Photocatalytic Hydrogen Production from Hantzsch 1,4-Dihydropyridines by Platinum(II) Terpyridyl Complexes in Homogeneous Solution

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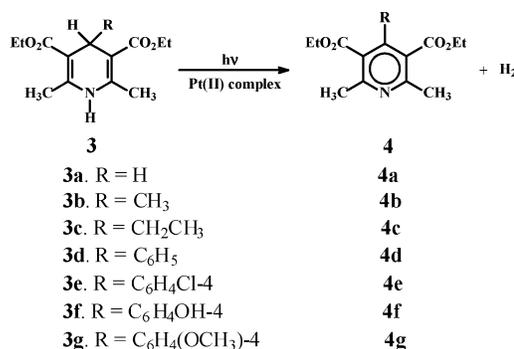
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Creation of molecular photocatalysts that promote the production of hydrogen from organic or inorganic protic solutions is of tremendous potential significance in the sense of solar energy conversion. Until now, the most successful photocatalysts for generation of hydrogen are heterogeneous systems involving transition metal complexes chemisorbed on the surface of semiconductors.[1−3] The semiconductor serves as a mediator to couple the 1e− equivalency provided by the photoexcited metal complex to the 2e− equivalency required for hydrogen production. Although photochemical production of hydrogen in the absence of a heterogeneous mediator has been realized, in most cases, such reactions occur only under stoichiometric conditions,[4,5] and photocatalytic examples are few.[6,7] Square-planar platinum(II) complexes have vacant coordination sites at the platinum center and can bind hydrogen atom(s), and thus may be capable of mediating the reaction of 2H to H_2. On the other hand, Hantzsch 1,4-dihydropyridines (dialkyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylates) may act as the source of two hydrogen atoms. Therefore, one might expect that platinum(II) complexes could be able to photocatalyze hydrogen production from 1,4-dihydropyridines. Here, we report that this is indeed the case for platinum-(II) terpyridyl complexes as the photocatalysts to oxidize Hantzsch 1,4-dihydropyridine derivatives. This hydrogen production proceeds in homogeneous solution in quantitative yield and with large catalytic turnover.

Hantzsch 1,4-dihydropyridine derivatives are often regarded as the models of the natural reduced nicotinamine adenine dinucleotide (NADH) coenzyme which functions as redox reagent for biological reactions.[8,9] Although the oxidation of NADH and its analogues is one of the ubiquitous issues in organic chemistry,[10−12] oxidative transformation of these compounds accompanying generation of hydrogen has never been reported. In the present work, we studied the photocatalytic oxidation of Hantzsch dihydropyridine and its 4-alkyl and 4-aryl substituted derivatives (**3a−3g** in Scheme 1 and **5a−5c** in Scheme 2) and found that **3a−3g** can photocatalytically produce hydrogen in quantitative yields, while **5a** and **5b** undergo photocatalytic dealkylation. The photocatalysts are platinum(II) 4′-*p*-tolyl-terpyridyl chlorine complex (**1**) and platinum(II) 4′-*p*-tolyl-terpyridyl acetylide complexes (**2a−2d**, Chart 1).

The solutions of **1** and **2a−2d** in acetonitrile show similar absorption spectra with the lowest energy bands in the region of 400−520 nm depending on the respective complexes, and extinction coefficients on the order of 10^3 dm^3 mol^{-1} cm^{-1}, which are assignable to the $d\pi$ (Pt) $\rightarrow$ π*(trpy) metal-to-ligand charge-transfer (MLCT) transition.[13] The absorption spectral property was found to follow Beer's law below the concentration of 1×10^{-4} M, suggesting no significant complex aggregation occurred. All of these complexes in degassed acetonitrile at room temperature display moderately intense photoluminescence with λ_{max} at 550−640 nm. The large Stokes shift for the photoluminescence suggests that the emission originates from a triplet parentage and is assigned as
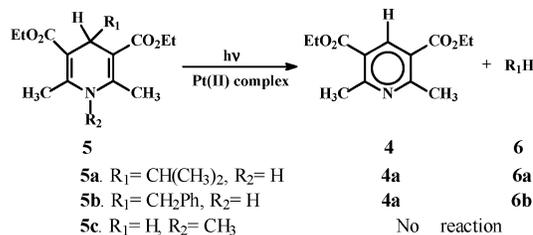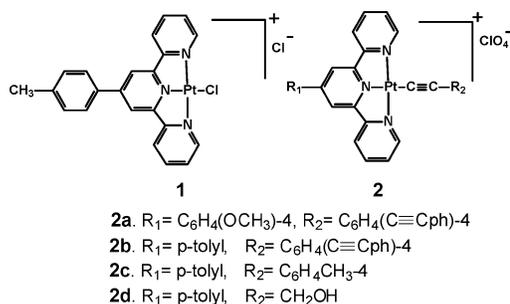
Scheme 1

