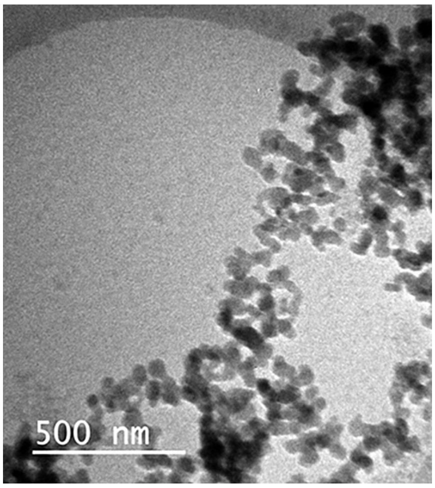

Figure 4. Cryo-TEM of aggregate formation between PSS (0.5 mM) and [Ru,Rh,Ru] (120 μM) in aqueous solution.

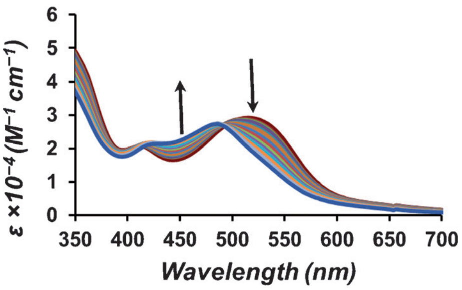

Figure 5. Electronic absorbance of [Ru,Rh,Ru] (65 μM) during photoreduction in deoxygenated aqueous solutions containing 1.1 M H_2A/HA^-. Spectra measured in 15 min intervals over 4 h.

polyanion but only requires 4 h to reach completion in the presence of PSS (Figure S7). The increased photoreduction rate to the active Rh^I species in PSS solutions is a promising result and may provide insight into H_2 photocatalysis for these systems.

In pH 4 H_2A/HA^- (1.1M), [Ru,Rh,Ru] functions as a photocatalyst to produce H_2 from water upon photolysis with visible light (470 nm). The catalytic efficiency of the complex is greatly reduced in deoxygenated aqueous solutions, achieving only 15 TON compared to 30 TON in CH_3CN using *N*,*N*-dimethylaniline (DMA) as sacrificial reductant.[4c] Upon the addition of PSS to deoxygenated aqueous solutions, substantially enhanced photocatalytic activity is observed, achieving up to 46 TON after 10 h of irradiation (Figure 6). H_2 production in the presence of 2.5 mM sodium *p*-toluenesulfonate (TS) was similar to aqueous solutions without PSS, indicating that the styrene sulfonate unit must be in the polymeric form to impact catalyst efficiency. Control experiments confirmed H_2 production was only achieved in the presence of the photocatalyst.

To investigate the impact of polyelectrolytes on catalyst function in the presence of O_2 (Table 2), photolysis was carried out in air-saturated aqueous solutions. In solutions without PSS or in those containing TS, H_2 production is not observed, even after 24 h of irradiation. However, upon the addition of 2.5 mM PSS, photocatalytic water reduction proceeds even in the presence of O_2, achieving 30 TON after 10 h of irradiation. The increased O_2 resistance in the presence of PSS is attributed to increased local ionic strength near the polyanion which decreases O_2 solubility.[8d]

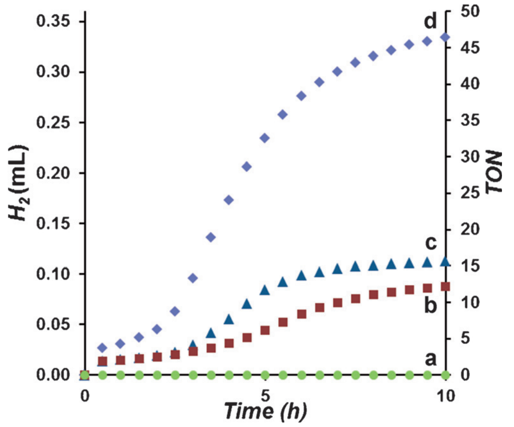

Figure 6. H_2 production of [Ru,Rh,Ru] in deoxygenated pH 4 H_2A/HA^- a) without catalyst, b) [catalyst] = 65 μM, [TS] = 2.5 mM, c) [catalyst] = 65 μM, d) [catalyst] = 65 μM, [PSS] = 2.5 mM.

Table 2: H_2 production of [Ru,Rh,Ru] in the presence and absence of PSS under argon-purged and air-saturated conditions.

Complex[a] [65 μM]	Solution[b]	Purge	H_2 [μmol]	TON[c]
[Ru,Rh,Ru]	2.5 mM PSS	argon	15.0 ± 0.5	46 ± 2
[Ru,Rh,Ru]	2.5 mM TS	argon	3.9 ± 0.3	12 ± 1
[Ru,Rh,Ru]	H_2O	argon	4.9 ± 0.5	15 ± 1
[Ru,Rh,Ru]	2.5 mM PSS	air	9.8 ± 0.4	30 ± 1
[Ru,Rh,Ru]	2.5 mM TS	air	none detected	none detected
[Ru,Rh,Ru]	H_2O	air	none detected	none detected

[a] Solution volume 5 mL containing 65 μM catalyst. [b] 1.1 M H_2A/HA^- (pH 4). [c] Turnovers per Rh catalyst center.

