



Photochemical hydrogen production catalyzed by polypyridyl ruthenium–cobaloxime heterobinuclear complexes with different bridges

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ABSTRACT

Two heterobinuclear complexes [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py)Co(dmgBF₂)₂(OH₂))(PF₆)₂ (**1**, dmgBF₂ = (difluoroboryl)dimethylglyoximato) and [(bpy)₂Ru(bpy-4-CH₃,4'-CONHCH₂(4-py)Co(dmgBF₂)₂(OH₂))(PF₆)₂ (**2**) were prepared, in which the polypyridyl ruthenium photosensitizer and the cobaloxime catalyst are connected either by a conjugated bridge (**1**) or by an unconjugated one (**2**). Complexes **1** and **2** were used as photocatalysts for hydrogen generation. Under optimal conditions, the turnover numbers (ton) for hydrogen evolution were 38 for **1** and 48 for **2** in the presence of 300 equiv of both Et₃N and [Et₃NH][BF₄] in the acetone solution during an 8-h irradiation of visible light (λ > ca. 400 nm). The complex **2** with an unconjugated bridge proved to be more efficient for photochemical hydrogen generation than the complex **1** with a conjugated bridge under the same reaction condition.

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1. Introduction

Hydrogen is known as a clean and efficient energy carrier, and is free from CO₂ emission. It has been considered as a promising alternative to fossil fuels to solve the current problems of energy and environment [1–4]. Conversion of solar energy into molecular hydrogen has attracted more and more attention in recent years. Many studies on the visible light-driven water splitting into hydrogen with either heterogeneous or homogeneous systems have been reported since late 1970s [5–8]. The key components of these photochemical H₂-evolving systems are usually a light-harvesting photosensitizer, a sacrificial electron donor, and a proton-reduction catalyst. With the aim of developing light-driven H₂-evolving devices, several photoinduced molecular devices for homogeneous hydrogen generation were constructed in recent years [9–11]. But efficient supramolecular photocatalysts for hydrogen production are relatively scarce [12–16]. Moreover, in most cases, the catalytic centers are noble metal-based (such as Pt, Pd and Rh) complexes [9–11,17–20]. In the long term, the photocatalysts used for a large-scale hydrogen production should rely on inexpensive metals rather than unsustainable noble metals. Some cobalt- and iron-based multi-component catalyst systems proved to be catalytically

active for photochemical hydrogen production in recent decades [21–29].

Homogeneous photochemical hydrogen production mediated by the cobaloxime was initially studied by Lehn and co-workers in 1980s [30]. Recently, Artero and co-workers employed supramolecular devices, with a ruthenium or an iridium chromophore coordinated to the cobaloxime catalyst, for photochemical hydrogen generation [15,16]. In these photocatalysts the two units, the chromophore and the catalyst, are linked with the fully conjugated bridge. It is assumed that the presence of this conjugated bridge could facilitate electron transfer (ET), either through conjugated bonds or by an outer-sphere ET pathway, which is favored by the spatial proximity of the photosensitizer and the catalyst center. In this paper, we prepared two heterobinuclear complexes [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py)Co(dmgBF₂)₂(OH₂))(PF₆)₂ (**1**, dmgBF₂ = (difluoroboryl)dimethylglyoximato) and [(bpy)₂Ru(bpy-4-CH₃,4'-CONHCH₂(4-py)Co(dmgBF₂)₂(OH₂))(PF₆)₂ (**2**), in which the polypyridyl ruthenium chromophore and the cobaloxime catalyst are connected either by a conjugated bridge (**1**, Chart 1) or by an unconjugated one (**2**). After studies on electrochemistry and the steady-state emission quenching of complexes **1** and **2**, the photo-induced hydrogen production mediated by supramolecular devices **1** and **2** was investigated to figure out the influence of the bridge linking the two units of the photocatalysts. The efficiency of such supramolecular devices might be improved by tuning either the nature of the bridge or the distance between two heteronuclear metal centers in the photocatalyst.

