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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · JULY 2011

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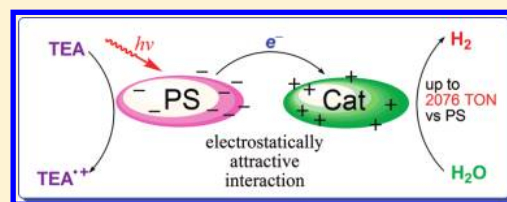
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# Promoting Effect of Electrostatic Interaction between a Cobalt Catalyst and a Xanthene Dye on Visible-Light-Driven Electron Transfer and Hydrogen Production

Jingfeng Dong,<sup>†</sup> Mei Wang,<sup>\*,†</sup> Pan Zhang,<sup>†</sup> Songqiu Yang,<sup>‡</sup> Jianyong Liu,<sup>‡</sup> Xueqiang Li,<sup>†</sup> and Licheng Sun<sup>\*,†,§</sup><sup>†</sup>State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China<sup>‡</sup>State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, China<sup>§</sup>Department of Chemistry, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden

Supporting Information

**ABSTRACT:** The readily obtained noble-metal-free molecular catalyst systems, with xanthene dyes (Rose Bengal, RB<sup>2-</sup>; Eosin Y, EY<sup>2-</sup>; and Eosin B, EB<sup>2-</sup>) as photosensitizers, [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> as catalyst, and triethylamine as sacrificial electron donor, are highly active for visible-light-driven ( $\lambda > 450$  nm) hydrogen production from water. The turnover frequency is up to 54 TON/min versus RB<sup>2-</sup> with a RB<sup>2-</sup>/[Co(bpy)<sub>3</sub>]Cl<sub>2</sub> molar ratio of 1:10 in CH<sub>3</sub>CN/H<sub>2</sub>O under optimal conditions in the first half hour of irradiation ( $\lambda > 450$  nm), and the turnover number is up to 2076 versus RB<sup>2-</sup>. Comparative studies show the following: (1) The photocatalytic H<sub>2</sub>-evolving activity of the cationic cobalt complex [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> is apparently higher than the neutral cobaloxime complexes with xanthene dyes as photosensitizers, and also much higher than the analogous system of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>/[Co(bpy)<sub>3</sub>]Cl<sub>2</sub>. (2) The UV–vis absorptions of xanthene dyes are red-shifted to different extents upon addition of [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> to the aqueous or CH<sub>3</sub>CN/H<sub>2</sub>O solutions of these dyes, while no change was observed in the UV–vis absorptions of photosensitizer with addition of the cobaloximes to the aqueous solution of RB<sup>2-</sup> or addition of [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> to the aqueous solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>. (3) The fluorescence of RB<sup>2-</sup> is significantly quenched by [Co(bpy)<sub>3</sub>]Cl<sub>2</sub>, but not by the cobaloximes. These special performances of [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> are attributed to the electrostatically attractive interaction between the anionic organic dyes and the cationic cobalt catalyst. The probable mechanism for photoinduced hydrogen production catalyzed by the system of RB<sup>2-</sup>, [Co(bpy)<sub>3</sub>]Cl<sub>2</sub>, and triethylamine is discussed in detail on the basis of fluorescence and transient absorption spectroscopic studies.



## 1. INTRODUCTION

The visible-light-driven hydrogen production from aqueous protons has been one of the most attractive subjects in the field of photochemistry for the past decades.<sup>1–4</sup> In addition to the extensively studied heterogeneous photocatalysts, the homogeneous systems for photoinduced hydrogen production have been actively studied in recent years.<sup>5–8</sup> In most reported molecular catalyst systems, the photosensitizer (PS) and the proton reduction catalyst in the H<sub>2</sub>-evolving system are complexes containing precious metals such as Ru,<sup>9,10</sup> Ir,<sup>11,12</sup> Pt,<sup>13,14</sup> Pd,<sup>15,16</sup> Rh,<sup>17,18</sup> etc. For large-scale hydrogen production, development of catalytic systems with PSs and catalysts based on earth-abundant elements is an alluring topic. Some proton reduction catalysts based on the first-row transition metals, such as FeFe-hydrogenase model complexes,<sup>19–24</sup> iron(0) all-carbonyl complexes,<sup>25</sup> and cobalt-based complexes,<sup>26–33</sup> proved effective for photoinduced H<sub>2</sub> production. However, these reported systems usually require precious metal-containing PSs, such as tris(2,2'-bipyridine)ruthenium(II) complexes,<sup>19,20,26</sup> heteroleptic iridium(III) complexes,<sup>22,25,27–29</sup> rhenium(I)-based complexes,<sup>23,29–31</sup> and terpyridine acetylide platinum(II) complexes.<sup>32,33</sup> Only a few examples of completely noble-metal-free molecular catalyst

systems for photoinduced hydrogen production have been reported.<sup>34–39</sup> The porphyrin-and-Fe-based catalyst systems so far reported displayed the photocatalytic efficiencies of H<sub>2</sub> evolution lower than 4 turnover number (TON). The systems comprising a xanthene dye and a cobaloxime complex, reported by Eisenberg and co-workers, gave turnovers of H<sub>2</sub> production from water up to 900 versus Eosin Y (EY<sup>2-</sup>) and 181 versus cobaloxime complex in the presence of an excess of the glyoximate ligand under optimal conditions in 12 h of irradiation.<sup>38</sup> In place of the oxygen in the xanthene ring with selenium, the H<sub>2</sub>-evolving efficiency of the modified xanthene dye/cobaloxime system was improved to 9000 TON versus PS and 450 TON versus Co<sup>III</sup> in 8 h of irradiation, which is the highest efficiency yet reported for the photoreduction of water to H<sub>2</sub> with molecular catalysts.<sup>39</sup>

In addition to cobaloxime complexes, tris(2,2'-bipyridine)cobalt(II) complex was used as catalyst in several hydrogen production systems in combination with Ru<sup>II</sup>- and Ir<sup>III</sup>-containing PSs.<sup>27,28,40</sup>

