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Published on Web 06/05/2007

Photogeneration of Hydrogen from Water Using an Integrated System Based on TiO_2 and Platinum(II) Diimine Dithiolate Sensitizers

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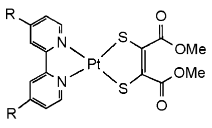
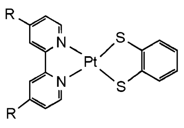
Received March 14, 2007

For the effective utilization of solar energy, the visible light-driven splitting of water into its constituent elements remains a continuing challenge. The reductive side of this reaction has been studied for three decades with the first reports describing systems containing $Ru(bpy)_3^{2+}$ as the chromophore, methyl viologen (MV^{2+}) as both quencher and electron relay, a metal colloidal catalyst, and a sacrificial electron donor.[1−5] Subsequent studies dealt with detailed analyses of individual steps and components of these systems[6−10] as well as variations of system architecture such as the attachment of chromophore to platinized TiO_2 particles for system integration.[11−15] Recent efforts to examine light-driven H_2 production include the photochemical reduction of HBr solutions using dinuclear Rh complexes,[16] the liberation of H_2 from Hantzsch 1,4-dihydropyridines employing Pt(terpy)(arylacetylide)$^+$ complexes as photocatalysts,[17] and the photogeneration of H_2 from water also using platinum terpyridyl complexes as chromophores.[18]

In this paper we report on a more integrated and photochemically stable system for light driven generation of H_2 that better utilizes visible light. In contrast with the Pt(terpy)(arylacetylide)$^+$ chromophore that absorbs only weakly at $\lambda > 450$ nm, related Pt(diimine)(dithiolate) complexes exhibit greater absorption in the visible region, owing to a charge-transfer transition from an orbital of mixed metal and dithiolate character to a π^* orbital localized on the diimine, designated in earlier work as ^{1}MMLL′CT (mixed metal−ligand to ligand′ charge transfer).[21,23] The spectroscopic properties of these Pt(II) complexes have been studied extensively.[19−27] In 2001, dicarboxybipyridine derivatives of these systems as sensitizers were studied for TiO_2 and found to bind to the semiconductor with photocurrent generated upon visible light irradiation (Voc of ∼600 mV; fill factors of ∼0.7 depending on the dithiolate).[24−27] These observations prompted us to examine photogeneration of H_2 employing Pt diimine dithiolate complexes as chromophores in an integrated system in which nanoscale TiO_2 would act as the electron relay in place of methyl viologen. The results for two of these complexes, Pt(dcbpy)(met) (**1**) and Pt(dcbpy)(bdt) (**2**) (R = COOH; dcbpy = 4,4′-dicarboxyl-2,2′-bipyridine; met = *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate; bdt = 1,2-benzenedithiolate), are reported herein.



1 R = COOH
3 R = *t*-Bu



2 R = COOH
4 R = COOEt

Complexes **1** and **2** were synthesized by the reaction of Pt(dcbpy)Cl_2 with the corresponding dithiolate ligand in THF/H_2O (1/1) in the presence of NaOH under nitrogen and fully characterized by elemental analyses, mass spectrometry, and ^{1}H and ^{13}C NMR and IR spectroscopies. For the purpose of control experiments in which binding between the Pt chromophore and TiO_2 would not be expected, two other diimine dithiolate complexes, Pt(dbbpy)(met) (**3**) (R = *t*-Bu; dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and Pt(ecbpy)(bdt) (**4**) (R = COOEt; ecbpy = 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine), were also prepared and fully characterized. Full experimental details and complex characterizations are given in the Supporting Information. Complexes **1** and **2** are poorly soluble in most organic solvents, moderately soluble in DMF and DMSO forming blue solutions, slightly soluble in water (pink solutions), and very soluble in aqueous base (red solutions) (see Figure S1 for representative UV/vis spectra in Supporting Information). While the organic solubility characteristics of **4** are similar to those of **1** and **2**, **3** exhibits solubility in most polar organic solvents, generating red to purple solutions.

Complexes **1** and **2** exhibit a moderately intense, solvatochromic absorption in the low-energy region of the visible spectrum, corresponding to the previously assigned ^{1}MMLL′CT transition. In THF/DMSO (50/1) solution, the absorption maxima are at 650 and 670 nm with molar extinction coefficients of 4710 and 9360 M^{-1} cm^{-1} for **1** and **2**, respectively (Figure S1). For complex **4**, the low-energy absorption appears at 685 nm ($\epsilon = 11120$ M^{-1} cm^{-1}), while for **3**, which has *t*-butyl substituents on the bipyridine, the MMLL′CT absorption in MeCN is seen at 510 nm ($\epsilon = 4770$ M^{-1} cm^{-1}). The low-energy charge transfer absorptions for **3** and **4** match closely with those reported previously for mnt and tdt systems (mnt = maleonitriledithiolate; tdt = toluene-3,4-dithiolate) having the same bipyridine ligand.[21] In H_2O/NaOH solution, the MMLL′CT absorption maxima of **1** and **2** occur at higher energies (500 and 505 nm, respectively), consistent with deprotonation of the dcbpy acid groups and existence of these complexes in solution as mono- or dianions. These results are consistent with (a) the bipyridine substituents controlling the LUMO energy and hence the energy of the ^{1}MMLL′CT transition and (b) **1** and **2** existing in neutral, protonated form in polar organic solvents, and as anionic species in basic aqueous media.

