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COMMUNICATIONS

Reductive Side of Water Splitting in Artificial Photosynthesis: New Homogeneous Photosystems of Great Activity and Mechanistic Insight

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Abstract: Rhodamine photosensitizers (PSs) substituting S or Se for O in the xanthene ring give turnover numbers (TONs) as high as 9000 for the generation of hydrogen via the reduction of water using [Co^{III}(dmgH)$_2$(py)Cl] (where dmgH = dimethylglyoximate and py = pyridine) as the catalyst and triethanolamine as the sacrificial electron donor. The turnover frequencies were 0, 1700, and 5500 mol H_2/mol PS/h for O, S, and Se derivatives, respectively (Φ_{H_2} = 0%, 12.2%, and 32.8%, respectively), which correlates well with relative triplet yields estimated from quantum yields for singlet oxygen generation. Phosphorescence from the excited PS was quenched by the sacrificial electron donor. Fluorescence lifetimes were similar for the O- and S-containing rhodamines (~2.6 ns) and shorter for the Se analog (~0.1 ns). These data suggest a reaction pathway involving reductive quenching of the triplet excited state of the PS giving the reduced PS^- that then transfers an electron to the Co catalyst. The longer-lived triplet state is necessary for effective bimolecular electron transfer. While the cobalt/rhodamine/triethanolamine system gives unprecedented yields of hydrogen for the photoreduction of water, mechanistic insights regarding the overall reaction pathway as well as system degradation offer significant guidance to developing even more stable and efficient photocatalytic systems.

For light-to-chemical energy conversion as embodied in artificial photosynthesis, the splitting of water into its constituent elements is the key reaction, both energetically and environmentally, that must be accomplished. Despite many proof-of-concept studies related to this problem,[1−20] great challenges remain regarding both the photogeneration of H_2 from aqueous protons and the oxidation of water in terms of system activity and robustness. This communication deals with important developments regarding the photogeneration of H_2 from water that describe new highly active systems incorporating dye sensitizers not previously studied for photoreduction of water with photochemical and photophysical measurements that provide critical insight into the light-driven steps of the catalysis.

In 2009, a homogeneous system for the photoreduction of water to H_2 was reported that did not contain a noble metal in either the photosensitizer (PS) or the catalyst.[21] The system employed the brominated fluorescein-based dye Eosin Y as the PS, [Co^{III}(dmgH)$_2$(py)Cl] where dmgH = dimethylglyoximate and py = pyridine as the catalyst, and triethanolamine (TEOA) as the sacrificial electron donor and produced >800 turnovers of H_2 with a quantum yield of 4% for 520−540 nm light. The system, however, was subject to photodecomposition, as was another active system using the iodine-containing dye Rose Bengal as the PS. Since unhalogenated fluoroscein did not yield H_2 in a similar system, it was proposed that the halogen substituent facilitated intersystem crossing (ISC) giving access to the $^3\pi\pi^*$ state from which bimolecular electron transfer chemistry leading to H_2 occurs.[22,23] However, the C−Br and C−I bonds of these dyes were also viewed as the source of their photodecomposition through reductive quenching and C−X cleavage from the reduced PS.

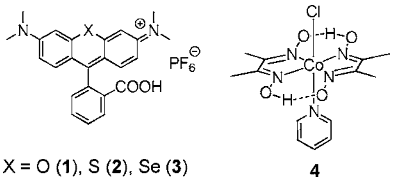

Figure 1. Structures of photosensitizers **1**−**3** and [Co^{III}(dmgH)$_2$(py)Cl] (**4**) (where dmgH = dimethylglyoximate, py = pyridine).

To eliminate this problem, we turned to rhodamine dye analogs containing S (**2**) or Se (**3**) in place of O (**1**) in the xanthene ring as shown in Figure 1. It is known that photophysical properties including the rate of ISC to the triplet $\pi\pi^*$ state of the dye are influenced by the heteroatom in the ring.[24−29] We report here a system with dye **3** as the PS that shows the highest TOF (turnover frequency) yet reported for the photoreduction of water (>5500 mol H_2/mol PS/h and a turnover number (TON) per PS of over 9000 after 8 h). In addition to finding the most active PS to date for the evolution of H_2 from water, we have been able to elucidate details of the system that were previously difficult to examine with less active systems. Through control of system component concentrations (catalyst, PS, and TEOA), the overall stability, turnover frquency (TOF), and length of the induction period are altered, yielding insight into the photochemical steps of the reaction system.

