铂–钴双核配合物：合成、光物理性质及可见光驱动分解水制氢

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摘要：合成了一种铂钴双核配合物,[Pt(^{t}Bu$_3$tpy)([C≡C-C$_6$H$_4$N])-Co(dmgH)$_2$PyCl,(**5**)](^{t}Bu$_3$tpy 为 4, 4′, 4″-叔丁基-2,2″6′, 2″三联吡啶, C$_6$H$_4$N 为吡啶基,dmgH 为丁二酮肟,Py 为吡啶),并研究其光物理和光化学性质。通过对配合物进行紫外、荧光光谱表征,表明该铂配合物在可见光区显示金属到配体电荷转移(MLCT)的特点及钴配合物猝灭其发光的性质。在电子给体三乙醇胺(TEOA)存在下,这种双核配合物可实现光驱动分解水产氢,光催化产氢性质受很多因素影响,比如 pH 值,溶剂等。通过质谱和紫外光谱表征表明这种双金属核分子催化剂不稳定,铂光敏剂和钴催化剂会在光照过程会分离。

关键词：铂；光敏剂；钴；产氢

Platinum-Cobalt Dinuclear Complex: Synthesis, Photophysical Properties and Visible Light-Driven Hydrogen Production from Water

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Abstract：A platinum sensitizer-cobalt dinuclear complex, [Pt(^{t}Bu$_3$tpy)([C≡C-C$_6$H$_4$N])-Co(dmgH)$_2$PyCl, **5**] (^{t}Bu$_3$tpy= 4,4′,4″-tri (tert-butyl)-2,2′:6′,2″-terpyridine, C$_6$H$_4$N=4-pyridyl, dmgH=dimethylglyoxime, Py=pyridine), has been synthesized and characterized. The complex **5** shows absorption spectra in the visible region, which are assigned to mainly metal-to-ligand charge transfer (MLCT) character from the platinum sensitizer part. The cobalt moiety in complex **5** could quench the luminescence of the platinum part, indicating a possible process of intramolecular electron transfer. This dinuclear complex has been used for light-driven catalytic hydrogen production from water in the presence of triethanolamine (TEOA). The hydrogen production is affected by many factors, such as pH value and solvent. And the results show that this molecular catalyst could be decomposed to release the platinum based photosensitizer, as confirmed by absorption spectra and mass spectrometry.

Key words: platinum; photosensitizer; cobalt; hydrogen production

0　Introduction

　　Visible light-driven water splitting is a great challenge and an attractive topic for solar energy conversion. The reduction side of this reaction to generate hydrogen fuel has been studied since 1970s and many proof-of-concept systems for hydrogen production have been reported [1-2]. Such systems generally contain a sacrificial electron donor, a photosensitizer (such as [Ru (bpy)$_3$]$^{2+}$, bpy =2,2′-

bipyridine), an electron relay and a metal colloidal catalyst. Recently, the discovery of long-lived excited states of platinum terpyridyl acetylide photosensitizers and iridium cyclometalated photosensitizers has led to the development of more efficient multi-component systems to replace $[Ru(bpy)_3]^{2+}$ for hydrogen production with both higher turnover frequencies (TOF) and overall turnover numbers (TONs)[3-5]. However, these systems also rely preferably on expensive and unsustainable noble metals as the catalysts. Recently, many different catalysts based on earth-abundant elements such as Ni, Co and Fe have been reported for hydrogen production in electrocatalytic or photocatalytic systems [6-7]. Cobaloxime (scheme 1) represents one example of Co based molecular catalysts and attracts much attention for visible light-driven hydrogen production from water in the presence of a photosensitizer and a sacrificial electron donor, in which the reaction mechanism has also been discussed[8-14].

Sol=H_2O or CH_3CN

$[Co(dmgH)_2PyCl]$ (1)　　　$[Co(dmg)_2(BF)_2(Sol)_2]$ (2)
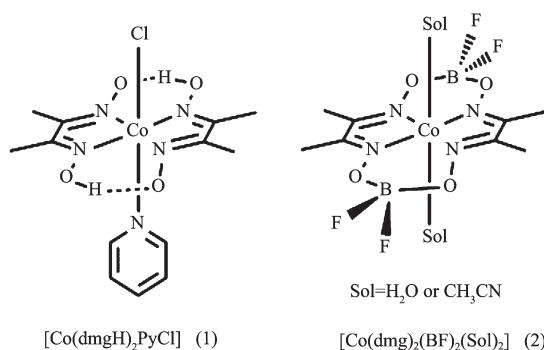
Scheme 1