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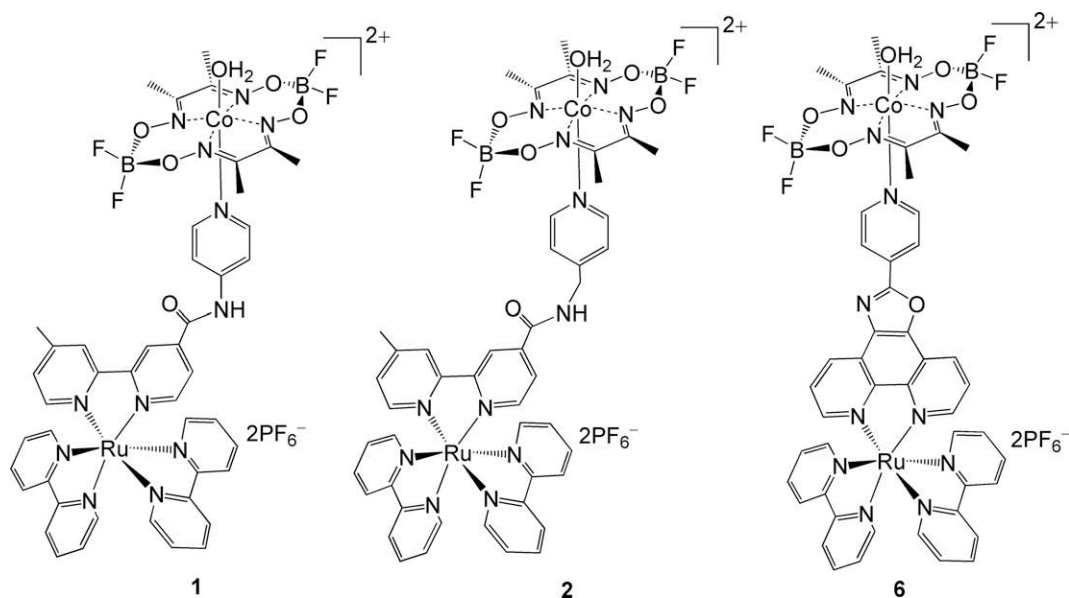


Chart 1. Structures of photocatalysts **1**, **2**, and **6**.

2. Results and discussion

2.1. Preparation and characterization of heterobinuclear complexes **1** and **2**

In the designed heterobinuclear complexes **1** and **2**, the polypyridyl ruthenium unit is used as a light-harvesting photosensitizer and the cobaloxime unit as a proton-reduction catalyst. Complexes **1** and **2** were conveniently prepared in good yields by the facile axial coordination of the pendant pyridyl group of the ruthenium chromophore to the cobalt center of the cobaloxime complex [31]. The HR-MS analyses with a positive ion mode show the doubly charged molecular ion, $[M-H_2O-2PF_6]^{2+}$, as the primary peak. The peaks of $m/z = 544.5924$ for **1** and 551.3936 for **2** are consistent with the calculated MS models for complexes **1** (Fig. S1, $m/z = 544.5986$) and **2** (Fig. S2, $m/z = 551.6064$). The structural difference between the two photocatalysts is that complex **1** possesses a conjugated bridge, while the conjugation of the bridge in complex **2** is broken by an inserted methylene group. The complexes $[(bpy)_2Ru(bpy-4-CH_3,4'-CONH(4-py))](PF_6)_2$ (**3**), and $[(bpy)_2Ru(bpy-4-CH_3,4'-CONHCH_2(4-py))](PF_6)_2$ (**4**), as well as $[Co(dmgBF_2)_2(OH_2)_2]$ (**5**) and the reported heterobinuclear complex **6** (Chart 1) [15], were also prepared to separately study the properties of the two units of the photocatalyst and to make a comparison of the catalytic results under the same reaction condition. The ruthenium complexes **3** and **4** display broad absorptions in the range of 400–500 nm in their UV-Vis spectra (Fig. S3), and the cobaloxime **5** exhibits a relatively positive reduction potential (-0.82 V vs. $Ag/AgNO_3$ in CH_3CN) for the $Co(II)/Co(I)$ process (Fig. S4). All of these merit properties ensure that the photoinduced ET from the excited polypyridyl ruthenium unit to the $Co(II)$ -based catalytic center is thermodynamically feasible in the heterobinuclear complexes **1** and **2**.

2.2. Electrochemistry

Electrochemistry of photocatalysts **1** and **2** were studied to evaluate their redox properties. The cyclic voltammograms of **1** and **2** were recorded in CH_3CN with 0.05 M $[Bu_4N][PF_6]$ as electrolyte (Figs. S4 and S5). The electrochemical data are given in Table 1. Complexes **1** and **2** each display four reversible reduction peaks.

