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Short Communication

Photocatalytic H_2 production from water based on platinum(II) Schiff base sensitizers and a molecular cobalt catalyst

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ABSTRACT

Three platinum(II) Schiff base complexes were synthesized and were used as efficient photosensitizers (PSs) for the photocatalytic H_2 production from mixed solvents under visible light irradiation with a molecular cobalt complex as catalyst. Their photophysical and electrochemical properties were investigated and catalytic activities were evaluated under different catalytic conditions. The turnover numbers (TONs) up to 601 for complex **1** was achieved under optimized conditions and the effects of different groups in the complexes on the photocatalytic activity were presented. The photocatalytic efficiencies of three PSs are in good agreement with obtained quenching rate constant of the MLCT excited state.

1. Introduction

Artificial photosynthesis is regarded as the most promising way to relieve humankind's tremendously growing requirement for fuels [1]. The conversion of solar energy into hydrogen fuel ultimately remains one of the greatest challenges in search of an economically and ecologically feasible fuel provision [2]. A number of systems of photogenerated hydrogen were developed in the past decade. Of particular interest is molecular photocatalysis [3]. Generally, photocatalytic multi-component systems consist of a metal such as Ru [4,5], Ir [6], Pt [7–9] complex as PS, a sacrificial electron donor such as triethylamine (TEA), triethanolamine (TEOA), and a proton reduction catalyst mostly based on the colloidal metal [10,11], cobalt-based complexes [12–16] or Fe-hydrogenase [17–19]. A key challenge in this area is to design more efficient and robust PS that can absorb visible light to produce long-lived excited states [20,21]. In 2006, Eisenberg's group reported firstly the utility of $[Pt(terpy)(arylacetylide)]^+$ (terpy = 2,2′:2″,6′-terpyridine) complexes as PS for photodriven production of H_2 from aqueous protons [22]. After that they achieved proton reduction at low overpotential with the same PS using $[Co(dmgH)_2PyCl]^{2+}$ (dmgH = dimethylglyoximate, Py = pyridine) as a catalyst [23]. Recently, Castellano and coworkers also employed a series of π-conjugated platinum(II) arylacetylide sensitizers for photocatalytic H_2 generation [24]. However, low TON for these platinum(II) complexes with respect to classical $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) is likely due to their weak absorption in visible-light region and instability under irradiation. It is therefore urgent and significant to seek robust platinum(II) complexes with more intense visible absorption and longer-lived excited states to act as a PS in photocatalytic multi-component systems.

The potential application of platinum(II) complexes with Schiff base ligands as PSs has been long overlooked, although they have been widely used in organic light-emitting diodes (OLEDs) [25–27]. Importantly, these complexes have longer-lived excited states and broader visible absorption relative to the classical cyclometalated platinum(II) complexes with C^N (2-phenylpyridine) and N′N (2,2-dipyridine) ligands. The flexibility of these complexes to control the photophysical and photochemical behaviors and their excellent photostability render them to be good candidates for photocatalysis. To the best of our knowledge, platinum(II) Schiff base complexes have not been utilized as a PS in photocatalytic systems for hydrogen production. In this communication, we demonstrate that the three platinum(II) Schiff base complexes (R = F, **1**; R = H, **2**; R = OCH_3, **3**) (Scheme 1) can be utilized as potent PSs in a three-component system containing $[Co(dmgH)_2PyCl]^{2+}$ as a catalyst and TEA or TEOA as a sacrificial electron donor. Some insights into the electronic effects on the photocatalysis were performed.

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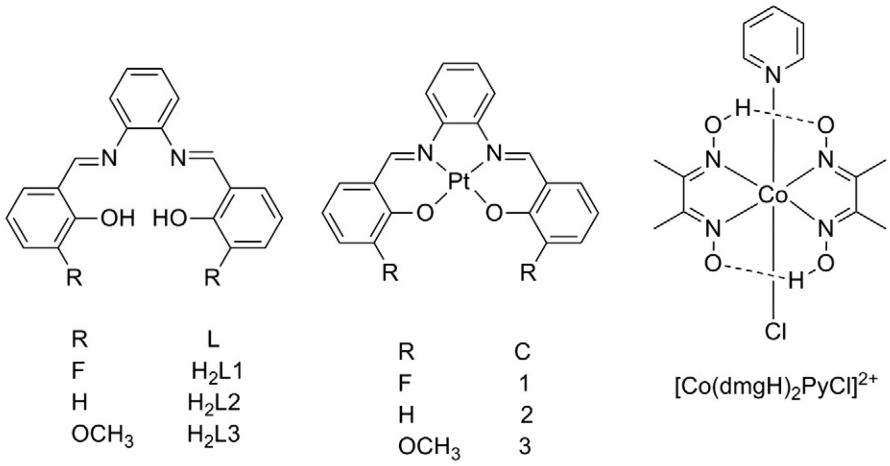

Scheme 1. Molecular structures of platinum(II) complexes and $[Co(dmgH)_2PyCl]^{2+}$.

2. Experimental

2.1. Synthesis of complexes 1 and 2

All of the complexes were synthesized according to the previously reported procedure [25,28] and were characterized by ^{1}H NMR spectroscopy and mass spectrometry.