Received: May 3, 2011

Revised: June 20, 2011

Published: June 29, 2011

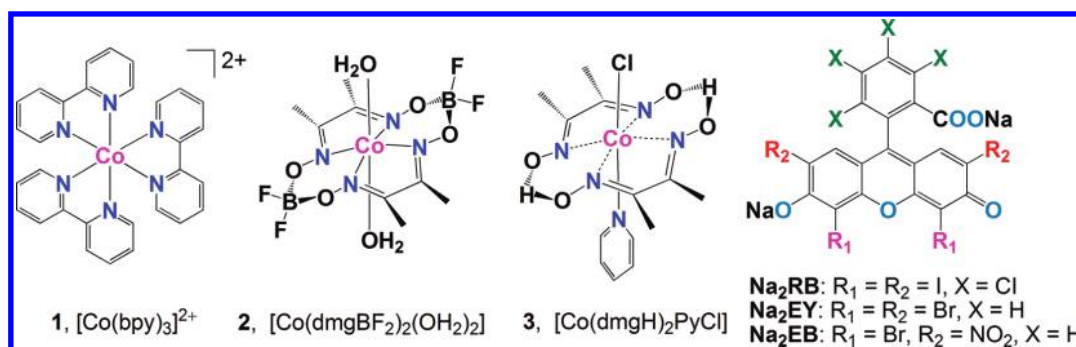


Figure 1. Structures of cobalt catalysts and xanthene dyes used in the present work.

We tried to replace the expensive noble-metal-containing PSs in these systems with commercially available cheap organic dyes, Rose Bengal ( $\text{RB}^{2-}$ ) and Eosins ( $\text{EY}^{2-}$  and  $\text{EB}^{2-}$ ), to build new noble-metal-free molecular catalyst systems (Figure 1). Besides the merits of being inexpensive and readily obtained, the more important advantage of these systems is that an electrostatically attractive interaction of the negatively charged xanthene dyes and the  $[\text{Co}(\text{bpy})_3]^{2+}$  cation may improve the efficiency of photochemical  $\text{H}_2$  production as compared to the previously reported systems with an electrostatically repulsive force between the positively charged Ru- or Ir-containing PSs and  $[\text{Co}(\text{bpy})_3]^{2+}$ .<sup>27,28,40</sup> To our delight, the three-component systems, comprising the xanthene dyes,  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ , and triethylamine (TEA), exhibited a high activity up to 2076 turnover number versus  $\text{RB}^{2-}$  in photoinduced hydrogen production with turnover frequencies (TOFs) of  $\text{H}_2$  evolution up to 54 TON/min versus  $\text{RB}^{2-}$  and 27 TON/min versus  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  in aqueous acetonitrile solution in the first half hour of visible light irradiation ( $\lambda > 450 \text{ nm}$ ). The electron transfer (ET) process and the  $\text{H}_2$ -evolving activity of the xanthene dye/ $[\text{Co}(\text{bpy})_3]^{2+}$  systems are compared with the  $[\text{Ru}(\text{bpy})_3]^{2+}$ / $[\text{Co}(\text{bpy})_3]^{2+}$  and  $\text{RB}^{2-}$ /neutral cobaloxime systems.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents and Instruments.** Complexes  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ ,<sup>27</sup>  $[\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$ ,<sup>41</sup> and  $[\text{Co}(\text{dmgH})_2\text{PyCl}]$ <sup>42</sup> were prepared according to the literature procedures. Rose Bengal and Eosin B were purchased from Aladdin, and Eosin Y was from Sigma-Aldrich. These xanthene dyes were used without further purification. Triethylamine was distilled prior to use. All solvents were of analytical purity and used without further treatment.

UV-vis absorption spectra were recorded on a Jasco-V-530 spectrophotometer. Photoluminescence spectra were recorded using a Spex Fluorolog fluorimeter by exciting the sample at 450 nm. The fluorescence decay times were obtained with a time-correlated single photon counting (TCSPC) setup (FluoroMax-4-TCSPC spectrofluorometer, HORIBA JOBIN YVON Corp,  $\lambda_{\text{exc}}$  460 nm). The instrument response function of the TCSPC system has a fwhm of 1 ns, and the time resolution is estimated at 200 ps. The time range is 0.055 ns/channel, in 4096 effective channels. Nanosecond transient absorption measurements were performed on a LP-920 laser flash photolysis setup (Exdinburgh). The excitation pulses were obtained from the unfocused second harmonic (532 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II), and the probe light was provided by a 75-W Xe arc lamp. The laser and analyzing light beam passed perpendicularly through a 1 cm quartz cell. The

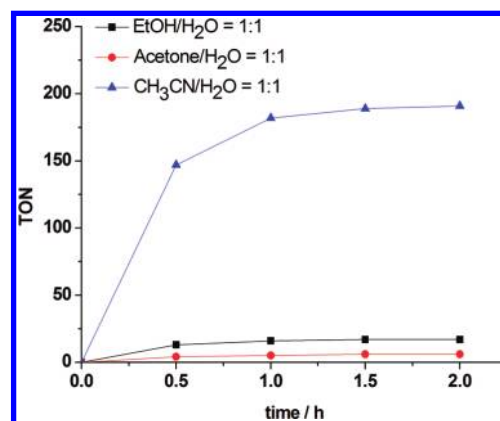


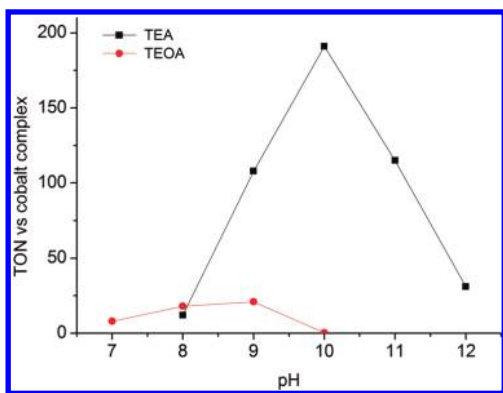
Figure 2. Turnovers of  $\text{H}_2$  evolution from the system containing  $\text{RB}^{2-}$  ( $4.0 \times 10^{-4} \text{ M}$ ), **1** ( $4.0 \times 10^{-4} \text{ M}$ ), and TEA (10%, v/v) in different solvents at pH 10 in irradiation.

signals were detected by Tektronix TDS 3012B oscilloscope and R928P photomultiplier, and finally analyzed by Edinburgh analytical software (LP900). All samples used in flash photolysis experiments were deaerated for 30 min with argon before measurements.