When H_2O/NaOH solutions of **1** or **2** (2.0×10^{-5} M, 25 mL) were mixed with TiO_2 (20 mg) overnight at room temperature, the pink solution color was transferred entirely to TiO_2, and after filtration, **1** or **2** was not detectable by UV/vis spectroscopy in solution (<1 μM). The pink coloration of the isolated TiO_2 was maintained after repeated washings with water and THF, and neither **1** or **2** could be detected in the washings. When these experiments were repeated using blue THF/DMSO solutions of **1** or **2**, the solution color again disappeared completely (neither **1** or **2** was detectable in solution by UV−vis spectroscopy) and TiO_2 with *pink* coloration was obtained. Similar experiments using MeCN solutions of **3** or THF/DMSO solutions of **4** and TiO_2 led to no change in solution color and maintenance of the initial white coloration of TiO_2. The results of these experiments are consistent with the view that **1** and **2** can bind effectively to TiO_2 through the bipyridyl carboxylate groups while **3** and **4**, lacking these functionalities, cannot.

10.1021/ja071789h CCC: $37.00 © 2007 American Chemical Society

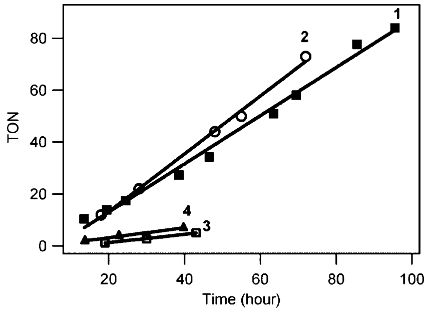


Figure 1. Turnovers of H_2 in photolyses of **1**−**4** with $\lambda > 410$ nm.

With establishment of the binding of **1** and **2** to TiO_2, attention turned to using these systems for the photogeneration of hydrogen from aqueous protons. In one set of experiments, $MeCN/H_2O$ solutions of **1** or **2** ($(2.0-3.3) \times 10^{-5}$ M, 25 mL) were mixed with platinized TiO_2 (TiO_2/Pt, 20 mg, Pt% = 3%) prepared from TiO_2 and K_2PtCl_6 according to a slightly modified published procedure[28] (see Supporting Information), to which was added triethanolamine (TEOA, 12.6 mM). The mixture was then degassed and exposed to visible light irradiation ($\lambda > 410$ nm). GC analysis of gases above the solution showed that H_2 was indeed generated from the system. With a fixed amount of methane as an internal GC standard in the reaction system, the amounts of photogenerated hydrogen were quantified, Figure 1. For **1**, 84 turnovers of H_2 were obtained after 95 h of irradiation, while for **2**, 72 turnovers of hydrogen were generated after 73 h of irradiation. A control experiment that omitted either chromophore **1** or **2** yielded no H_2 evolution on irradiation with $\lambda > 410$ nm. From the linear plots of H_2 turnover versus time in Figure 1, both **1** and **2** appear to maintain their reactivity, but further irradiation led to lower turnover rates. However, when irradiation of **2** was conducted with $\lambda > 455$ nm, the generation of H_2 which occurred at a slightly reduced level from that with $\lambda > 410$ nm continued at a constant rate for more than 180 h. For complexes **3** and **4** that do not bind to TiO_2, analogous experiments generated H_2, but far less effectively than either **1** or **2**. After 40 h of irradiation ($\lambda > 410$ nm), only five and seven turnovers of H_2 were obtained for **3** and **4**, respectively. The origin of H_2 as aqueous protons has been confirmed in a separate experiment using a related chromophore in $D_2O/MeCN$ with platinized TiO_2 and TEOA present.

In a second series of experiments, $MeCN/H_2O$ solutions of **1** or **2** (3.3×10^{-5} M for **1**, 2.0×10^{-5} M for **2**, 25 mL) were stirred with platinized TiO_2 (TiO_2/Pt, 20 mg, Pt% = 3%) at room temperature for 10 h, after which the chromophore-derivatized TiO_2/Pt was isolated, washed repeatedly with H_2O and THF, and dried. The resultant chromophore/TiO_2/Pt powder was then stirred in water and TEOA (12.6 mM), degassed, and exposed to visible light irradiation ($\lambda > 410$ nm). GC analysis of these reaction systems revealed photogeneration of H_2 in amounts similar to those described above. One additional protocol that also yielded photogeneration of H_2 involved the preparation and isolation of **1**-derivatized TiO_2, to which a solution of H_2PtCl_6 (2.2×10^{-4} M, 25 mL) and TEOA (12.6 mM) was added. The mixture was degassed and irradiated ($\lambda > 410$ nm) as before, followed by GC analysis that showed hydrogen in amounts comparable to the **1**/TiO_2/Pt system described above. This last result suggests that upon radiation, H_2PtCl_6 is reduced to metallic Pt by TEOA, generating in situ the TiO_2-attached Pt metal sites necessary for catalysis of proton reduction.

In summary, the results reported here describe an integrated system of chromophore-electron relay-catalyst for the reductive side of the water splitting reaction, that is, the visible light-driven generation of hydrogen from aqueous protons and a sacrificial electron donor. In the present system, TiO_2 serves as both the electron relay and the scaffold to which the Pt diimine dithiolate chromophore and the metallic Pt catalyst for proton reduction are attached. Further studies to improve both system efficiency and robustness for the photogeneration of H_2 are in progress.

Acknowledgment. We wish to thank the Department of Energy, Division of Basic Sciences for support of this research (Grant DE-FG02-90ER14125). We thank Mr. Tom Darrah for running the hydrogen isotope mass spectrum.

Supporting Information Available: Synthesis and spectroscopic characterization of complexes and experimental details for water reduction process. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA071789H