The TOFs for systems using **1**−**3** as the PS with irradiation from 520-nm LEDs (0.15 W, 5% TEOA in 1:1 CH_3CN/H_2O, pH 7) are 0, 1700, and 5500 TON/h respectively. While the system containing **1** as the PS does not produce H_2, quantum yields for H_2 production (Φ_{H_2}) for the systems containing **2** and **3** are very high, 12.2 ± 1.2% and 32.8 ± 1.4%, respectively, as calculated using power meter measurements of the incident photon flux and analysis of photogenerated H_2 by the pressure change in the reaction flask and GC analysis. These are among the highest yet reported.[20] In the quantum yield analysis, two electrons per incident photon are assumed since TEOA upon oxidation decomposes with transfer of a second reducing electron. Since the redox potentials and emission energies of **1**, **2**, and **3** are similar (Table 1), the inactivity of the system containing **1** cannot lie with the energetics of its excited state, but rather with the kinetics of the excited state from which electron transfer occurs.

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Table 1. Electrochemical and Photophysical Properties of Dyes **1**−**3** and Rates of H_2 Generation for Systems with **4** as the Catalyst

	Red. (V)[b]	Ox. (V)[b]	λ_{max} abs (nm) (ϵ M^{-1} cm^{-1})[c]	λ_{max} em (nm)[d]	Φ_F emission[d]	τ_{FL} (ns)[d]	$\Phi(^1O_2)$[d]	TOF[e]	Φ_{H_2}
1	−0.75	+1.23[a]	547 nm (59 000)[c]	580	0.43 ± 0.08	2.69 ± 0.02	0.05 ± 0.03	0	0%
2	−0.66[a]	+1.28	560 nm (72 000)	590	0.47 ± 0.09	2.55 ± 0.04	0.17 ± 0.01	1700	12.2%
3	−0.54	+1.46	570 nm (51 000)	600	0.075 ± 0.019	0.118 ± 0.007	0.67 ± 0.01	5500	32.8%

[a] Quasireversible with $i_p^c/i_p^a < 0.8$ for oxidations or $i_p^a/i_p^c < 0.8$ for reductions, scan speed of 0.25 V s^{-1}; irreversible at 0.1 V s^{-1}. [b] Measured in acetonitrile. [c] Acetonitrile with 0.1% 1 M HCl added. [d] In methanol. [e] Mol of H_2/mol of photosensitizer per hour.

While the fluorescence lifetimes, τ_{Fl}, for dyes **1** and **2** are similar and 20-fold shorter for **3** (2.69 ± 0.02 ns for **1**, 2.55 ± 0.04 ns for **2**, and 0.118 ± 0.007 ns for **3**) (Table 1), the presence of S and Se in **2** and **3** facilitates ISC that leads to population of the longer-lived triplet excited states from which electron transfer occurs. The intersystem crossing efficiencies of **1**−**3** can be estimated from quantum yields for singlet oxygen generation [$\Phi(^1O_2)$] through $^3PS^*$ quenching by molecular oxygen. Experimentally determined values of $\Phi(^1O_2)$ are 0.05 ± 0.01 for **1**, 0.17 ± 0.04 for **2**, and 0.67 ± 0.04 for **3** (Table 1). Although the triplet lifetimes for **2** and **3** were not measured, the analogs of **2** and **3**, not having the −COOH substituent (a tetramethylrosamine dye analog), have a reported triplet excited-state lifetime, τ_T, of 1−2 μs and ~340 ns in MeOH at 293 K respectively, both of which are >1000-fold longer than the corresponding singlet excited state.[27]

The ^3PS excited state is therefore long enough lived for bimolecular electron transfer leading to H_2 generation to be favorable relative to radiative and nonradiative decay back to the ground state. Electron transfer quenching of the ^3PS excited state can be either oxidative or reductive, leading respectively to PS^+ with electron transfer *from* the dye to the catalyst or PS^- with electron transfer *to* the dye from the sacrificial reductant TEOA. For **2** and **3** with their higher ISC efficiencies, electron-transfer quenching provides the path to H_2 generation. In fact, an excellent correlation can be seen in Table 1 between the $^1O_2$ yields for these dyes and both the TOF and Φ_{H_2}.

Electron transfer from the ^3PS excited state of **3** was confirmed through emission quenching studies. As expected, neither TEOA nor the catalyst **4** quenches the singlet state ($^1PS^*$) fluorescence (600 nm) of **3**. In contrast, the triplet state phosphorescence of **3** (750 nm)[27] is quenched by TEOA, but *not* by Co complex **4**, as shown in emission spectra of **3** that decreases only with the addition of TEOA and not with **4** (see Supporting Information). These observations indicate that electron transfer comes from the ^3PS excited state through a reductive quenching mechanism only.