3a. R = H   **4a**
3b. R = CH_3 **4b**
3c. R = CH_2CH_3 **4c**
3d. R = C_6H_5 **4d**
3e. R = C_6H_4Cl-4   **4e**
3f. R = C_6H_4OH-4   **4f**
3g. R = $C_6H_4(OCH_3)$-4   **4g**

Scheme 2

5a. R_1= $CH(CH_3)_2$, R_2= H   **4a**   **6a**
5b. R_1= CH_2Ph, R_2= H   **4a**   **6b**
5c. R_1= H, R_2= CH_3 No reaction

Chart 1

2a. R_1= $C_6H_4(OCH_3)$-4, R_2= $C_6H_4(C{\equiv}Cph)$-4
2b. R_1= *p*-tolyl, R_2= $C_6H_4(C{\equiv}Cph)$-4
2c. R_1= *p*-tolyl, R_2= $C_6H_4CH_3$-4
2d. R_1= *p*-tolyl, R_2= CH_2OH

arising from the ^{3}MLCT state.[13] This photoluminescence is readily quenched by **3** and **5**. For example, we have examined the emission lifetimes of **2a** in the presence of various concentrations of **3** and **5**. In all cases, the photoluminescence decays monoexponentially. In the absence of **3** and **5**, the emission lifetime of **2a** is ca. 340 ns. As the concentration of the substrate increases, the lifetime of **2a** decreases. The quenching process follows Stern−Volmer kinetics, the quenching constants (k_q) were calculated from these lifetimes, and some data are listed in Table 1. These values of k_q are consistent with those obtained from emission intensity measurements in the presence of substrate.

Hydrogen production was carried out in dry degassed acetonitrile solutions. Typically, 40 mL of the solution of the substrate (1×10^{-2} M) and the photocatalyst (1×10^{-5} to 1×10^{-4} M) in a Pyrex reactor was irradiated by a 500 W high-pressure Hanovia

Table 1. Data of k_q and Φ in the Case of **2a** as the Photocatalyst

substrate	3a	3a-*d*-1	3a-*d*-4	3b	3c	3d	3g	5a	5c
k_q ($\times 10^9$ M^{-1})	8.7	6.1	8.7	5.7	5.6	4.5	3.8	4.5	no quenching
Φ		0.38	0.31	0.32	0.23	0.29	0.16	0.20	0.28	no reaction

mercury lamp. A glass filter was employed to cut off light with wavelength below 450 nm; thus only the photocatalyst was irradiated. The generated hydrogen was collected and analyzed by GC and a hydrogen detector (Oldham Detector Ltd., Arras, France), and its volume was measured at the atmosphere pressure and constant temperature. After irradiation, the solvent was removed under reduced pressure, and the oxidized products were isolated by extraction with ethyl acetate and identified by ^{1}H NMR spectroscopy and on the basis of known retention times of authentic compounds on GC. Control experiments showed that both the photocatalyst and light were necessary for hydrogen production. For substrates **3**, only the dehydrogenated products **4** (Scheme 1) were produced, and no trace of the dealkylated product was detected. The molar ratio of hydrogen to **4** was ca. 1:1, and the yield of **4** (therefore the yield of hydrogen) was ca. 100% based on the consumption of the starting material for any substrate of **3a**−**3g**. The quantum yields (Φ) of the photocatalytic hydrogen production in the case of **2a** as the photocatalyst were determined for the substrates with the initial concentration of 1×10^{-2} M and are listed in Table 1.

In contrast, irradiation of the solutions of **5a** and **5b** in acetonitrile in the presence of a photocatalyst under similar conditions described above resulted in dealkylated pyridine **4a** and alkanes **6** (Scheme 2), and no trace of hydrogen was produced. The molar ratio of **4a** to **6** was 1:1, and the mass balance was greater than 95%.