Table 1

Electrochemical potentials of heterobinuclear complexes **1**, **2**, and the cobaloxime **5**^a.

Complex	$(E_{pc} + E_{pa})/2$ ($Co(II)/Co(I)$), V	$(E_{pc} + E_{pa})/2$ (L/L ⁻), V
$[Co(dmgBF_2)_2(OH_2)_2]$	-0.82	
1	-0.75	-1.63, -1.82, -2.10
2	-0.72	-1.62, -1.82, -2.08

^a Cyclic voltammetry was carried out at a scan rate of 100 mV/s in 0.05 M $[Bu_4N][PF_6]$ in CH_3CN . All potentials are vs. Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN).

The reduction peaks, at -0.75 V (All potentials measured are versus $Ag/AgNO_3$ in CH_3CN .) for **1** and -0.72 V for **2**, are ascribed to the $Co(II)/Co(I)$ couple. Typical bpy-based reduction peaks of the polypyridyl ruthenium moiety are observed at -1.63 , -1.82 , -2.10 V for **1** and -1.62 , -1.82 , -2.08 V for **2**, which are similar to the reduction potentials reported for the Tris(bipyridine)ruthenium(II) complex [32].

Cyclic voltammograms of **1** and **2** show that the reversible processes of the $Co(II)/Co(I)$ couple shift by 70 mV for **1** and 100 mV for **2** to more positive potentials relative to the starting cobaloxime **5**, which gives a further proof for the coordination of the ruthenium chromophore to the cobalt center via the axial pyridyl bridge. According to the $Co(II)/Co(I)$ reduction potentials of **1** and **2**, the driving force for the ET from the excited state of the polypyridyl ruthenium moiety to the cobalt center of the catalyst unit is enough and it is somewhat increased as compared to the non-bonded bicomponent system [33].

2.3. Steady-state emission quenching

The fluorescence spectra of the two photocatalysts **1** and **2**, and the corresponding polypyridyl ruthenium complexes **3** and **4** in the deoxygenated acetone solution were studied (Fig. 1). The polypyridyl ruthenium complexes **3** and **4** displayed a strong fluorescence emission, thus they can be employed as a sensitive probe for excited state quenching. If ET and/or energy transfer occurs from the excited state of the polypyridyl ruthenium moiety to the cobaloxime unit in complexes **1** and **2**, the fluorescence quenching should be readily detected. Indeed, we found that the fluorescence of the excited ruthenium moiety was quenched in complexes **1** and **2** in contrast to the corresponding ruthenium complexes without

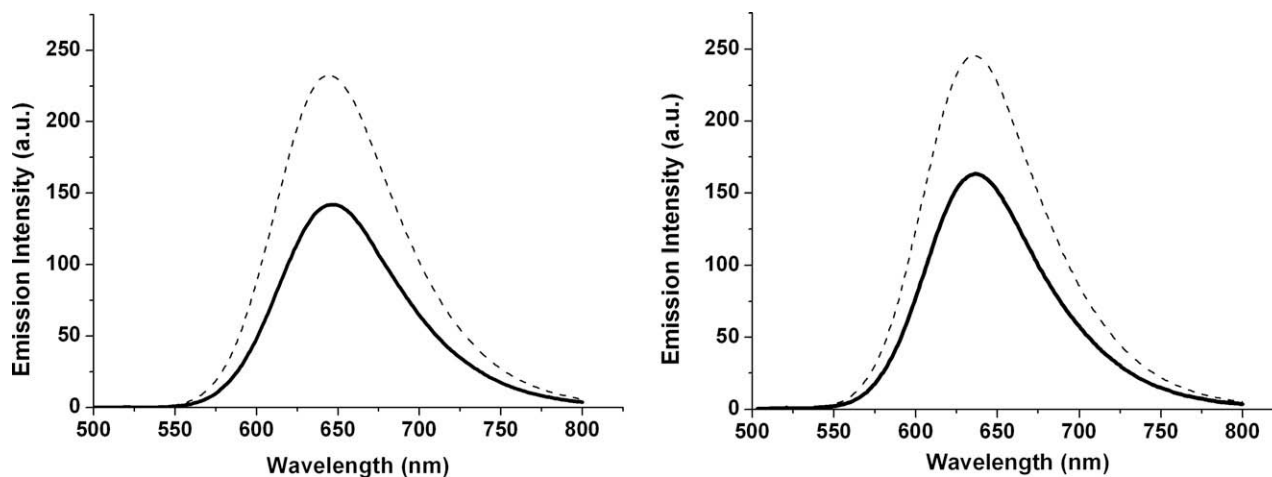


Fig. 1. Fluorescence spectra of complexes **1** (left, solid line) and **2** (right, solid line), and the corresponding polypyridyl ruthenium complexes **3** (left, dashed line) and **4** (right, dashed line) in the deoxygenated acetone (2×10^{-5} M).