Plots of H_2 generation as a function of different component concentrations from irradiation at 520 nm are shown in Figure 2. In these plots, rapid and nearly linear initial rates give way to photodecomposition and cessation of H_2 production. Figure 2a shows the effect of PS concentration, whereas Figure 2b reveals the influence of Co catalyst concentration. As seen in Figure 2a, both the initial rate and the total amount of H_2 produced increase as the PS concentration is increased, although the TONs based on mol of H_2 per mol of PS actually decrease as [PS] increases, possibly due to greater collisional deactivation of the ^3PS excited state. The influence of [PS] on the H_2 generation rate suggests that the reduction of the PS is rate limiting. This is supported by the pseudolinear rate dependence for H_2 formation on TEOA concentration, since the TEOA would be involved in the reductive quenching of the PS excited state (see Supporting Information).

In Figure 2b, the initial rates of H_2 generation are similar for all three catalyst concentrations, [**4**], in the range of 5×10^{-5}−2×10^{-4} M, but the system longevity for making H_2 is affected. At higher values of [**4**], H_2 generation lasts longer, resulting in greater total amounts of H_2. These data are consistent with two competing pathways for the reduced PS: nondestructive electron transfer to the catalyst and a competitive unimolecular degradation pathway for PS^-. The partitioning of PS^- between these two pathways is affected by [**4**]; at higher concentrations of **4**, H_2 formation is more favorable relative to first-order decomposition of PS^-.

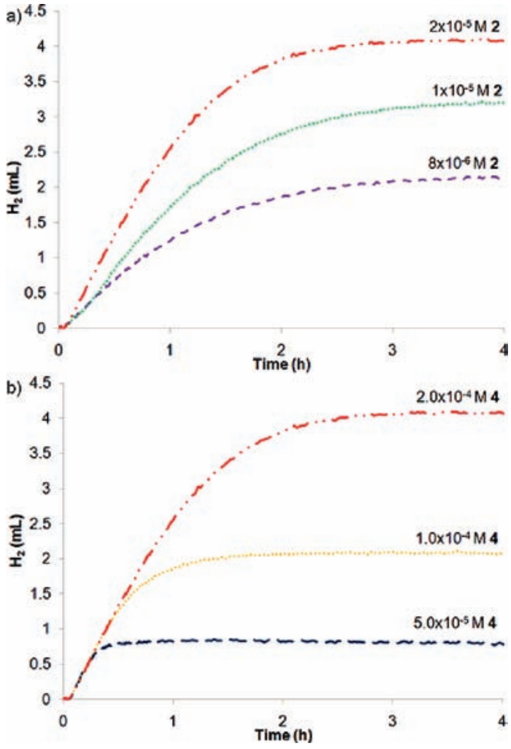
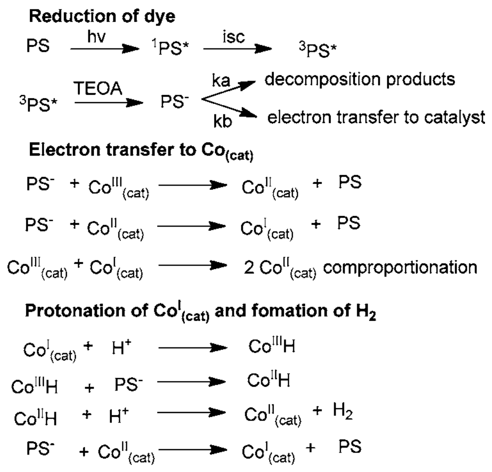


Figure 2. Hydrogen generation in 5% TEOA in 1:1 CH_3CN/H_2O, pH 7 (irradiated with 520 nm LED): (a) effect of varying [**2**] in a system containing 2.0×10^{-4} M **4**; (b) effect of varying [**4**] with 2.0×10^{-5} M **2**.

As [**4**] is increased beyond 5×10^{-4} M, an induction period for H_2 production is noted and the TONs based on PS concentration decrease (see Supporting Information). It has previously been proposed based on studies using **4** with a different PS that H_2 generation occurs with reduction of Co(II) to Co(I) followed by protonation to form a Co(III) hydride intermediate. For **4** which is a Co(III) complex, initial reduction of Co(III) to Co(II) must occur prior to H_2 generation, and at higher values of [**4**] this initial reduction leads to the observed induction period. This hypothesis is supported by running the reaction with $Co^{II}(BF_4)_2 \cdot 6H_2O$ and free dmgH as the catalyst precursors; no induction period is observed under these conditions.