To ascertain the photocatalytic character for the hydrogen production and the dealkylation reaction, we measured the yield of the oxidation products (**4**) as a function of irradiation time and found that the product formation rate was constant during the irradiation, indicating the absence of photocatalyst decomposition. On the basis of the molar ratio of the oxidation product to the catalyst, the total turnover at the end of irradiation was over 1000.

To provide information on the mechanism of the photocatalytic oxidation, we performed the deuterium substitution of the hydrogen atom at the 1-position (**3a**-*d*-1) and the two hydrogen atoms at the 4-position (**3a**-*d*-4) of **3a**. As **3a**, the deuterated compounds also quench the photoluminescence of **2a**, and the quenching constant for **3a**-*d*-1 is evidently smaller than those for **3a** and **3a**-*d*-4 (Table 1). However, the quantum yield of production formation for **3a**-*d*-1 is comparable to **3a**-*d*-4 and smaller than **3a** (Table 1).

The mechanism for this photocatalytic hydrogen production and dealkylation is not yet well understood. We believe that the lowest energy excited state (^{3}MLCT) of the photocatalyst is responsible for these reactions. This triplet state can be considered to have biradical character. Furthermore, as in the ground-state chemistry, vacant coordination sites in the metal center of the platinum(II) terpyridyl complexes also would play a role in the photocatalysis.[14] As shown in Scheme 3, the radical character and the availability of open coordination sites make the ^{3}MLCT state able to abstract a hydrogen atom from the 1,4-dihydropyridines **3** (or **5**) to form [Pt complex]·H and radical **3•** (or **5•**). We proposed that the first step for the photocatalytic reaction involves the hydrogen atom abstraction from the 1-position rather than the 4-position of **3** (or **5**) on the basis of the following observations: (1) The k_q of **3a**-*d*-1

Scheme 3

$$[\text{Pt complex}]^* + \mathbf{3} \rightarrow [\text{Pt complex}]\cdot\text{H} + \mathbf{3\cdot} \quad (1)$$

$$[\text{Pt complex}]\cdot\text{H} + \mathbf{3\cdot} \rightarrow [\text{Pt complex}] + \mathbf{3} \quad (2)$$

$$[\text{Pt complex}]\cdot\text{H} + \mathbf{3\cdot} \rightarrow [\text{Pt complex}]\cdot\text{H}_2 + \mathbf{4} \quad (3)$$

$$[\text{Pt complex}]\cdot\text{H}_2 \rightarrow [\text{Pt complex}] + \text{H}_2 \quad (4)$$

is smaller than those for **3a** and **3a**-*d*-4. (2) The N-alkyl substituted substrate **5c** cannot be photocatalyzed to dealkylation by the photocatalyst. (3) **5a** and **5b** undergo photocatalytic dealkylation rather than dehydrogenation. The generated radical pair, [Pt complex]·H and **3•** (or **5•**), in a solvent cage undergoes either back hydrogen atom transfer to yield the starting materials or disproportionation (step 3, Scheme 3) to produce pyridines **4**, and [Pt complex]·H$_2$ (in the case of **3** as the substrate) or [Pt complex]· HR$_1$ (in the case of **5** as the substrate). Finally, elimination of hydrogen and alkane from the respective intermediates [Pt complex]· H$_2$ and [Pt complex]·HR$_1$ regenerates the photocatalyst Pt(II) complex and completes the photocatalytic cycle. The data of k_q and Φ for deuterated **3a** in Table 1 support the above mechanism. Steps 1 and 3 in Scheme 3 involve the transfer of the hydrogen atom at the 1- and 4-positions of the 1,4-dihydropyridines, respectively. Deuterium substitution of these hydrogen atoms would retard the atom transfer, and thus decrease the quantum yield for product formation.

To summarize, we have proved that platinum(II) terpyridyl complexes can photocatalyze hydrogen production from Hantzsch dihydropyridine derivatives in quantitative yields. Our further efforts will be focused on expanding the scope of the photocatalyst and the substrate, which can produce hydrogen in high quantum yield with large catalytic turnover.

Supporting Information Available: The synthesis and identity of **2**, **3**, **5**, and deuterated **3a**, absorption spectra and emission quenching of **2**, measurements of photocatalytic quantum yields and turnover, data of ^{1}H NMR spectroscopy of **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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