**2.2. General Procedure for Photocatalysis.** In a typical experiment, Rose Bengal disodium salt (2 mg,  $2 \mu\text{mol}$ ) and the cobalt catalyst ( $2 \mu\text{mol}$ ) were added to a 10% TEA aqueous acetonitrile solution (5 mL) in a Schlenk bottle with magnetic stirring under  $\text{N}_2$  atmosphere. The solution was then freeze-pump-thaw degassed three times and then exposed to  $\text{N}_2$ . The mixture was irradiated using a Xe lamp (500 W) with a cutoff filter ( $\lambda > 450 \text{ nm}$ ). The pH value of the solution was adjusted by addition of hydrochloric acid as required and measured on a PHS-25 pH meter. The gas phase of the reaction system was analyzed on a GC 7890T instrument with a thermal conductivity detector, a 5 Å molecular sieve column (2 mm  $\times$  2 m), and  $\text{N}_2$  as carrying gas. The hydrogen dissolved in solution was neglected.

## 3. RESULTS AND DISCUSSION

**3.1. Optimization of Conditions for Photocatalytic Hydrogen Production with  $\text{RB}^{2-}$  as PS.** First, the influence of solvents on the  $\text{H}_2$ -evolving reaction was explored with the system of  $\text{RB}^{2-}$  and  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  in a 1:1 molar ratio in the 10% TEA solution at pH 10 in irradiation of visible light ( $\lambda > 450 \text{ nm}$ ). Solvents have an apparent influence on the photoinduced  $\text{H}_2$  production. When the mixture of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1, v/v) was used as solvent, the turnover of  $\text{H}_2$  evolution was 191 versus the



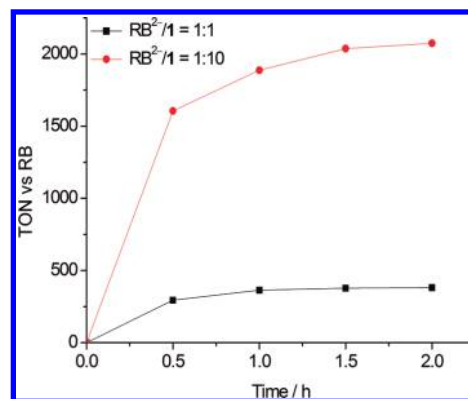
**Figure 3.** Influence of pH and electron donors on the photocatalytic  $\text{H}_2$  evolution from the system comprising  $\text{RB}^{2-}$  ( $4.0 \times 10^{-4}$  M), **1** ( $4.0 \times 10^{-4}$  M), and an electron donor (10%) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) over 2 h irradiation.

cobalt catalyst and the  $\text{H}_2$  evolution leveled off after 2 h of irradiation (Figure 2). In contrast, 17 and 6 TON were obtained, respectively, in the mixed solvents of  $\text{EtOH}/\text{H}_2\text{O}$  (1:1) and  $\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$  (1:1).

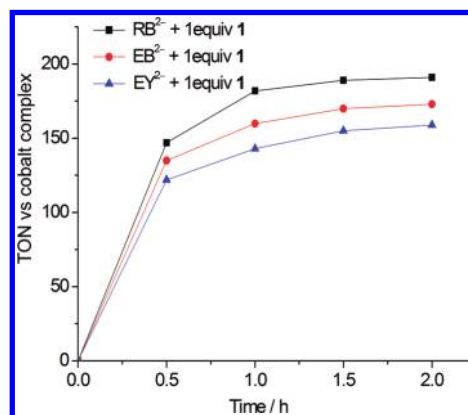
The influence of the volume ratio of  $\text{CH}_3\text{CN}$  to  $\text{H}_2\text{O}$  on the  $\text{H}_2$  evolution was explored (Figure S1 in Supporting Information). The maximal turnover (191 vs  $\text{Co}^{\text{II}}$ ) of  $\text{H}_2$  evolution was obtained in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) at pH 10. With increase of the  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  ratio to 2:1 or decrease of it to 1:2, the turnover was apparently reduced to 116 and 29 versus  $\text{Co}^{\text{II}}$ , respectively. Although increase in the ratio of acetonitrile to water can improve the solubility of TEA, the quantum yield and lifetime of  $^3\text{RB}^{2-}$  can be considerably influenced with addition of a large amount of acetonitrile to water, due to the decrease of the static dielectric constant of the solution.

Considering the aforementioned catalytic results, the influence of pH on  $\text{H}_2$  production was studied using  $\text{RB}^{2-}$  and  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ , both in the concentration of  $4.0 \times 10^{-4}$  M, with TEA (10%) as electron donor in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) over 2 h irradiation. The pH value of the solution was adjusted by dropwise addition of hydrochloric acid. The maximal value of turnover of  $\text{H}_2$  evolution was reached at pH = 10, and it decreased sharply in a more acidic or more basic medium (Figure 3). Decrease in the pH value may cause the protonation of TEA to a considerable extent, while increase of the pH of the solution to the value higher than 10 is not favorable for protonation of the reduced cobalt catalyst to form the cobalt hydride species, which is an accredited intermediate for proton reduction to hydrogen at the metal center of a molecular catalyst.<sup>43,44</sup> When the 10% triethanolamine (TEOA) was used as electron donor in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1), the highest turnover of hydrogen evolution obtained is 23 at pH 9 (Figure 3).

The concentrations of  $\text{RB}^{2-}$  and  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  have apparent influences on the photocatalytic hydrogen evolution. The turnover of  $\text{H}_2$  evolution is 382 versus  $\text{RB}^{2-}$  in a 1:1 molar ratio of  $\text{RB}^{2-}$  to the cobalt catalyst under optimal conditions. When the concentration of  $\text{RB}^{2-}$  was reduced to  $4 \times 10^{-5}$  M in a 10:1 molar ratio of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  to  $\text{RB}^{2-}$  with the other conditions unchanged, 2076 TON versus  $\text{RB}^{2-}$  was attained in a 10% TEA aqueous acetonitrile solution at pH 10 in 2 h irradiation (Figure 4) and the TOF is 54 TON/min in the first half hour of irradiation. In a contrasting experiment, 631 TON versus cobalt complex was obtained in a 1:10



**Figure 4.** Plots of turnover numbers (based on  $\text{RB}^{2-}$ ) of  $\text{H}_2$  evolution vs time with  $\text{RB}^{2-}$  and **1** ( $4.0 \times 10^{-4}$  M) in a 1:1 or 1:10 molar ratio in a 10% TEA  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) solution at pH 10.