bonding to the cobalt ion. The fluorescence intensity of the polypyridyl ruthenium moiety was quenched as much as 35% in complex **1** and 25% in complex **2**. This is probably because the distance between the two units is shorter in complex **1** than that in complex **2**, and because the outer-sphere and the through-bond mechanisms occur in competition for the intramolecular ET in **1** and **2**. We assume that the fluorescence quenching is mainly caused by an intramolecular oxidative process with ET from the excited photosensitizer to the cobalt center in both heterobinuclear complexes. The catalytic activity of **1** and **2** for photoinduced hydrogen evolution, described in the following section, gives a support for this argument.

2.4. Photocatalysis

Complexes **1** and **2** were used as photocatalysts for light-driven hydrogen production with Et_3N as a sacrificial electron donor and $[\text{Et}_3\text{NH}][\text{BF}_4]$ as a proton source. The reaction solution was irradiated at 25 °C using an Xe lamp (500 W) with a Pyrex-glass filter ($\lambda > \text{ca. } 400 \text{ nm}$). The amount of hydrogen evolved was determined by GC analysis of the gas phase of the reaction system. The influences of the loading amount of Et_3N and $[\text{Et}_3\text{NH}][\text{BF}_4]$, the concentration of the photocatalyst, and different solvents on the hydrogen production were studied. The results are summarized in Table 2.

When the loading amount of both Et_3N and $[\text{Et}_3\text{NH}][\text{BF}_4]$ was varied from 100 to 300 equiv relative to that of the photocatalyst, the turnovers (mol H_2 produced per mol of photocatalyst) apparently increased from 15 to 38 (run 1 vs. 2) for **1**, and from 19 to 48 (run 4 vs. 5) for **2** during an 8-h irradiation in the deoxygenated acetone. With increase in the loading amount of both Et_3N and $[\text{Et}_3\text{NH}][\text{BF}_4]$ to 500 equiv, the turnovers of the hydrogen evolved slightly decreased to 36 (run 3) and 42 (run 6) for **1** and **2**, respectively (Figs. S7 and S8). Therefore, in the following experiment, 300 equiv of both Et_3N and $[\text{Et}_3\text{NH}][\text{BF}_4]$ was used for photoinduced hydrogen production.

The turnovers went up from 23 to 38 (run 7 vs. 2) for **1** and from 29 to 48 (run 9 vs. 5) for **2** when the concentration of the photocatalyst was enhanced from 0.25 to 0.50 mM in the solution (Figs. S9 and S10). Further increase of the concentration to 0.75 mM resulted in decrease of the turnovers to 31 (run 8) for **1** and 39 (run 10) for **2**. The condition with 0.5 mM of the photocatalyst in acetone together with 300 equiv of both Et_3N and $[\text{Et}_3\text{NH}][\text{BF}_4]$ proved to be more efficient for photoinduced hydrogen generation mediated by **1** and **2**.

Lower turnovers were obtained when the catalytic reactions were carried out in CH_3CN (25 for **1** and 37 for **2**, runs 11 and 13) and in DMF (8 for **1** and 15 for **2**, runs 12 and 14), respectively. Runs 15 and 16 show that in replacement of $[\text{Et}_3\text{NH}]^+$ with H_2O as the proton source, the turnovers obtained are 29 and 38 for **1** and **2**, respectively, in an acetone solution during an 8-h irradiation.