In contrast with the multi-component systems, many molecular photochemical devices by covalently or coordinately linking a photosensitizer with a molecular catalyst have been constructed with the aim of higher efficiency for hydrogen production because electron transfer processes would be possibly more favorable in the devices. Various photosensitizer-catalyst dyads have been reported as molecular photochemical devices for hydrogen production. In some of the systems reported, a Pt(Ⅱ) or Pd(Ⅱ) molecular catalyst is covalently linked to the ruthenium sensitizer without any electron relays[15-16]. In the presence of a sacrificial donor, the systems do produce hydrogen upon visible light irradiation and give

TONs as 4.8 and 56 for Pt(Ⅱ) and Pd(Ⅱ), respectively. Furthermore, a Rh(Ⅱ) catalyst was directly attached to the ruthenium photosensitizer to make a molecular device, $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ (bpy =bipyridine, dpp =2,3-bis (2-pyridyl)pyrazine), for hydrogen production[17]. Artero and co-workers[18-19] employed [Ru (bpy)_3]^{2+} with cobaloximes (1 and 2) or iridium-cobaloxime system for photochemical H_2 generation in organic solvents, but system efficiency decreased dramatically in the presence of small amounts of water. Sun and co-workers [8] examined a Znic porphyrin-[2Fe-2S] system for a TONs of 22 under visible light. Some other photosensitizer-catalyst hybrids could also be found in recent literatures[14,21].

In this contribution, we report the photophysical properties and visible light-driven hydrogen production from water based on a heterodinuclear platinum-cobalt complex.

1　Experimental

1.1　Materials

Acetonitrile, methanol, and triethanolamine (TEOA) were purchased (Sigma-Aldrich) and used without further purification. [Pt (^{t}Bu$_3$tpy)Cl]PF$_6$ was synthesized following the reported procedure [22]. All of the new complexes were synthesized, and were characterized by ^{1}H-NMR, ESI-MS spectrometry and elemental analysis.

1.2　Synthesis of complex 3 and complex 5

$[Pt(^tBu_3tpy)([C \equiv C-C_6H_4N])]$ (3, ^{t}Bu$_3$tpy=4, 4′, 4″-tri (tert-butyl)-2,2′,6′,2″-terpyridine). 5 mg CuI, 5 mL triethylamine (TEA) and 10 mg 4-Ethynylpyridine were added in 10 mL dimethylformamide (DMF), followed by addition of 50 mg [Pt(^{t}Bu$_3$tpy)Cl]PF$_6$ (0.064 mmol). The mixture was stirred at room temperature for 3 d. TEA was then evaporated and the DMF solution was filtered into an aqueous solution of NH$_4$PF$_6$. The orange precipitate was collected by a frit and washed twice by methanol and diethyl ether to yield a reddish orange solid (38 mg, yield, 71%). ^{1}H NMR (DMSO-d_6, 400.1 MHz): 8.97 (2H, d), 8.72 (4H, m), 7.89 (d, 2H), 7.75 (d, 2H), 7.46 (d, 2H), 1.50 (s, 9H), 1.40 (s, 18H) ESI-MS Calcd. for $M^+(C_{34}H_{39}N_4Pt)$ 698.79, Found 698.67 (M^+).

Complex **5**. Complex **3** (30 mg, 0.036 mmol) and complex **4** (13 mg, 0.036 mmol) were added in 10 mL methanol followed by addition of 1 equivalent triethylamine. The mixture was stirred at room temperature for 6 h and the yellow precipitate was collected by a frit. The crude product was washed by methanol and diethyl ether twice to yield a product of 29 mg (yield: 80%). ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): 8.82 (2H, d), 8.70 (4H, m), 7.95 (d, 2H), 7.80 (d, 2H), 7.43 (d, 2H), 2.35 (s, 12H), 1.50 (s, 9H), 1.40 (s, 18H). Infrared Spectra (IR, cm^{-1}): 3 438.52 (broad), 2 965.54, 2 118.51, 1 610.96, 1 563.19, 1 474.66, 1 425.30, 1 372.21, 1 241.29, 1 092.96, 1 028.87, 840.88. ESI-MS Calcd. for M$^+$(C$_{42}$H$_{53}$ClCoN$_8$O$_4$Pt) 1023.40, Found: 1022.83. Anal. Calcd. (C$_{42}$H$_{53}$ClCoN$_8$O$_4$PtPF$_6$·MeOH): C, 43.02; H, 4.79; N, 9.33. Found: C, 42.53; H, 4.35; N, 9.17.