**Figure 5.** Plot of the TON of hydrogen evolution vs time. Reaction conditions: xanthene dye and **1**, both in  $4.0 \times 10^{-4}$  M, TEA (10% v/v) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) at pH 10.

molar ratio of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  to  $\text{RB}^{2-}$  under similar conditions (Figure S2).

**3.2. Comparison of the  $\text{H}_2$ -Evolving Efficiencies of Xanthene Dye/ $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  Systems and Other Analogous Cobalt-Based Catalyst Systems.** The  $[\text{Co}(\text{bpy})_3]^{2+}$ -based catalyst systems with  $\text{EY}^{2-}$  and  $\text{EB}^{2-}$  as PSs displayed similar photocatalytic behaviors as compared to that with  $\text{RB}^{2-}$  as light-harvesting chromophore for hydrogen production. The turnovers, 320 versus  $\text{EY}^{2-}$  and 346 versus  $\text{EB}^{2-}$ , are slightly lower than that obtained with  $\text{RB}^{2-}$  as PS in a 1:1 molar ratio of dye to the cobalt catalyst under optimal conditions (Figure 5), and the  $\text{H}_2$  evolution also leveled off after 2 h irradiation.

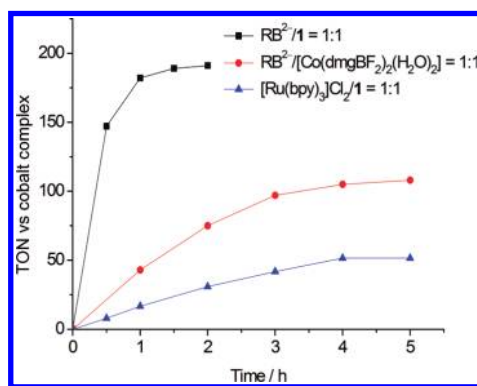
To make a comparison, the performances of the neutral cobalt complexes  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  and  $[\text{Co}(\text{dmgH})_2\text{PyCl}]$  were also studied for hydrogen production with  $\text{RB}^{2-}$  as PS in a 10% TEA aqueous acetonitrile solution at pH 10. It was found that the optimal conditions for hydrogen evolution with  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  as catalyst are similar to those determined for  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ . The system of  $\text{RB}^{2-}$  and  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  in a 1:1 molar ratio gave a TON of hydrogen evolution up to 108 versus  $\text{Co}^{\text{II}}$  (Figure 6), which was enhanced to 212 versus  $\text{Co}^{\text{II}}$  in an 8:1 molar ratio of  $\text{RB}^{2-}$  to the cobaloxime (Table 1).<sup>45</sup> Eisenberg and co-workers reported that approximately 540 TON versus  $\text{RB}^{2-}$  molecule and 54 TON versus  $\text{Co}^{\text{III}}$  were obtained with  $[\text{Co}(\text{dmgH})_2\text{PyCl}]$  as



**Table 1.** Comparison of Efficiencies for Photoinduced H<sub>2</sub> Evolution with the RB<sup>2−</sup>/[Co(bpy)<sub>3</sub>]Cl<sub>2</sub> Systems and Other Analogous Cobalt-Based Catalyst Systems

catalyst	PS	PS to catalyst (mol/mol)	TON vs Co	TON vs PS
[Co(bpy) <sub>3</sub> ]Cl <sub>2</sub> <sup>a</sup>	RB <sup>2−</sup>	1:1	191 (382 μmol)	382
[Co(bpy) <sub>3</sub> ]Cl <sub>2</sub> <sup>b</sup>	RB <sup>2−</sup>	10:1	631 (126 μmol)	126
[Co(bpy) <sub>3</sub> ]Cl <sub>2</sub> <sup>c</sup>	RB <sup>2−</sup>	1:10	104 (208 μmol)	2076
[Co(dmgBF <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>d</sup>	RB <sup>2−</sup>	1:1	108 (216 μmol)	216
[Co(dmgBF <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>e</sup>	RB <sup>2−</sup>	8:1	212 (54 μmol)	54
[Co(dmgH) <sub>2</sub> PyCl] <sup>f</sup>	RB <sup>2−</sup>	1:5	54 (268 μmol)	540
[Co(bpy) <sub>3</sub> ]Cl <sub>2</sub> <sup>a</sup>	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	1:1	52 (104 μmol)	104
[Co(bpy) <sub>3</sub> ]Cl <sub>2</sub> <sup>g</sup>	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	1:50	2 (50 μmol)	100

<sup>a</sup> Reaction conditions: PS (4.0 × 10<sup>−4</sup> M), [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> (4.0 × 10<sup>−4</sup> M), and TEA (10%, v/v) at pH 10 in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1), λ > 450 nm. <sup>b</sup> RB<sup>2−</sup> (4.0 × 10<sup>−4</sup> M), [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> (4.0 × 10<sup>−5</sup> M). <sup>c</sup> RB<sup>2−</sup> (4.0 × 10<sup>−5</sup> M), [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> (4.0 × 10<sup>−4</sup> M). <sup>d</sup> Under similar conditions, RB<sup>2−</sup> (4.0 × 10<sup>−4</sup> M), [Co(dmgBF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (4.0 × 10<sup>−4</sup> M), ref 45. <sup>e</sup> RB<sup>2−</sup> (4.0 × 10<sup>−4</sup> M), [Co(dmgBF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (5.0 × 10<sup>−5</sup> M). <sup>f</sup> RB<sup>2−</sup> (5.0 × 10<sup>−5</sup> M) and [Co(dmgH)<sub>2</sub>PyCl] (2.48 × 10<sup>−4</sup> M) with 5% TEOA in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) at pH 7 over 5 h irradiation, ref 38. <sup>g</sup> [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (5.0 × 10<sup>−5</sup> M) and [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> (2.5 × 10<sup>−3</sup> M) with TEOA (0.57 M) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) in irradiation from 465-nm LEDs, ref 27.