The addition of PSS to aqueous solutions of [Ru,Rh,Ru] has a profound impact on the photophysics and H_2 production of the supramolecule. Quenching of the ^{3}MLCT excited state is greatly decreased in PSS solutions because of the strong interaction between the polypyridyl ligands and the hydrophobic backbone of the polymer resulting in an increased Φ^{em} and τ for the supramolecule, favorable for photocatalyst functioning. Cryo-TEM studies show evidence for aggregate formation between the photocatalyst and PSS which may greatly impact electron-transfer efficiency as well as quenching of the ^{3}MLCT excited state. An unprecedented increase in photocatalyst activity was observed in aqueous solutions containing PSS, producing over three times as much H_2 fuel as that without PSS. A photocatalytic system resistant to high levels of O_2 has also been achieved with addition of PSS, taking advantage of the decreased O_2 solubility due to high local ionic strength near the polyanion. The increased efficiency and O_2 resistance observed with the addition of a low-cost, abundant polyelectrolyte is a promising method to optimize hydrogen-evolving catalysts is easily incorporated into many other photocatalytic schemes. Current work is focused on investigating electron transfer processes using transient absorption techniques.

Acknowledgements

Acknowledgement is made to the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Sciences, U.S. Department of Energy (grant number DE FG02-05ER15751) and Virginia Tech Institute for Critical Technology and Applied Science (ICTAS) for the generous financial support for our research. Acknowledgement is also made to Hannah M. Rogers for assistance with manuscript preparation.

Keywords: hydrogen · photocatalysis · polyelectrolytes · rhodium · ruthenium

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12819–12822
Angew. Chem. **2015**, *127*, 13010–13013

[1] J. R. McKone, N. S. Lewis, H. B. Gray, *Chem. Mater.* **2014**, *26*, 407–414.
[2] a) H. I. Karunadasa, C. J. Chang, J. R. Long, *Nature* **2010**, *464*, 1329–1333; b) H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* **2012**, *335*, 698–702; c) B. D. Stubbert, J. C. Peters, H. B. Gray, *J. Am. Chem. Soc.* **2011**, *133*, 18070–18073; d) C. C. L. McCrory, C. Uyeda, J. C. Peters, *J. Am. Chem. Soc.* **2012**, *134*, 3164–3170; e) T. Sakai, D. Mersch, E. Reisner, *Angew. Chem. Int. Ed.* **2013**, *52*, 12313–12316; *Angew. Chem.* **2013**, *125*, 12539–12542.
[3] a) J.-P. Sauvage, Jean-Marie Lehn, *Nouv. J. Chim.* **1977**, *1*, 0; b) M. Kirch, J.-M. Lehn, J.-P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345–1384; c) C. Creutz, A. D. Keller, N. Sutin, A. P. Zipp, *J. Am. Chem. Soc.* **1982**, *104*, 3618–3627.
[4] a) M. Schulz, M. Karnahl, M. Schwalbe, J. G. Vos, *Coord. Chem. Rev.* **2012**, *256*, 1682–1705; b) K. Sakai, H. Ozawa, *Coord. Chem. Rev.* **2007**, *251*, 2753–2766; c) M. Elvington, J. Brown, S. M. Arachchige, K. J. Brewer, *J. Am. Chem. Soc.* **2007**, *129*, 10644–10645; d) T. Stoll, M. Gennari, J. Fortage, C. E. Castillo, M. Rebarz, M. Sliwa, O. Poizat, F. Odobel, A. Deronzier, M.-N. Collomb, *Angew. Chem. Int. Ed.* **2014**, *53*, 1654–1658; *Angew. Chem.* **2014**, *126*, 1680–1684; e) M. Elvington, K. J. Brewer, *Inorg. Chem.* **2006**, *45*, 5242–5244; f) K. Kalyanasundaram, M. Graetzel, M. K. Nazeeruddin, *J. Phys. Chem.* **1992**, *96*, 5865–5872.
[5] V. Balzani, L. Moggi, F. Scandola in *Supramolecular Photochemistry*, *Vol. 214* (Ed.: V. Balzani), Springer, Amsterdam, **1987**, pp. 1–28.
[6] a) K. Rangan, S. M. Arachchige, J. R. Brown, K. J. Brewer, *Energy Environ. Sci.* **2009**, *2*, 410–419; b) T. A. White, S. L. H. Higgins, S. M. Arachchige, K. J. Brewer, *Angew. Chem. Int. Ed.* **2011**, *50*, 12209–12213; *Angew. Chem.* **2011**, *123*, 12417–12421; c) T. A. White, B. N. Whitaker, K. J. Brewer, *J. Am. Chem. Soc.* **2011**, *133*, 15332–15334.
[7] a) J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590; b) P. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439–1478; c) J. Van Houten, R. J. Watts, *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.
[8] a) E. R. Alvarez-Roa, N. E. Prieto, C. R. Martin, *Anal. Chem.* **1984**, *56*, 1939–1944; b) M. W. Espenscheid, A. R. Ghatak-Roy, R. B. Moore, R. M. Penner, M. N. Szentirmay, C. R. Martin, *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 1051–1070; c) J. W. Park, M. H. Kim, S. H. Ko, Y. H. Paik, *J. Phys. Chem.* **1993**, *97*, 5424–5429; d) G. L. Duveneck, C. V. Kumar, N. J. Turro, J. K. Barton, *J. Phys. Chem.* **1988**, *92*, 2028–2032; e) C. Turro, S. H. Bossmann, S. Niu, J. K. Barton, N. J. Turro, *Inorg. Chim. Acta* **1996**, *252*, 333–338; f) E. M. Tuite, D. B. Rose, P. M. Ennis, J. M. Kelly, *Phys. Chem. Chem. Phys.* **2012**, *14*, 3681–3692.
[9] D. Meisel, M. S. Matheson, *J. Am. Chem. Soc.* **1977**, *99*, 6577–6581.
[10] C. Ruthard, M. Maskos, U. Kolb, F. Gröhn, *J. Phys. Chem. B* **2011**, *115*, 5716–5729.
[11] S. Frühbeißer, F. Gröhn, *J. Am. Chem. Soc.* **2012**, *134*, 14267–14270.

Received: July 16, 2015