1.3 Photophysical properties and photocatalysis

Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200~1 100 nm). Emission spectra were obtained using a Spex Fluoromax-P fluorometer corrected for instrument response. Monochromators were positioned with a 2-nm band-pass, and solution samples were degassed by at least three freeze-pump-thaw cycles before mesurements.

For photoinduced hydrogen evolution, each sample was made in a 100 mL round bottom flask with volume of 25 mL in acetonitrile:water (24:1, V/V). Typically, the sample contained 4.0×10^{-5} mol·L^{-1} Pt chromophore or Pt-Co molecular catalyst. Hydrochloric acid or sodium hydroxide solution were used to adjust the pH value. The flask was sealed with a rubber septum and degassed by bubbling nitrogen for 15 min under atmospheric pressure at room temperature, after which 5 mL nitrogen was removed from the flask and replaced with 5 mL of methane (1.013 kpa) to serve as the internal standard. The samples were irradiated under a 200W Mercury Xexon lamp. A cut-off filter was used to remove off light with $\lambda < 400$ nm. The amount of H$_2$ generated was determined by GC analysis using a chromatograph (Shimadzu) with a molecular sieve 0.5 nm (30 m×0.53 mm, PLOT column, df =50 μm) and thermal conductivity detector. The gas samples were directly injected by a syringe (100 μL/ each) and non split stream was applied. The temperature for column is 60 ℃ and the temperature for detector is 90 ℃. The temperature for the injection port is 90 ℃. Nitrogen was used as the carrier gas and the rate is 30 mL·min^{-1}.

2　Results and discussion

2.1 Photophysical properties of complex 3 and complex 5

The steady-state spectroscopy of complexes 3 and 5 were examined at room temperature. The spectroscopic data are consistent with a cationic Pt(Ⅱ) complex having a square-planar geometry with three of the four coordination sites occupied by the terpyridyl ligand and the fourth site occupied by acetylide [23-24]. The UV-Vis absorption spectra of 3 and 5 measured in MeCN/H$_2$O (24:1, V/V) are shown in Fig.1 (a). The absorption spectra exhibit a broad low energy absorption band between 371~480 nm with λ_{max} at 405 nm ($\varepsilon \sim 6800$ dm^3·mol^{-1}·cm^{-1}) for complex 3 and λ_{max} at 396 nm ($\varepsilon \sim 9300$ dm^3 mol^{-1}cm^{-1}) for complex 5, which mainly corresponds to the $d\pi$(Pt)-π(terpy) metal-to-ligand charge transfer (MLCT) transition based on previous assignments made for this class of
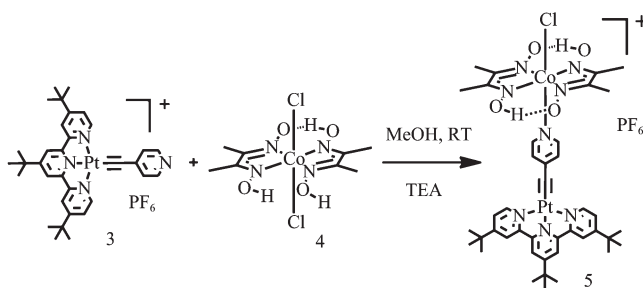
Scheme 2

complexes [23-24]. The absorption bands in the range of 210~371 nm correspond to spin-allowed intraligand (π-π*) transitions (ε>2×10^4 dm^3·mol^{-1}·cm^{-1}).

The emission spectra was also investigated in MeCN/H$_2$O (24:1, V/V) at room temperature. When complex **3** is excited at 400 nm (Fig.1 (b)), the emission spectra show a broad weak emission band from 480 nm to 700 nm with a maximum emission peak at 538 nm, giving a luminescence quantum yield (Φ) of ~0.009, based on [Ru(bpy)$_3$](PF$_6$)$_2$ (Φ= 0.062) [25]. According to previous photophysical studies of closely related [Pt(terpyridyl)(acetylide)]$^+$