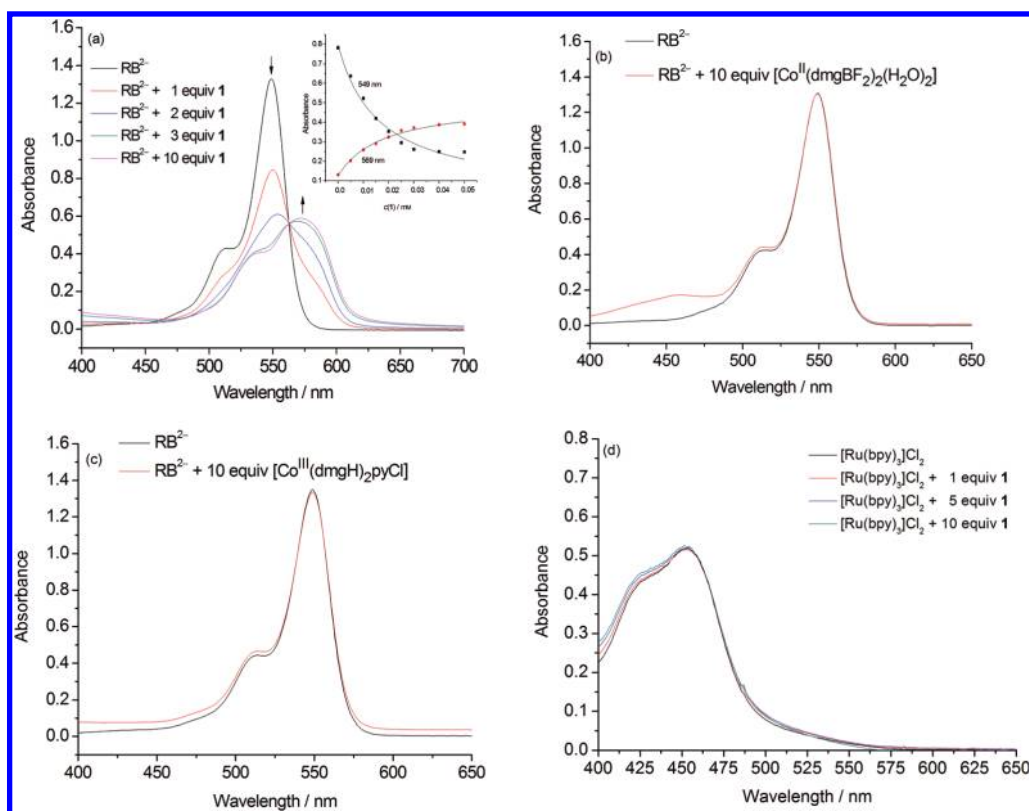
**Figure 6.** Comparison of plots for turnover numbers (based on Co<sup>II</sup>) of H<sub>2</sub> evolution versus time with a PS (4.0 × 10<sup>−4</sup> M) and a Co<sup>II</sup>-based catalyst (4.0 × 10<sup>−4</sup> M) in a 10% TEA CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) solution at pH 10.

catalyst in a 1:5 molar ratio of RB<sup>2−</sup> to the cobaloxime in 5% TEOA CH<sub>3</sub>CN/H<sub>2</sub>O (1:1 v/v) over 5 h irradiation (λ > 450 nm).<sup>38</sup> The other reference system containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Co(bpy)<sub>3</sub>]<sup>2+</sup>, in which both PS and catalyst possess two positive charges in each molecule, also displayed a considerably lower TON (52 vs Co<sup>II</sup>) for photoinduced H<sub>2</sub> production as compared to the system comprising the RB<sup>2−</sup> dianion and [Co(bpy)<sub>3</sub>]<sup>2+</sup> (Figure 6). In addition, 2 TON versus [Co(bpy)<sub>3</sub>]<sup>2+</sup> and 100 TON versus [Ru(bpy)<sub>3</sub>]<sup>2+</sup> were reported for the same system with triethanolamine (TEOA) as electron donor in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1 v/v) with irradiation from 465-nm LEDs.<sup>27</sup> The similar system comprising [Co(bpy)<sub>3</sub>]<sup>2+</sup> and [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup> displays 10 TON versus the cobalt complex and 7 TON versus the Ir-containing sensitizer in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1 v/v) with irradiation from 420-nm LEDs.<sup>28</sup> In general, the systems of the xanthene dye dianions and the complex [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> display apparently higher activity than the neutral cobaloxime catalyst systems with RB<sup>2−</sup> as PS and the system of [Co(bpy)<sub>3</sub>]-Cl<sub>2</sub> in combination with the positively charged sensitizer [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, but the lifetime of the xanthene dye/[Co(bpy)<sub>3</sub>]<sup>2+</sup> systems is shorter than the other cobalt-based molecular catalyst systems.

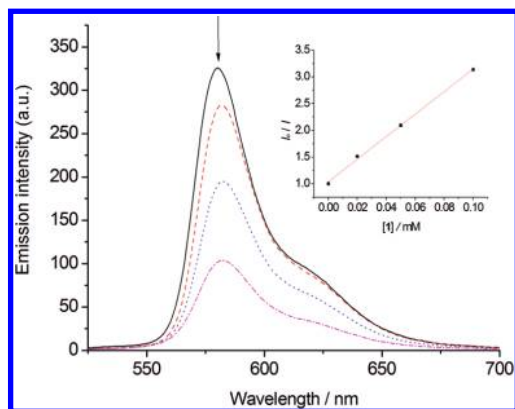
Some experiments were run to figure out which component is responsible for the deactivation of the system. Addition of either

extra Na<sub>2</sub>RB or extra [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> after the 2-h photocatalytic reaction fails to recover hydrogen generation under irradiation, indicating the decomposition of both photosensitizer and catalyst. In a second set of experiments, the H<sub>2</sub>-evolving activity of the system is partially regenerated with addition of extra Na<sub>2</sub>RB when the hydrogen production just starts to level off (1 h of irradiation, Figure S3), while addition of extra [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> cannot resume the H<sub>2</sub>-evolving activity of the system. The results suggest that the degradation of RB<sup>2−</sup> is faster than the decomposition of the [Co(bpy)<sub>3</sub>]<sup>2+</sup> catalyst in this system. Furthermore, the UV–vis absorption spectra were measured before and after the photolysis experiments (Figure S4). It was found that after the 2-h photocatalytic reaction the absorptions of RB<sup>2−</sup> in the range 480–580 nm completely disappeared. It is imperative to improve the stabilities of the photosensitizer and the catalyst.