Complex **1**: ^{1}H NMR (400 MHz, DMSO-d_6): 9.52 (s, 2H), 8.42 (dd, 2H, $J = 6.2$ and 3.3 Hz), 7.68 (d, 2H, $J = 8.1$ Hz), 7.49 (dd, 2H, $J = 11.3$ and 8.2 Hz), 7.44 (dd, 2H, $J = 6.2$ and 3.3 Hz), 6.72 (td, 2H, $J = 7.8$ and 4.4 Hz). MS (MALDI-TOF): *m/z* calcd for $[C_{20}H_{14}N_2O_2Pt + H]^+$ 545.05; found: 545.10.
Complex **2**: ^{1}H NMR (400 MHz, DMSO-d_6): 9.54 (s, 2H), 8.46 (dd, 2H, $J = 6.1$ and 3.3 Hz), 7.88 (d, 2H, $J = 7.2$ Hz), 7.58 (t, 2H, $J = 7.1$ Hz), 7.46 (dd, 2H, $J = 6.1$ and 3.0 Hz), 7.12 (d, 2H, $J = 8.6$ Hz), 6.80 (t, 2H, $J = 7.3$ Hz). MS (MALDI-TOF): *m/z* calcd for $[C_{20}H_{14}N_2O_2Pt + H]^+$ 510.07; found: 510.10.
Complex **3**: ^{1}H NMR (400 MHz, $CDCl_3$): 8.44 (br, 2H), 7.63 (br, 2H), 7.09 (br, 2H), 6.93 (d, 2H, $J = 7.3$ Hz), 6.73 (d, 2H, $J = 6.8$ Hz), 6.53 (t, 2H, $J = 7.8$ Hz), 3.80 (s, 6H). MS (MALDI-TOF): *m/z* calcd for $[C_{22}H_{18}N_2O_4Pt + H]^+$ 570.09; found: 570.10.
$[Co(dmgH)_2PyCl]^{2+}$: ^{1}H NMR (400 MHz, $CDCl_3$): 8.28 (d, 2H, $J = 5.2$ Hz), 7.70 (t, 1H, $J = 7.6$ Hz). 7.23 (t, 2H, $J = 7.4$ Hz), 2.4 (s, 12H).

2.2. Photocatalytic hydrogen evolution

In a typical homogeneous catalytic experiment, a total of 30 mL of DMF/water (1:1, v/v) or CH_3CN/water (1:1, v/v) solution containing TEA or TEOA, PS and catalyst was added to a quartz tube. The tube was degassed by bubbling N_2 for at least 30 min and sealed with a rubber stopper. The samples were then irradiated under a 500 W metal-halogen lamp and optical filter was employed to block light with a wavelength below 420 nm. The photogenerated hydrogen from the system was monitored and quantified by gas chromatography on a Shimadzu GC-2014 which was equipped with a 5 Å molecular sieve column (3 m × 2 mm), thermal conductivity detector and N_2 carrier gas. $TON = 2n(H_2) / n(PS)$.

3. Results and discussion

The photophysical properties of complexes were tested in degassed DMF solutions and the results were summarized in Table 1. The complexes display intense absorption bands below 400 nm and broad charge transfer absorption in the visible-region with a tail extending up to 580 nm. The intense visible absorption band was ascribed previously to a mixture of the spin-allowed ^{1}MLCT (low-lying $d\pi(Pt) \rightarrow \pi^*$ metal-to-ligand charge transfer transition) and ^{1}IL (intraligand) transitions [25]. The absorption maxima are obviously red-shifted compared to those of reported cyclometalated platinum(II) complexes with C^N and N^N ligands. Inducing electron-donating group into the ligand results in a red-shift of the emission bands. Upon laser pulse by 355 nm light, the transient absorption spectra of **1**, **2** and **3** exhibit strong bands centered at around 450 nm. The decay lifetimes of excited states for the complexes are all limited to microsecond scale and match well with corresponding emission lifetimes, suggesting that the transient absorptions and emissions could come from the same triplet excited state.

Cyclic voltammograms of the PSs as well as the $[Co(dmgH)_2PyCl]^{2+}$ catalyst were recorded in degassed DMF. All of the complexes display a irreversible oxidation wave and a reversible single-electron-reduction couples, the reduction peak is assigned to the reduction of the ligand. The catalyst $[Co(dmgH)_2PyCl]^{2+}$ exhibits one irreversible reduction of Co(III) to Co(II) ($E_{pc} = -0.55$ V vs SCE) followed by a reversible Co(II)/Co(I) process at −0.93 V. The more negative reduction potentials of PSs compared with those of the catalyst show that electron transfer from PS^- to the catalyst is thermodynamically feasible [29].

The luminescence quenching of PS by both the catalyst $[Co(dmgH)_2PyCl]^{2+}$ (oxidative quenching) and TEA (reductive quenching) was investigated. The electronic effects of the ligands have a profound influence on the excited-state dynamic of the corresponding complexes, as reflected in the lifetime (τ_0) of the emissive MLCT excited state. Complex **1** was quenched by TEA and catalyst following linear

Table 1
Photophysical and electrochemical data for complexes **1**–**3** in degassed DMF.

	λ_{abs} [nm] ($[mol^{-1}\ dm^3\ cm^{-1}]$)	λ_{em} [nm]	μs	Φ_{em}[a]	E_{pa} [V][b]	E_{pc} [V]
1	314 (24,000), 365 (33,000), 385 (35,000), 452 (5100), 498 (6900), 520 (7000)	608	1.79	0.10	1.25	−1.10
2	312 (19,000), 363 (29,000), 381 (30,000), 453 (7000), 500 (6700), 523 (6500)	610	1.87	0.17	1.15	−1.25
3	330(17,500), 355 (17,800), 375 (24,500), 397 (26,000), 512 (5000), 550 (6000)	650	2.24	0.03	1.25	−1.27

[a] The quantum yields (Φ_{em}) are relative to $Ru(bpy)_3Cl_2$ in degassed acetonitrile as a standard value.
[b] Potential (V vs. SCE) in DMF/n-Bu_4NPF_6 (0.1 M) at room temperature.