Electrocatalytic and photocatalytic hydrogen generation from water by a water-soluble cobalt complex supported by 2-ethyl-2-(2-hydroxybenzylideneamino)propane-1,3-diol

Ling-Zhi Tang, Chen-Neng Lin, Yun-Xiao Zhang, Shu-Zhong Zhan*

College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

ABSTRACT:

The reaction of 2-ethyl-2-(2-hydroxybenzylideneamino)propane-1,3-diol (H₃L) with Co(NO₃)₂·6H₂O affords a dinuclear cobalt complex, [Co₂(HL)₂(H₂O)₂](NO₃) **1**, an efficient catalyst for both electrocatalytic and photocatalytic hydrogen evolution from aqueous buffer. **1** is a water-soluble molecular species, that is among the most rapid homogeneous catalysts for water reduction and can electrocatalyze hydrogen evolution from a neutral buffer (pH 7.0) with a turnover frequency (TOF) of 1301 mol of hydrogen per mole of catalyst per hour at an overpotential (OP) of 638 mV. Additionally, under photoirradiation with blue light ($\lambda_{\text{max}} = 469$ nm), **1**, together with ascorbic acid and [Ru(bpy)₃]Cl₂ (bpy = 2,2'-bipyridine) in an aqueous buffer (pH 6.0), also affords hydrogen with a remarkable turnover number (TON) of 4314 mol of H₂ per mol of catalyst.

Keywords: Cobalt complex; molecular electrocatalyst; molecular photocatalyst; water reduction; hydrogen evolution.

* Corresponding author. Fax: +86 20 87112053.

E-mail address: shzhzhan@scut.edu.cn (S.-Z. Zhan).

1. Introduction

Ever-increasing energy and environmental concerns are encouraging researchers to explore sustainable and renewable alternatives of conventional fossil fuels, such as hydrogen energy with zero carbon emission [1]. Water is the only waste-free electron-source substrate that could sustain the scale of the process required to supply our energy demands. Thus water splitting is an important method for hydrogen production in high purity and large quantities [2]. However, the kinetically slow oxygen evolution reaction exhibits a significant efficiency loss in water-splitting systems [3,4]. In order to increase the turnover frequency for hydrogen generation, it is necessary to use an efficient hydrogen evolution reaction (HER) catalyst. So far, several complexes that contain cobalt [5-10], iron [11-13], nickel [14,15], copper [16-19] and molybdenum [20-22] have been developed as electrocatalysts for H₂ generation via the reduction of water. Compared to the studies on the electrocatalytic systems, the development of photocatalytic system intended to drive hydrogen evolution from water using visible light still remains a challenging subject [23,24]. Among these, cobalt complexes supported by tetra- or pentadentate ligands have been reported for the catalytic production of H₂ in aqueous media [25-28]. Despite much

progress in water reduction catalysis for hydrogen generation, major improvements in several areas, including simplifying structural complexity, increasing catalyst solubility in water, and operating in neutral medium (pH 7.0), are needed before efficient catalytic water reduction can be realized. Within this context, we have been designing molecular catalysts based on the water-soluble complexes by modification of ligands. As a continuous work [29], reported here is a cobalt electrocatalyst, $[\text{Co}_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ **1** that exhibited remarkable activity in both electro- and photo-catalytic reduction of water. In our photocatalytic system, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was chosen as the photosensitizer: 1) soluble in both organic and aqueous media; 2) strong absorption in the visible region [30,31]; 3) the oxidized species, $\text{Ru}(\text{bpy})_3^{3+}$ and the reduced species, $\text{Ru}(\text{bpy})_3^+$ can react with most of the sacrificial donors, such as ascorbic acid (H_2A) and with most of the catalysts, respectively [31,32]. We hope this can offer an efficient method in water reduction catalysis in purely aqueous media.

2. Experimental

2.1. Materials and physical measurements

$[\text{Co}_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ **1** was prepared by the literature procedure [33]. Elemental analysis for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. UV-Vis spectra were measured on a Hitachi U-3010 spectrometer. ^1H and ^{13}C NMR analysis were conducted by using a Bruker AM-500 instrument in DMSO-d_6 .