It has been reported that RB<sup>2−</sup> could form an ion pair with the pyridium cation in the aqueous solution.<sup>46</sup> The interaction between the RB<sup>2−</sup> dianion and [Co(bpy)<sub>3</sub>]<sup>2+</sup> was explored by the UV–vis spectroscopy. The typical absorption of RB<sup>2−</sup> at 555 nm displayed 25 and 6 nm red-shifts with addition of 10 equiv of [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> to the aqueous (Figure 7a) and the aqueous acetonitrile solution (Figure S5), respectively. The binding constants of RB<sup>2−</sup> and [Co(bpy)<sub>3</sub>]<sup>2+</sup>, calculated according to the insets of Figure 7a and Figure S5, are 5.46 × 10<sup>4</sup> M<sup>−1</sup> in H<sub>2</sub>O and 1.41 × 10<sup>4</sup> M<sup>−1</sup> in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1). The concentrations of the ion-pair adduct RB<sup>2−</sup>⋯[Co(bpy)<sub>3</sub>]<sup>2+</sup> formed in the ground state were estimated to be 2.8 × 10<sup>−6</sup> M in H<sub>2</sub>O and 1.1 × 10<sup>−6</sup> M in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) on the basis of the binding constants. Although the binding constant of RB<sup>2−</sup> and [Co(bpy)<sub>3</sub>]<sup>2+</sup> is somewhat larger in H<sub>2</sub>O than in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1), GC analysis showed that only a trace of H<sub>2</sub> was evolved from the photocatalytic reaction in H<sub>2</sub>O, presumably due to the poor solubility of TEA in H<sub>2</sub>O. By contrast, the absorptions of RB<sup>2−</sup> did not show any shift when 10 equiv of the neutral cobalt complex Co(dmgBF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> or Co(dmgH)<sub>2</sub>(Py)Cl was added to the aqueous solution of RB<sup>2−</sup> (Figures 7b,c). Furthermore, addition of [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> to the aqueous solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> did not cause any red shift of the absorptions of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> either (Figure 7d). The results indicate that a close interaction exists between the RB<sup>2−</sup> dianion and the [Co(bpy)<sub>3</sub>]<sup>2+</sup> dication in an aqueous or CH<sub>3</sub>CN/H<sub>2</sub>O solution. Such interaction may facilitate a fast intracomplex ET from the excited state of the organic dye to the [Co(bpy)<sub>3</sub>]<sup>2+</sup>



**Figure 7.** UV-vis spectra observed with addition of **1** (a),  $[\text{Co}^{\text{II}}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  (b), and  $[\text{Co}^{\text{III}}(\text{dmgH})_2(\text{Py})\text{Cl}]$  (c) to the aqueous solution of  $\text{RB}^{2-}$  ( $1.0 \times 10^{-5} \text{ M}$ ), and with addition of **1** to the aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  ( $5.0 \times 10^{-5} \text{ M}$ ) (d). Inset in part a: Plot for changes of absorptions at 549 and 569 nm.

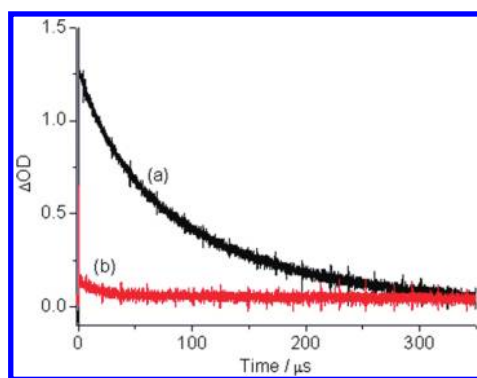


**Figure 8.** Fluorescence spectra of  $\text{RB}^{2-}$  ( $1.0 \times 10^{-5} \text{ M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) upon addition of 0, 2, 5, and 10 equiv of **1**. Inset: The Stern-Volmer plot for the quenching of fluorescence.

catalyst to form the important  $\text{Co}^{\text{I}}$  intermediate for hydrogen production although the presence of the free xanthene dye in the solution cannot be excluded.

**3.3. Probable ET Processes for Photoinduced Hydrogen Evolution.** To investigate the possibility for the ET from the singlet excited state  $^1\text{RB}^{2-}$  to the cobalt catalyst, we studied the fluorescence and the lifetime of  $^1\text{RB}^{2-}$  in the presence of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ . Because  $\text{RB}^{2-}$  displays a strong fluorescence at 560–580 nm depending on the solvent,<sup>47</sup> this band can be employed as a sensitive probe for the quenching of  $^1\text{RB}^{2-}$ . Figure 8 shows that the intensity of fluorescence of  $\text{RB}^{2-}$  was

quenched by ca. 70% upon addition of 10 equiv of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  to the  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) solution of  $\text{RB}^{2-}$ . On the basis of the Stern–Volmer plot (the inset in Figure 8), the quenching constant  $k_{\text{q}01}$  calculated by the equation of  $I_0/I = 1 + K_{\text{sv}}[\text{Q}] = 1 + k_{\text{q}}\tau_0[\text{Q}]$  is  $8.5 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ . In a sharp contrast, the fluorescence of  $\text{RB}^{2-}$  was not quenched in the presence of 10 equiv of  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  (Figure S6) or  $[\text{Co}(\text{dmgH})_2(\text{Py})\text{Cl}]$  (Figure S7).<sup>38,45</sup> The results suggest that the direct ET from  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  may occur in the photoinduced  $\text{H}_2$ -evolving reaction, while the intermolecular ET from  $^1\text{RB}^{2-}$  to the neutral cobaloxime complexes does not take place in the  $\text{RB}^{2-}$ -cobaloxime catalyst systems, although it is thermodynamically feasible according to the oxidation potential of  $^1\text{RB}^{2-}$  ( $E^\circ(\text{RB}^-/{}^1\text{RB}^{2-}) = -1.24 \text{ V}$  versus NHE)<sup>48</sup> and the reduction potentials of  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  ( $E(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = -0.29 \text{ V}$ ) and  $[\text{Co}(\text{dmgH})_2(\text{Py})\text{Cl}]$  ( $E(\text{Co}^{\text{III}}/\text{Co}^{\text{II}}) = -0.43 \text{ V}$ ).<sup>33</sup> The quenching process was further verified by fluorescence lifetime measurements. The lifetime of  $^1\text{RB}^{2-}$  was determined to be 0.6 ns in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1) in the absence of the cobalt complex, while the fluorescence decay time of  $^1\text{RB}^{2-}$  is too short in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  to be detected by the nanosecond fluorometer in the presence of 1 equiv of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ . Therefore, the lifetime of  $^1\text{RB}^{2-}$  was measured in  $\text{CH}_3\text{CN}$ . It was shortened from 2.7 to 0.38 ns when 5 equiv of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  was added to the acetonitrile solution. By varying the concentration of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  from 0.01 to 0.05 mM, the calculated rate constant ( $k'_{\text{q}01}$ ) for the oxidative quenching of  $^1\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  is  $9.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{CH}_3\text{CN}$ , which is in good agreement with the  $k_{\text{q}01}$  calculated by the Stern–Volmer equation. Presumably, the fast ET rate from  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  is due to the electrostatically

