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Photocatalytic Generation of Hydrogen from Water Using a Platinum(II) Terpyridyl Acetylide Chromophore

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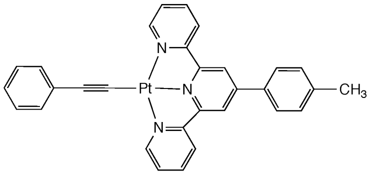
Photochemical water splitting using visible light represents one of the “grand challenges” in artificial photosynthesis. The reduction side of this reaction is the light-driven generation of H_2 from aqueous protons and an electron source. Numerous studies have dealt with this conversion, commencing in the 1970s with reports describing multiple component systems containing Ru(bpy)$_3^{2+}$ as the chromophore, methyl viologen (MV^{2+}) as both quencher and electron transfer mediator, a metal colloidal catalyst, and a sacrificial electron donor.[1−3] Subsequent studies have dealt with variations of these systems, including attachment of the chromophore to platinized TiO_2 particles,[4−8] and the use of different chromophores, such as Zn(II) porphyrins[9−11] and cyclometalated [Ir(C∧N)$_2$(N∧N)]-Cl complexes.[12,13] Other recent studies on the light-driven generation of H_2 have included the photochemical reduction of HBr solutions (along with bromine trapping) using dinuclear Rh complexes[14] and the liberation of H_2 from Hantzsch 1,4-dihydropyridines using Pt(terpy)(arylacetylide)$^+$ complexes (terpy = 2,2′:6′,2′′-terpyridine) as photocatalysts via a proposed H atom abstraction.[15] In the present communication, we report the use of the same and related Pt(terpy)-(arylacetylide)$^+$ complexes as chromophores for the light-driven production of H_2 from aqueous protons in the presence of a sacrificial electron donor. This is the first time that such platinum terpyridyl complexes have been used in this capacity.

Complex **1** was synthesized as reported previously[16] by the reaction of [Pt(4′-*p*-tolyl-terpy)Cl]Cl with phenylacetylene in the presence of CuI as the catalyst in triethylamine/DMF. Complex **1** exhibits a broad low energy absorption band in MeCN:water (2:3 v/v) between 375 and 540 nm with λ_{max} at 420 nm ($\epsilon \sim 7700$ dm^3 mol^{-1} cm^{-1}) (Figure 1) that corresponds to the dπ(Pt)−π*(terpy) metal-to-ligand charge transfer (MLCT) transition. The absorption wavelength differs from that reported previously (433 and 482 nm) because of a solvent change from dichloromethane to MeCN:water.[16]



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Complex **1** exhibits a strong photoluminescence in the range of 500−800 nm with λ_{max} at 605 nm and an emission quantum yield ϕ of 0.025 based on [Ru(bpy)$_3$](PF$_6$) in degassed MeCN as the reference ($\phi = 0.062$).[17] The luminescence is readily quenched by either triethanolamine (TEOA) as an electron transfer donor or by MV^{2+} as an electron transfer acceptor. Both reductive and oxidative quenching processes follow Stern−Volmer behavior with k_q values being 1.43×10^9 and 3.25×10^9 M^{-1} s^{-1} for TEOA and MV^{2+}, respectively, consistent with dynamic quenching (see Supporting Information). From ^{1}H NMR measurements of the reaction solutions, **1** was found to be stable under photolytic quenching conditions after 10 h of irradiation ($\lambda > 410$ nm). With TEOA present as the quencher, however, the TEOA resonances become complex and a new resonance grows in at 9.60 ppm, indicative of TEOA decomposition leading to glycolaldehyde formation. For the MV^{2+} oxidative quenching solution, no significant changes in the resonances of both Pt chromophore **1** and MV^{2+} are noted.