Under the optimal condition, both photocatalysts **1** and **2** were more active in hydrogen production than the corresponding non-bonding multi-component system (run 20), which gave a relatively low turnovers (7 TON). The maximum turnovers of **1** and **2** are 38 and 48, respectively, in the presence of 300 equiv of Et_3N together with 300 equiv of $[\text{Et}_3\text{NH}][\text{BF}_4]$ during an 8-h irradiation (Fig. 2). The turnover frequency (TOF) of the photocatalyst is 4.75 h^{-1} for **1** and 6 h^{-1} for **2**. It has been reported that the cobaloxime-based catalysts are relatively stable under irradiation of visible light and do not decompose after irradiation for more than 10 h [15,16,27,30]. After a continuous 8-h hydrogen evolution, the irradiation was stopped to let the xenon lamp cool down for a while. We found that the photocatalysts **1** and **2** are still active for hydrogen generation when the solution was re-freeze-pump-thaw degassed and exposed to light.

To make a comparison, we also used the previously reported heterobinuclear photocatalyst **6** [15] as a photocatalyst for hydrogen generation (run 21) under the same condition. Complex **1** with a conjugated bridge displays a comparable catalytic activity to that of **6**, while complex **2** with an unconjugated bridge exhibits a higher activity than **6**. Presumably, the higher activity of **2** results from the influence of the linking bridge. Complexes **1** and **6** with a conjugated bridge may render the unwanted back ET (see Eq. (6) in Scheme 1) easier through the conjugated bonds following the photoinduced ET.

As expected, control experiments show that omission of either moiety of the photocatalyst did not generate hydrogen under irradiation of visible light (runs 17–19), indicating both parts of the photocatalyst were essential to the photoinduced hydrogen production. Moreover, hydrogen formation was not observed when the reaction was carried out in the dark. The results of control experiments indicate that the hydrogen evolution catalyzed by photocatalysts **1** and **2** is indeed via the photoinduced ET from the excited ruthenium moiety to the cobalt center. Considering the much faster reaction rate for the intramolecular ET than that for the intermolecular ET, the intramolecular ET process is assumed to be a dominant mechanism, but the intermolecular ET process could not be totally excluded. We did observe that the

Table 2
Photochemical hydrogen production using Et₃N as a sacrificial electron donor^a.

Run	Photocatalyst	ton
1	1	15 ^b
2	1	38
3	1	36 ^c
4	2	19 ^b
5	2	48
6	2	42 ^c
7	1	23 ^d
8	1	31 ^e
9	2	29 ^d
10	2	39 ^e
11	1	25 ^f
12	1	8 ^g
13	2	37 ^f
14	2	15 ^g
15	1	29 ^h
16	2	38 ^h
17 ⁱ	[(bpy) ₂ Ru(bpy-4-CH ₃ ,4'-CONH(4-py))(PF ₆) ₂]	0
18 ⁱ	[(bpy) ₂ Ru(bpy-4-CH ₃ ,4'-CONHCH ₂ (4-py))(PF ₆) ₂]	0
19 ⁱ	[Co(dmgBF ₂) ₂ (OH ₂) ₂]	0
20	[(bpy) ₂ Ru(bpy-4-CH ₃ ,4'-COOH))(PF ₆) ₂ + 1 equiv [Co(dmgBF ₂) ₂ (OH) ₂]	7
21	6	36

^a Reaction conditions for all runs except for additionally mentioned special conditions in other footnotes: catalyst 0.5 mM, acetone as solvent 10 mL, Et₃N 300 equiv, [Et₃NH][BF₄] 300 equiv, irradiation time 8 h.

^b Both Et₃N and [Et₃NH][BF₄] 100 equiv.

^c Both Et₃N and [Et₃NH][BF₄] 500 equiv.

^d Photocatalyst 0.25 mM.

^e Photocatalyst 0.75 mM.

^f In CH₃CN (10 mL).

^g In DMF (10 mL).

^h Using H₂O (1 mL) as a proton source.

ⁱ Irradiation time 4 h.