complex [23-24], the excited state that gives rise to the observed emission in complex 3 is a triplet metal-to-ligand charge transfer (^{3}MLCT) involving a dπ (Pt) metal orbital as the HOMO and the π*(^{t}Bu$_3$tpy) orbital as the LUMO. However, complex **5** is almost non-emissive (φ<0.000 5) in fluid solution, indicating the intramolecular electron transfer is very efficient from the Pt photosensitizer unit to the cobalt center. The emission property is consistent with previous observations made with the closely related dyad based on the Pt photosensitizers or Ru photosensitizers[26-27].
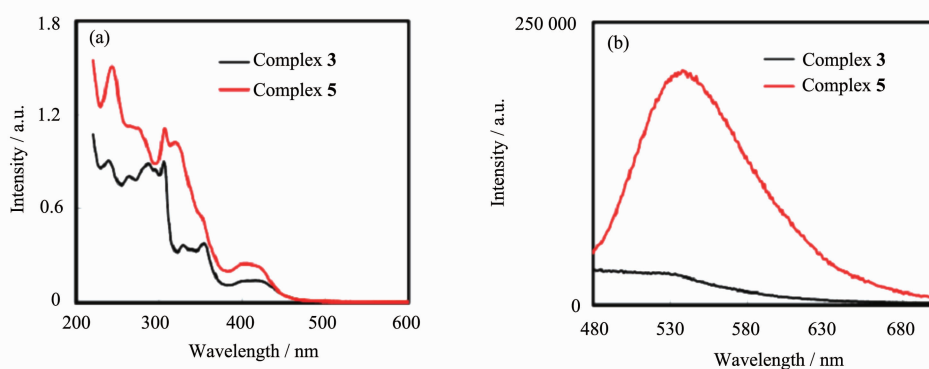

Fig.1　Absorption spectra (a) and emission spectra (b) of complexes **3** and **5** in MeCN/H$_2$O (24:1, V/V) at 2.0×10^{-5} mol·L^{-1}, room temperature. The excitation wavelength is λ=400 nm for both **3** and **5**

2.2　Visible light-driven hydrogen production

Using complex **5** as the hydrogen production catalyst, when TEOA is present as the sacrificial electron donor, the system does produce hydrogen upon visible light irradiation (long pass cut filter, λ > 400 nm). The reaction condition is as follows: room temperature, 4.0×10^{-5} mol·L^{-1}catalyst 5, 1.60×10^{-2} mol·L^{-1} TEOA in MeCN/H$_2$O (24:1, V/V). Quantitative determination of generated H$_2$ was conducted by gas chromatography (GC) analysis with added methane as an internal standard. The turnover numbers (TONs) are defined with respect to the mole numbers of catalyst 5.

The production of hydrogen by photocatalyst 5 is impacted by many factors. At pH value of 8.5, hydrogen is generated with a turnover number of 105 after 10 hours (run 1). Within the same reaction time, the system gives a turnover number of 5 and 37 for

pH value of 5.0 and 11 (run 2 and 3), respectively. At higher pH values, the required redox potential for water reduction is increased, which might decrease the rate of hydrogen production. At lower pH values, the sacrificial electron donor of TEOA will be protonated and therefore weaken the electron donating ability, which could decrease the rate of hydrogen production from water. This observation is consistent with previous results for pH dependence of cobaloxime catalysts. [12] Control experiments indicate that all of the components - molecular catalyst 5, TEOA and water are essential for hydrogen production. The absence of any one of them yields insignificant amounts of hydrogen, as shown in Table 1, run 4~6. The activity of catalyst 5 also varies with different solvents (run 7~10), showing the following order for hydrogen production: MeCN >MeOH > acetone>DMF.

Table 1　Photocatalytic hydrogen production under different conditions[a]

Run	Complex	Irrad. Time / h	TONs
1	**5**	10	105
2	**5**	10	5
3	**5**	10	37
4	**5**	5	<1
5	**5**	5	<5
6	–	5	<1
7	**3**	5	<1
8	**5**	10	25
9	**5**	10	56
10	**5**	10	75

[a]General conditions: The reaction was run in MeCN/water (24:1, *V/V*) in the presence of $1.60×10^{-2}$ mol·L^{-1} TEOA, $4.0×10^{-5}$ mol·L^{-1} complex **5** or **3**; run 1: pH=8.5; run 2 :pH=5.0; run 3: pH=11; run 4: No TEOA; run 5: No water; run 6: No catalyst; run 7: complex **3** at pH= 8.5; run 8: in DMF:water (*V/V*=24:1); run 9: in acetone/water (24:1, *V/V*); run 10: in MeOH/water (24:1, *V/V*)

2.3　Mechanism of the photocatalytic reaction

The mechanism of the visible light-driven hydrogen production in the multi-component system containing the Pt photosensitizer and the cobaloxime catalyst has been fully discussed in previous reports, in which the first step could be either oxidative quenching or reductive quenching upon visible light irradiation[4c,13]. In the present system, the emission spectra of the molecular catalyst 5 indicates the first step might be oxidative quenching via fast intramolecular electron transfer from the Pt photosensitizer part to the cobalt catalytic center [12b]. Subsequently, the electron transfer from TEOA to the Pt photosensitizer unit may regenerate the ground state of the photosensitizer and prevent the non-productive back electron transfer. Further electron transfer from the Pt photosensitizer to Co(II) catalytic center will produce the Co(I) species,
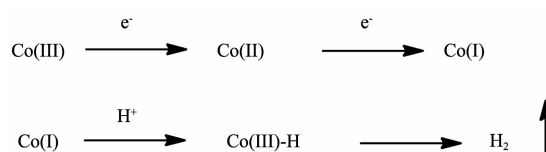
Scheme 3

which are then protonated to give the important Co(III) hydride intermediates for further hydrogen production (Scheme 3).