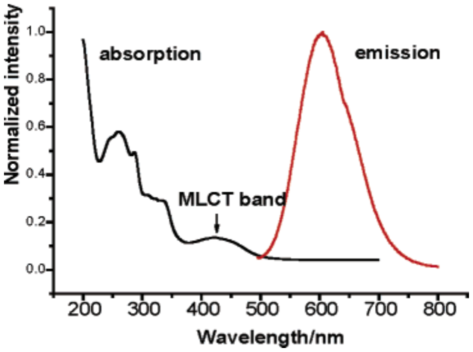

Figure 1. Electronic absorption spectra of **1** in MeCN:water (2:3 v/v).

While degassed solutions of **1** + MV^{2+} remain colorless on irradiation, solutions of **1** that contain *both* TEOA and MV^{2+} develop a persistent deep blue color characteristic of the $MV^{+\bullet}$ species. UV−vis spectra are consistent with the absorption band of the methyl viologen radical cation with λ_{max} at 605 nm. The $MV^{+\bullet}$ concentration increases with irradiation time but levels off after 50 min. Upon exposure to air, the blue color is quickly discharged and the resultant spectrum resembles that of the initial solution, indicating the oxidation of $MV^{+\bullet}$ back to MV^{2+}. The absence of the blue color from the solution of **1** + MV^{2+} on irradiation suggests that, while quenching is occurring, back electron transfer is rapid and efficient, whereas the persistent presence of $MV^{+\bullet}$ in the solution that also contains TEOA is consistent with reductive quenching followed by the oxidative decomposition of TEOA and a second electron transfer leading to glycolaldehyde formation. Similar observations with oxidized TEOA and MV^{2+} have been reported previously.[2]

Addition of colloidal Pt (5−7 nm size stabilized by sodium polyacrylate[18]) to the solution of **1** + TEOA + MV^{2+} led to H_2 generation upon irradiation. Since the MLCT band of **1** has a maximum at 420 nm and extends to 540 nm, a cutoff filter was used to remove all light with $\lambda < 410$ nm. Photogenerated H_2 thus produced was identified by GC analysis using a 5 Å molecular sieve column, thermal conductivity detector, and nitrogen carrier gas. The amount of hydrogen generated was quantified employing a calibration plot based on measured mixtures of H_2 and N_2 with CH_4 as a calibrant. The reaction medium was a 2:3 v/v ratio of MeCN:water. Control experiments indicated that all of the components—**1**, TEOA, MV^{2+}, and colloidal Pt—were essential for H_2

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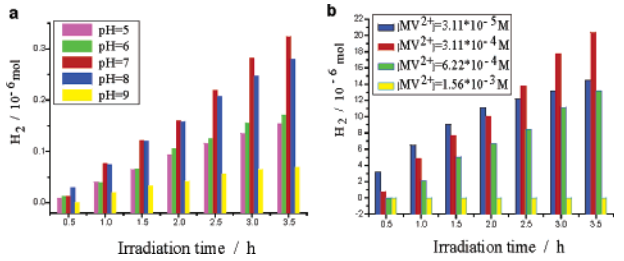

Figure 2. (a) The effect of pH on hydrogen evolution. (b) The effect of [MV^{2+}] on hydrogen evolution.

Scheme 1

$$1 \longrightarrow 1^{*} \qquad (1)$$

$$1^{*} + MV^{2+} \longrightarrow 1^{+} + MV^{+\cdot} \qquad (2)$$

$$1^{*} + TEOA \longrightarrow 1^{-} + TEOA^{+} \qquad (3)$$

$$1^{-} + MV^{2+} \longrightarrow 1 + MV^{+\cdot} \qquad (4)$$

$$1^{+} + MV^{+\cdot} \longrightarrow 1 + MV^{2+} \qquad (5)$$

$$TEOA + 1^{+} \longrightarrow TEOA^{+} + 1 \qquad (6)$$

$$TEOA^{+} \xrightarrow{-H^{+}} TEOA^{\cdot} \xrightarrow[MV^{2+} \to MV^{+\cdot}]{} \longrightarrow CH_2(OH)CHO + NH(CH_2CH_2OH)_2 \qquad (7)$$