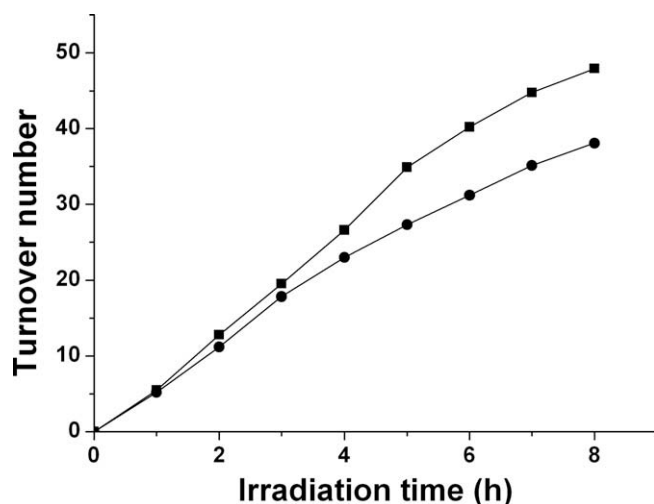
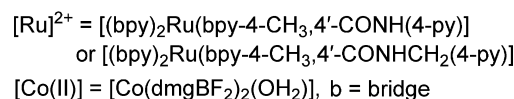
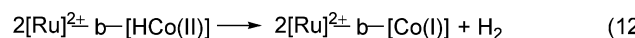
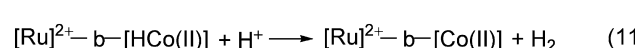
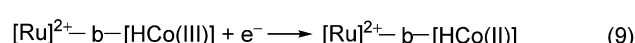
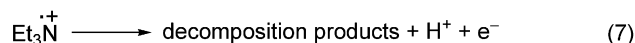
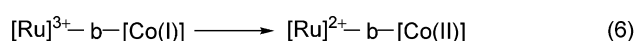
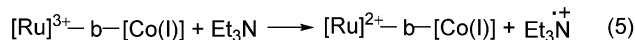
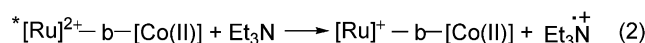


Fig. 2. Photochemical hydrogen evolution from an oxygen-free acetone solution (10 mL) of Et₃N (300 equiv) and [Et₃NH][BF₄] (300 equiv) catalyzed by **1** (●) and **2** (■) (0.5 mM).

color of the reaction solution turned from orange to dark blue after irradiation for several minutes, which was a characteristic of formation of the Co(I) species [6,30]. The thereby generated Co(I) species is assumed to be an important active intermediate for hydrogen production [30].

2.5. Discussion on the mechanism

The processes for the photocatalytic hydrogen generation by the non-bonding photosensitizer/cobaloxime systems have been



Scheme 1. Plausible mechanism for photoinduced hydrogen generation mediated by **1** and **2**.

studied [30,34]. According to the previous report [24,30], the reductive quenching of the excited ruthenium moiety by the electron donor Et₃N and the oxidative quenching by the Co(II) center are both possible in the case of **1** and **2** (Eqs. (2) and (4), Scheme 1). We assume that the latter is the dominant process because it is an intramolecular ET with a large driving force ($E = \text{ca. } -0.79 \text{ V}$ for ${}^*[\text{Ru}]^{2+}/[\text{Ru}]^{3+}$ [33], and $\text{ca. } -0.55 \text{ V}$ for the $[\text{Co(II)}]/[\text{Co(I)}]$ [35], both potentials vs. SCE in CH₃CN). Moreover, the steady-state emission quenching experiment shows that Et₃N is not a good reductive quencher for the excited $[(\text{bpy})_2\text{Ru}(\text{bpy-4-CH}_3,4'-\text{CONH(4-py)})(\text{PF}_6)_2]$ and $[(\text{bpy})_2\text{Ru}(\text{bpy-4-CH}_3,4'-\text{CONHCH}_2(4\text{-py)})(\text{PF}_6)_2]$ in the deoxygenated acetone solution. Upon addition of 500 equiv of Et₃N to the deoxygenated acetone solution of the ruthenium photosensitizer, no apparent fluorescence quenching was observed (Fig. S6). Further studies on the ET reaction are needed to determine the quenching pathway in the polypyridyl ruthenium-cobaloxime bonding photocatalysts. The photochemically formed $[\text{Ru}]^{3+}$ moiety in $[\text{Ru}]^{3+}-\text{b}-[\text{Co(I)}]$ is readily reduced by the sacrificial electron donor Et₃N to the crucial intermediate $[\text{Ru}]^{2+}-\text{b}-[\text{Co(I)}]$ (Eq. (5)). In competition, the unwanted energy-wasting intramolecular ET from the $[\text{Co(I)}]$ center to the oxidized chromophore $[\text{Ru}]^{3+}$ could also happen in $[\text{Ru}]^{3+}-\text{b}-[\text{Co(I)}]$ (Eq. (6)). The decomposition of Et₃N⁺ proceeds via a well-known process to release a proton and an electron (Eq. (7)) [10]. Since the $[\text{Co(I)}]$ center could not be further reduced by the excited $[\text{Ru}]^{2+}$ moiety, protonation of the $[\text{Co(I)}]$ species is a plausible process to generate a Co(III)-hydride intermediate (Eq. (8)) [34–37]. The presence of [Et₃NH]⁺ could facilitate the protonation step. Since [Et₃NH]⁺ is not able to protonate Co(III)-H to generate molecular hydrogen via the heterolytic way, the $[\text{Ru}]^{2+}-\text{b}-[\text{Co(III)-H}]$ could get an electron to form another intermediate $[\text{Ru}]^{2+}-\text{b}-[\text{Co(II)-H}]$ (Eq. (9)). There are three possible pathways for hydrogen generation in the catalytic system [35–37]: (1) by the homolytic cleavage of the Co(III)-H bond (Eq. (10)), (2) by subsequent reduction and further protonation of the Co(II)-H species, leading to heterolytic