The activity of the system can be prolonged leading to greater H_2 formation by the addition of extra $dmgH_2$ ligand to the system. A system with 5×10^{-5} M of **4** and 2×10^{-4} M of extra $dmgH_2$ (3×10^{-4} M dmgH total) is longer lived (2 h) and produces more H_2 than a system with more Co, but less *total* dmgH, with 1×10^{-4} M of **4** (2×10^{-4} M of *coordinated* dmgH), and is shorter

Scheme 1. Reaction Scheme for H_2 Photogeneration



lived than a system with 2×10^{-4} M **4** (4×10^{-4} M *coordinated* dmgH) (4 h) (Supporting Information). It thus appears that the dimethylglyoxime ligand is being degraded during the course of the photolysis and is a key cause of system instability. It also suggests that the coordinated dmgH ligand is labile and undergoes exchange with free $dmgH_2$ in solution. Nevertheless, through the addition of extra $dmgH_2$ during the course of the photolysis, *more than 9000 turnovers/PS of H_2 in 8 h has been achieved with irradiation at 520 nm.*

When the concentration of **4** is low enough such that the catalyst is rate limiting, there is a *linear* dependence of the initial rate of H_2 generation with respect to the concentration of **4** (Supporting Information). This observation is consistent with previous reports in which the H_2-generating mechanism is found to be first order in cobalt.[11,21] At a low concentration of catalyst, however, the system degrades quickly as can be observed by the cessation of H_2 evolution and a color change associated with a bleach of the PS. Addition of either **4** or PS alone does not restart H_2 generation indicating that both catalyst and PS undergo decomposition when H_2 production stops. Addition of *both* catalyst and PS is needed for the system to restart H_2 generation. The actual mechanism by which the Co(III) hydride reacts further to form H_2, by either monometallic or bimetallic pathways, remains uncertain and may in fact be system dependent. The pathway favored by us based on the linear relationship of H_2 formation with [**4**] is shown in Scheme 1, along with the photochemical steps of the system.

Bleaching of photosensitizers **2** and **3** during H_2 generation contrasts with the fact that they are stable under continuous irradiation with $\lambda > 455$ nm in $MeCN/H_2O$ solutions. However, a solution of only the PS and TEOA degrades very rapidly under irradiation. The lifetime of the dye in the presence of TEOA can be prolonged, by the addition of **4** as an electron acceptor. When followed by UV−vis spectroscopy for a system containing **3**, the band assigned to $Co(II)(dmg)_2$ at 440 nm grows in over a few minutes, followed by a slow bleach of this band over the next hour, indicating catalyst decomposition. The intensity of the PS absorption at 570 nm for **3** decreases only slightly for the first 30 min of irradiation and then rapidly when the 440 nm band becomes weak (Supporting Information). It thus appears that decomposition of the PS and the catalyst are coupled.

The fact that reductive quenching leads to H_2 formation and at the same time leads to PS decomposition when $Co(II)(dmgH)_2$ is no longer present suggests a branch point in the photochemical cycle. At high concentrations of $[Co(II)(dmgH)_2]$, electron transfer from PS^- to the catalyst results in H_2 generation, while, at very low concentrations of $[Co(II)(dmgH)_2]$, unimolecular photodecomposition of the PS becomes favored over electron transfer and subsequent productive chemistry. Figure 2 is consistent with this analysis. The rate of H_2 generation is initially constant, indicating constant PS concentration. However, during the photolysis, the concentration of **4**, initially present in sizable excess, declines. While this is not observed as a change in H_2 production rate, when the concentration of catalyst becomes too low, partitioning of the PS to decomposition becomes increasingly favored, as a rapid decline and cessation of H_2 production occur as first the catalyst and then the PS photodecompose.

The activity and stability of the systems we have reported rely on both favorable thermodynamics and kinetics for the steps leading to H_2 generation. There are several branch points in Scheme 1 from which two competing paths exist; appropriate conditions must be used so that the desired path can dominate. First, the ^3PS excited state is crucial for H_2 generation because its longer lifetime allows *bimolecular* electron transfer to compete effectively with radiative and nonradiative decay paths. Second, the operating stability of the PS depends on the rate of electron transfer by PS^- to the Co catalyst relative to unimolecular decomposition. Third, added $dmgH_2$ extends the functional lifetime of the system, most likely through ligand exchange. Each of these factors is under active study going forward including new sacrificial electron donors, catalysts more resistant to decomposition, and PSs that can either tolerate reductive quenching or function by an oxidative quenching pathway.

In summary, S- and Se-substituted rhodamine dyes have been used as PSs for the photogeneration of H_2 from water in a system containing $Co(dmgH)_2pyCl$ as the catalyst and TEOA as the sacrificial electron donor. The system is highly active and has allowed elucidation of the photochemical steps for H_2 production and system decomposition. Knowledge of these steps is essential for the design of more effective systems for the reductive side of water splitting.

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Supporting Information Available: Detailed experimental procedures, luminescence of singlet oxygen, quantum yield calculations, H_2 vs time under various conditions, phosphorescent quenching, UV−vis of reaction mixture over time. This material is available free of charge via the Internet at http://pubs.acs.org.

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