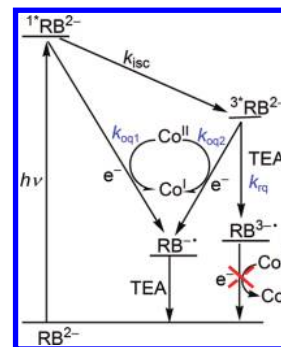


**Figure 9.** Transient decay of the photogenerated  $^3\text{RB}^{2-}$  followed at 620 nm in a deoxygenated acetonitrile solution that contains (a)  $\text{RB}^{2-}$  ( $1.0 \times 10^{-5}$  M) and (b)  $\text{RB}^{2-} + 1$  equiv **1** under pulse irradiation of 532 nm.

attractive interaction of the  $\text{RB}^{2-}$  dianion and the cationic  $[\text{Co}(\text{bpy})_3]^{2+}$  catalyst.

According to the reduction potential of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  ( $E(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = -0.74$  V vs NHE),<sup>40</sup> the ET from the triplet excited state ( $^3\text{RB}^{2-}$ ) of  $\text{RB}^{2-}$  ( $E^\circ(\text{RB}^{\cdot-}/^3\text{RB}^{2-}) = -1.02$  V vs NHE)<sup>38</sup> to  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  is thermodynamically feasible. The possibility of photoinduced ET from  $^3\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  was studied using nanosecond flash photolysis technique. It was reported that the typical absorption of  $^3\text{RB}^{2-}$  is at 610 nm in an aqueous solution.<sup>48</sup> The transient decay of the photogenerated  $^3\text{RB}^{2-}$  at 620 nm was recorded in the deoxygenated acetonitrile solution (Figure 9). The decay kinetic traces show that, in the absence of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ , the triplet excited state of  $\text{RB}^{2-}$  is a long-lived species with the lifetime of 84  $\mu\text{s}$ , which is significantly shortened to 24  $\mu\text{s}$  in the presence of an equivalent of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ . These results indicate that the ET from  $^3\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  possibly occurs as well in the catalyst system. By varying the concentration of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  from 0.01 to 0.05 mM, the apparent rate constant ( $k_{\text{eq2}}$ ) for the oxidative quenching of  $^3\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]^{2+}$  is estimated to be  $8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{CH}_3\text{CN}$ , which is slightly faster than that  $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  measured for the quenching of  $^3\text{RB}^{2-}$  by  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ . The rate constant  $k_{\text{eq1}}$  is 3 orders of magnitude faster than  $k_{\text{eq2}}$ , suggesting that the ET from  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  is more favored than that from  $^3\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$ , while the ET from  $^1\text{RB}^{2-}$  to the neutral  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  cobaloxime complexes cannot occur in the catalytic systems. Although the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  and  $\text{RB}^{2-}/\text{cobaloxime}$  systems display distinct properties in the aspect of ET from  $^1\text{RB}^{2-}$  to cobalt catalyst, these systems exhibit similar rate constants of ET from  $^3\text{RB}^{2-}$  to cobalt catalyst. The results suggest that the electrostatically attractive interaction of the  $\text{RB}^{2-}$  dianion and the cationic  $[\text{Co}(\text{bpy})_3]^{2+}$  catalyst greatly facilitates the ET from the short-lived  $^1\text{RB}^{2-}$  to the cobalt catalyst, but has slight influence on the ET from the long-lived  $^3\text{RB}^{2-}$  to cobalt catalyst. These phenomena can be rationally explained by the lifetime of  $^1\text{RB}^{2-}$  and  $^3\text{RB}^{2-}$ . The lifetime of  $^1\text{RB}^{2-}$  is so short that the slow intermolecular ET cannot take place before  $^1\text{RB}^{2-}$  changes to  $^3\text{RB}^{2-}$ . The formation of an ion-pair adduct can greatly shorten the distance of PS and catalyst so as to facilitate the ET from the short-lived  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  catalyst. The

**Scheme 1.** Proposed ET Pathways Involved in Photoinduced Hydrogen Production Catalyzed by the System of  $\text{RB}^{2-}$ ,  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ , and TEA



long lifetime of  $^3\text{RB}^{2-}$  can allow not only the intra-ion-pair ET but also intermolecular ET.

On the basis of the static and transient spectroscopic evidence as well as the thermodynamic analysis, the ETs from both  $^1\text{RB}^{2-}$  and  $^3\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  are presumably involved in the photoinduced  $\text{H}_2$ -evolving reaction. We propose that the initially photogenerated  $^1\text{RB}^{2-}$  can be either quenched by  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  or take place an intersystem crossing to form the triplet excited state  $^3\text{RB}^{2-}$  (Scheme 1), which is then oxidatively quenched by the cobalt complex. These two oxidative quenching pathways lead to the formation of the important  $\text{Co}^{\text{I}}$  intermediate.