$$2\,MV^{+\cdot} + H_2O \xrightarrow{\text{Pt colloid}} H_2 + 2\,OH^{-} + 2\,MV^{2+} \qquad (8)$$

generation; the absence of any one of them yielded unobservable to insignificant amounts of hydrogen. In subsequent studies of the reaction system, the concentrations of **1** and the colloidal catalyst were maintained at 2.23 × 10^{-5} M and 6.0 × 10^{-5} M Pt, respectively.

The rate of H_2 evolution was found to depend on both solution pH and the concentration of MV^{2+}. Figure 2a shows the amounts of H_2 produced as each of these parameters is varied. At pH 7, the maximum rate for H_2 generation is observed, while significant amounts of H_2 are also measured at pH 5 and 9. As with the previously reported $Ru(bpy)^{3+}$/TEOA/MV^{2+} and $Ru(bpy)^{3+}$/EDTA/MV^{2+} systems,[1-3,19] the pH dependence for hydrogen evolution from the present system is complex, depending on a number of factors, including its influence on the H^+/H_2 reduction potential, its effect on $TEOA^+$ deprotonation and decomposition, the destructive hydrogenation of MV^{2+}, and the effect of pH on the polyacrylate stabilizer charge.[2,19]

The variation of hydrogen obtained as a function of MV^{2+} is shown in Figure 2b. Interestingly, at a MV^{2+} concentration of 1.56 × 10^{-3} M or greater, no hydrogen is produced. The negative effect of higher MV^{2+} concentration in the present system may relate to competitive oxidative and reductive quenching by MV^{2+} and TEOA, respectively, and the facility of subsequent unproductive back reaction for each, or to hydrogenation of MV^{2+} as reported earlier for the Ru-based systems.[3b,19a,b] The optimal value of [MV^{2+}] for the **1**/TEOA/MV^{2+} system reported here was found to be 3•1 × 10^{-4} M at pH 7. After 10 h of irradiation with $\lambda > 410$ nm, the system with an initial [TEOA] of 5.6 × 10^{-3} M produced 84 turnovers of H_2 (relative to **1**) corresponding to a 34% yield based on the sacrificial donor. Further photolysis led to additional hydrogen but at a declining rate. Photogeneration of H_2 was also found to occur when $Rh(bpy)_3^{3+}$ was used in place of MV^{2+} as originally reported by Lehn, but in reduced amounts.[1]

On the basis of all of the measurements and observations described here, we formulate the mechanism for light-driven reduction of aqueous protons using **1**/TEOA/MV^{2+} as in Scheme 1. While **1*** is capable of both oxidative and reductive quenching with MV^{2+} and TEOA, respectively (eqs 2 and 3), the relative quenching rate constants suggest that oxidative quenching with MV^{2+} dominates. The reductive quenching by TEOA agrees with recent results reported by Schmehl[20] that **1** and related analogues are strong excited state oxidants. As proposed in earlier studies by Grätzel,[2] the resultant $TEOA^+$ radical cation that is generated by TEOA reduction of $Ru(bpy)_3^{3+}$ loses H^+ and transfers an electron to MV^{2+} on its decomposition path to form glycolaldehyde and di(ethanol)amine (eq 7). Electron transfer from $MV^{+\bullet}$ to the colloidal catalyst is then followed by proton reduction at the Pt surface (eq 8).

Further studies are in progress to optimize and modify the current system by chromophore variation to capture more of the visible spectrum and to link related triads based on **1** for rapid photoinduced charge separation to the colloidal catalyst directly for more efficient H_2 generation.

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Supporting Information Available: Synthesis of complex **1** and ^{1}H NMR data, emission quenching of **1** by TEOA and MV^{2+}, and NMR evidence of photostability under both reductive and oxidative quenching conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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