Experimentally, the transformation of Co species could be monitored by UV-Vis spectroscopy in a solution containing complex **5** and TEOA at different pH values during visible light-driven catalytic reactions, as shown in Fig.2. At pH=8.5, the absorption spectra are shown in Fig.2 (top). The spectra show a slight increase in the range between 420 nm and 520 nm, which is tentatively assigned to the absorption of Co
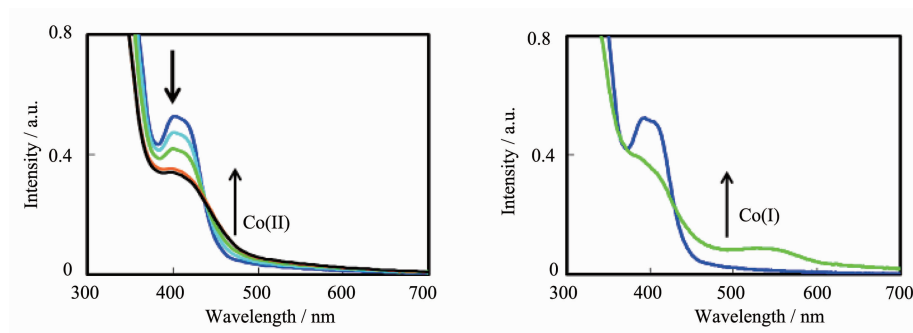

Fig.2　UV-Vis spectra of photocatalytic reaction solutions initially containing $1.60×10^{-2}$ mol·L^{-1} TEOA, $4.0×10^{-5}$ mol·L^{-1} complex **5** in a mixture of MeCN/water (24:1, *V/V*) at pH=8.5 (top) and 11(bottom)

(II) species. At higher pH values, the system has a slower rate for hydrogen production but the Co (I) species could be observed in the range between 480 nm and 650 nm after 6 h irradiation, as shown in Fig.2 (bottom)[28].

However, after carefully examining the absorption spectra before and after photoirradiation at pH=8.5, it seems that complex **5** might be decomposed during reaction. The final absorption spectrum in Fig.2 (left) shows a decreasing extinction coefficient at maximum peak 405 nm, which is closer to complex **3** under the same concentration. It's reasonable to propose that complex **3** is partly released from complex 5 during photoinduced electron transfer, as demonstrated in scheme 4 (inset). This process could be confirmed by mass spectrometry (scheme 4), which mainly shows two separate peaks at 698.58 (*m/z* of 3) and 1 022.83 (*m/z* of 5) after 20 min photoirradiation. A recent paper has reported the unstability of a fluorecein-cobaloxime catalyst for photoinduced hydrogen production, [14] in which the first step is reductive quenching during photoirradiation. While oxidative quenching is the first step during photoirradiation, the present platinum-cobalt catalyst shows another example for decompostion of photosensitizer-catalyst dyad during catalysis.
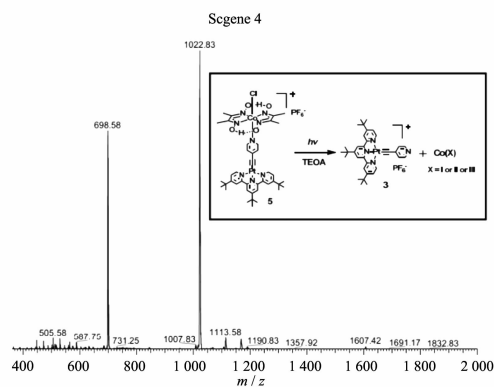
Scheme 2

3 Conclusions

In conclusion, we have demonstrated photoinduced electron transfer process and visible light-driven H_2 production in a platinum-cobaloxime dyad. Mechanistic study shows the formation of Co(II) and Co(I) species upon irradiation. However, the dyad is probably

decomposed to separate the photosensitizer and the catalyst. Further study is in progress to stabilize the cobalt catalytic center.

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