The ET from TEA to  $^1\text{RB}^{2-}$  (reductive quenching) is thermodynamically unfeasible, which was proved by fluorescence spectroscopy.<sup>45</sup> Although  $^3\text{RB}^{2-}$  can be reductively quenched by TEA to form a radical anion  $\text{RB}^{3-}$ , the rate constant ( $k_{\text{rq}} = 3.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>45</sup> of the reductive quenching of  $^3\text{RB}^{2-}$  by TEA is much slower than the  $k_{\text{q1}}$  ( $9.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ ) for oxidative quenching of  $^1\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]^{2+}$  and  $k_{\text{eq2}}$  ( $8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) for the oxidative quenching of  $^3\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]^{2+}$ . Furthermore, the ET from the reduced species  $\text{RB}^{3-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  is thermodynamically unfeasible according to the oxidation potential of  $\text{RB}^{3-}$ . ( $E^\circ(\text{RB}^{2-}/\text{RB}^{3-}) = -0.51$  V vs NHE) and the reductive potential of  $[\text{Co}(\text{bpy})_3]^{2+}$  ( $E(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = -0.74$  V vs NHE).<sup>40,49</sup> The kinetic traces of flash photolysis at 425 nm, the typical absorption band of the  $\text{RB}^{3-}$  radical anion,<sup>48</sup> show that the lifetime (1.4 ms) of the  $\text{RB}^{3-}$  species did not change when  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  was added to the photogenerated  $\text{RB}^{3-}$  solution, which gives experimental proof that the  $\text{RB}^{3-}$  species cannot reduce  $[\text{Co}(\text{bpy})_3]^{2+}$  to the  $\text{Co}^{\text{I}}$  intermediate. Therefore, we assume that the reductive quenching pathway has no contribution to photocatalytic  $\text{H}_2$  production by the  $\text{RB}^{2-}-[\text{Co}(\text{bpy})_3]^{2+}$ -TEA system.

The further reaction of the  $\text{Co}^{\text{I}}$  intermediate with protons from water to form the  $\text{Co}^{\text{III}}$ -hydride is probably similar to the cobaloxime catalysts.<sup>43,44</sup> The protonation of the  $[\text{Co}(\text{bpy})_n]^+$  species has been proposed by Sutin and co-workers as one of the steps in the photoinduced  $\text{H}_2$  evolution with the  $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Co}(\text{bpy})_3]^{2+}$  catalyst system.<sup>50</sup> The generation of hydrogen from the  $\text{Co}^{\text{III}}$ -hydride may undergo by a bimolecular reaction of two  $\text{Co}^{\text{III}}$ -hydrides (a homolytic route), as the basic condition (pH 10) in the present system should disfavor the further reaction of the  $\text{Co}^{\text{III}}$ -hydride with protons to form hydrogen by the heterolytic route. Further investigation is



needed on the details of reaction mechanism, particularly, on how the  $\text{Co}^{\text{I}}(\text{bpy})_n$  is involved in the catalytic H–H bond formation.

#### 4. CONCLUSION

The  $\text{H}_2$ -evolving efficiency (up to 2076 turnovers vs  $\text{RB}^{2-}$ ) of the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  system is considerably higher than that displayed by the analogous system of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{bpy})_3]^{2+}$  as well as the systems of  $\text{RB}^{2-}$  and the neutral cobaloxime complexes. The noticeable photochemical property of the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  system is that the singlet excited state  $^1\text{RB}^{2-}$  can be quenched by  $[\text{Co}(\text{bpy})_3]^{2+}$ . The large rate constant  $k_{\text{OQ1}}$  for oxidative quenching of  $^1\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]^{2+}$  suggests the possibility of fast ET from  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$ , which is presumably due to the electrostatically attractive interaction of  $\text{RB}^{2-}$  and  $[\text{Co}(\text{bpy})_3]^{2+}$ . Such interaction is evidenced by the apparent red-shifts of the absorptions of  $\text{RB}^{2-}$  in the UV–vis spectra upon addition of  $[\text{Co}(\text{bpy})_3]\text{Cl}_2$  to the solution of  $\text{RB}^{2-}$ . The transient spectroscopic studies show that the other ET pathway ( $k_{\text{OQ2}}$ ) from  $^3\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  is also possible, but the rate constant  $k_{\text{OQ1}}$  ( $9.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ ) is more than 3 orders of magnitude larger than the rate constant  $k_{\text{isc}}$  (ca.  $10^6$ – $10^8 \text{ s}^{-1}$ ) of intersystem crossing reported for the homologous xanthene dyes<sup>47,51</sup> and the rate constant  $k_{\text{OQ2}}$  ( $8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) for oxidative quenching of  $^3\text{RB}^{2-}$  by  $[\text{Co}(\text{bpy})_3]^{2+}$ , implying that the fast ET from  $^1\text{RB}^{2-}$  to  $[\text{Co}(\text{bpy})_3]^{2+}$  may play an important role in the photoinduced  $\text{H}_2$  evolution reaction with the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  system. The reductive quenching of  $^3\text{RB}^{2-}$  by TEA is not considered as an effective pathway for photocatalytic  $\text{H}_2$  production by the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  system because the further ET from the reduced  $\text{RB}^{3-}$  species to  $[\text{Co}(\text{bpy})_3]^{2+}$  cannot occur. Although the  $\text{RB}^{2-}/[\text{Co}(\text{bpy})_3]^{2+}$  system displayed relatively high activity (45 TON/min vs  $\text{RB}^{2-}$ ) in the first half hour of irradiation, the durability of the catalyst systems of xanthene dyes and  $[\text{Co}(\text{bpy})_3]^{2+}$  needs to be improved. Studies on the preparations of more stable organic dyes and cobalt polypyridine complexes and their catalytic properties for photoinduced  $\text{H}_2$  evolution are in progress.

#### ■ ASSOCIATED CONTENT

**S Supporting Information.** Seven figures including plots of photocatalytic  $\text{H}_2$  production and UV–vis and fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*Fax: +86-411-83702185 (M.W.). E-mail: [symbuono@dlut.edu.cn](mailto:symbuono@dlut.edu.cn) (M.W.). Fax: +46-8-7912333 (L.S.). E-mail: [lichengs@kth.se](mailto:lichengs@kth.se) (L.S.).

#### ■ ACKNOWLEDGMENT

We are grateful to the Natural Science Foundation of China (Grant 20633020), the Basic Research Program of China (Grant 2009CB220009), the Program for Changjiang Scholars and Innovative Research Team in University (IRT0711), the Swedish Energy Agency, the Swedish Research Council, and the K & A Wallenberg Foundation for financial support of this work.

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