cleavage of the Co(II)–H bond (Eq. (11)), and/or by a bimolecular reaction of two Co(II)–H species with homolytic cleavage of the Co(II)–H bond (Eq. (12)).

3. Experimental

3.1. Reagents and instruments

All reactions were carried out under N₂ atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. 4,4'-Dimethyl-2,2'-bipyridyl (dmbpy), 2,2'-bipyridyl (bpy), 4-aminopyridine, and 4-(aminomethyl)pyridine were purchased from Aldrich and used as received. 4'-Methyl-2,2'-bipyridine-4-carboxylic acid was prepared according to the literature procedure [37]. Complexes [(bpy)₂Ru(bpy-4-CH₃,4'-COOH)](PF₆)₂ and [Co(dmgBF₂)₂(OH₂)₂] (**5**) were synthesized following the literature protocol [31,38].

NMR spectra were collected on a Varian INOVA 400NMR spectrometer. Mass spectra were recorded on ESI-Q-TOF MS (Micro) instrument.

3.2. Preparation of 1–4

3.2.1. [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py))](PF₆)₂ (**3**)

Complex [(bpy)₂Ru(bpy-4-CH₃,4'-COOH)](PF₆)₂ (200 mg, 0.22 mmol) and *N*-hydroxysuccinimide (40 mg, 0.34 mmol) were dissolved in acetonitrile (15 mL) at room temperature followed by addition of *N,N'*-dicyclohexylcarbodiimide (DCC, 68 mg, 0.33 mmol). The mixture was stirred for 2 h, and 4-aminopyridine (22 mg, 0.24 mmol) was then added. The color of the solution turned from dark red to bright red. The mixture was stirred for another 24 h. After the solvent was removed on a rotary evaporator, the crude product was purified by column chromatography on an alumina column with acetonitrile/toluene (1:1, v/v) as eluent. Product **3** was obtained in a yield of 102 mg (53%). ¹H NMR (400 MHz, acetone-*d*₆): δ = 2.61 (s, 3H), 7.35 (d, 2H), 7.47 (d, 1H), 7.59 (m, 4H), 7.92 (t, 2H), 7.97 (d, 2H), 8.06 (d, 3H) 8.13 (d, 1H) 8.21–8.25 (m, 5H), 8.83–8.86 (m, 5H), 8.88 (s, 1H), 9.14 (s, 1H). ESI-TOF-MS: *m/z* = 849.43 [M–PF₆]⁺, 352.21 [M–2PF₆]²⁺.

3.2.2. [(bpy)₂Ru(bpy-4-CH₃,4'-CONHCH₂(4-py))](PF₆)₂ (**4**)

Complex **4** was prepared using the same amount of the starting compounds and the identical procedure as described for **3** by replacing 4-aminopyridine with 4-(aminomethyl)pyridine (26 mg, 0.24 mmol). Product **4** was obtained in a yield of 98 mg (50%). ¹H NMR (400 MHz, acetone-*d*₆): δ = 2.61 (s, 3H), 4.77 (d, 2H), 7.36 (d, 2H), 7.48 (d, 1H), 7.60 (m, 4H), 7.95 (t, 2H), 8.07 (d, 3H), 8.14 (d, 1H), 8.21–8.25 (m, 5H), 8.51 (d, 2H), 8.83–8.85 (m, 5H), 8.89 (s, 1H), 9.17 (s, 1H). ESI-TOF-MS: *m/z* = 863.53 [M–PF₆]⁺, 359.25 [M–2PF₆]²⁺.

3.2.3. [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py)Co(dmgBF₂)₂(OH₂))](PF₆)₂ (**1**)

Complexes [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py))](PF₆)₂ (40 mg, 0.04 mmol) and [Co(dmgBF₂)₂(OH₂)₂] (17 mg, 0.04 mmol) were dissolved in acetone (15 mL) and the solution was stirred for 4 h. Removal of the solvent gave a dark red solid of **1** (54 mg, 94%), which was washed with diethyl ether for several times. ESI-TOF-MS: *m/z* = 544.5924 [M–H₂O–2PF₆]²⁺ (calc. 544.5986, see Fig. S1).

3.2.4. [(bpy)₂Ru(bpy-4-CH₃,4'-CONHCH₂(4-py)Co(dmgBF₂)₂(OH₂))](PF₆)₂ (**2**)

Complex **2** was prepared using the same amount of the starting compounds and the identical procedure as described for **1** by replacing [(bpy)₂Ru(bpy-4-CH₃,4'-CONH(4-py))](PF₆)₂ with [(bpy)₂Ru(bpy-4-CH₃,4'-CONHCH₂(4-py))](PF₆)₂ (40 mg, 0.04 mmol). Complex **2** was obtained in a yield of 52 mg (91%). ESI-TOF-MS: *m/z* = 551.3936 [M–H₂O–2PF₆]²⁺ (calc. 551.6064, see Fig. S2).

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3.3. Electrochemistry

Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV/s. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disk (diameter, 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min. The auxiliary electrode was a platinum wire. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN). Acetonitrile (Aldrich, spectroscopy grade) used for performance of electrochemistry was dried with molecular sieve (4 Å) and then freshly distilled from CaH₂ under N₂. A solution of 0.05 M [Bu₄N][PF₆] in CH₃CN was used as electrolyte. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement.

3.4. Steady-state emission quenching

Steady-state absorption measurements were carried out on a Jasco-V-530 spectrophotometer. Photoluminescence spectra were recorded using a Spex Fluorolog fluorimeter by exciting the sample at 450 nm. Samples of ruthenium complexes were purged with N₂ gas for 15 min prior to measurement.

3.5. Photocatalysis

In a typical experiment, the photocatalyst (5 μmol) was dissolved in acetone (10 mL) and 300 equiv of Et₃N together with 300 equiv of [Et₃NH][BF₄] was added in a Schlenk tube (70 cm³). The mixture was magnetically stirred under N₂ atmosphere for 10 min. The solution was freeze-pump-thaw degassed for three times and then warmed to room temperature prior to irradiation. The gas phase volume is ca. 60 cm³. The reaction solution was irradiated at 25 °C using an Xe lamp (500 W) with a special cut-off filter (JB 400, λ > ca. 400 nm). The gas phase of the reaction system was analyzed on a GC 7890T instrument with a 5 Å molecular sieve column, a thermal conductivity detector, and with N₂ as carrier gas. The amount of hydrogen generated was determined by the external standard method.

4. Conclusion

Heterobinuclear complexes **1** and **2** are both efficient photocatalysts for hydrogen generation in the presence of 300 equiv of both Et₃N and [Et₃NH][BF₄] in the acetone solution in the action of visible light, which indicates that the conjugated bridge is not an essential factor for the hydrogen-production photocatalysts. Furthermore, the complex **2** with an unconjugated bridge proved to be more efficient for photochemical hydrogen generation in all cases than the complexes **1** and **6** with conjugated bridges under the same reaction condition, which is consistent with the Ru–Re photocatalysts reported by Ishitani et al. [39]. The photoinduced ET from the excited chromophore to the cobalt centers in these supramolecular photocatalysts may take place in competition by an outer-sphere and a through-bond ET pathway. The higher catalytic activity of **2** (48 TON during an 8-h irradiation) in photoinduced hydrogen evolution as compared to that **1** (38 TON) and **6** (36 TON) suggests that the unconjugated bridge between the chromophore and the catalyst center may prevent the unwanted back ET reaction to a certain extent. Further studies are under way to enhance the efficiency of the photocatalyst in hydrogen generation

by tuning the nature of the bridge and the distance between the chromophore and the catalyst.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.04.041](https://doi.org/10.1016/j.jorganchem.2009.04.041).

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