ESI-MS experiments were performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing samples directly into the ESI source using a syringe pump. Electrochemical studies were conducted on a CHI-660E electrochemical analyzer under N₂ using a three-electrode cell in which a glassy carbon electrode (1 mm in diameter) was the working electrode, a saturated Ag/AgNO₃ or Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. In organic media, the ferrocene/ferrocenium (1+) couple was used as internal standard and the solution of 0.10 M [(n-Bu)₄N]ClO₄ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) experiments in DMF were conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgNO₃ reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL DMF solution with 1.0 mM acetic acid, while the auxiliary compartment was filled with 35 mL of 0.10 M [(n-Bu₄N)]ClO₄ DMF solution, resulting in equal solution levels in both compartments. After adding complex **1** to working compartment, both compartments were sparged for 1.5 h with N₂ and cyclic voltammograms (CVs) were recorded as controls. CPE experiments in aqueous media were conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgCl reference electrode, and filled with 50 mL of 0.25 M buffer solution (pH 7.0). The auxiliary compartment was fitted with a Pt gauze electrode,

and filled with 35 mL buffer solution (pH 7.0). After adding complex **1**, both compartments were bubbled for 1.5 h with nitrogen and CVs were recorded as controls. After electrolysis, a 0.5 mL aliquot of the headspace was taken and replaced with 0.5 mL of CH₄, and the headspace sample was injected into the gas chromatograph (GC). For the photocatalytic system, each sample was prepared in a 5 mL flask containing 4 mL of buffer solution with ascorbic acid, [Ru(bpy)₃]Cl₂, and complex **1**. Then, the flask was sealed with a septum under air or Ar. Each sample was irradiated by blue light (469 nm) at room temperature. The amounts of H₂ produced during photocatalysis were determined by GC. GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument (Column: 19091J-413, No. USC184265H; Detector: TCD; Injection volume: 1 mL).

2.2. Synthesis of 2-ethyl-2-(2-hydroxybenzylideneamino)propane-1,3-diol (*H₃L*)

To a solution of salicylaldehyde (12.21 g, 0.10 mol) in 20 mL methanol, 2-amino-2-ethyl-1,3-propanediol (11.92 g, 0.10 mol) in methanol (30 mL) was added and the mixture was refluxed for 5 h. Upon cooling, a large quantity of beige solid formed. The solvents were decanted, and the remaining solid residue was washed with cold methanol to give a pure, yellow powder (18.97 g, 85%). Anal. calcd for C₁₂H₁₇NO₃: C, 64.55; H, 7.67; N, 6.27%. Found C, 64.46; H, 7.65; N, 6.38%. ¹H NMR (400 MHz, DMSO-d₆) δ 14.55 (s, 1H), 8.55 (s, 1H), 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 – 7.27 (m, 1H), 6.83 – 6.79 (m, 2H), 4.77 (t, *J* = 5.2 Hz, 2H), 3.55 (d, *J* =

4.7 Hz, 4H), 1.66 (q, $J = 7.5$ Hz, 2H), 0.85 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 164.4, 163.2, 132.7, 132.5, 117.9, 117.6, 66.2, 63.0, 25.1, 7.8.

2.3. Synthesis of cobalt complex, $[\text{Co}_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ **1**

To a solution containing H_3L (0.223 g, 1.0 mmol) and triethylamine (0.20 g, 2.0 mmol) in methanol (20 mL), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 g, 1.0 mmol) in 10 mL methanol was added and the mixture was stirred for 30 min. Red crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried in *vacuo* (0.201 g, 61%). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Co}_2\text{N}_3\text{O}_{11}$: C, 43.78; H, 5.21; N, 6.38%. Found: C, 43.38; H, 5.25; N, 6.49%.

3. Results and discussion

3.1. General characterization

The reaction of 2-ethyl-2-(2-hydroxybenzylideneamino)propane-1,3-diol (H_3L) (Fig. S1) with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ affords a dinuclear complex, $[\text{Co}_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ **1** (Scheme 1), which is in agreement with the result of ESI-MS analysis in methanol. The electrospray mass spectrum of **1** exhibits one ion at a mass-to-charge ratio (m/z) of 578.0877, with mass and isotope distribution pattern corresponding to $[\text{Co}_2(\text{HL})_2(\text{H}_2\text{O})]^+$ (calculated m/z of 578.39) (Fig. S2). As shown in Fig. S3, complex **1** shows one absorption peak at 388 nm, which can be assigned to ligand-metal or metal-ligand transition. From Fig. S4, in the pH range 3.0 to 11.0, the intensity of the

absorption band at 379 nm decreases, but no new peak appears, indicating no new component is formed under these conditions.

Scheme 1 The synthesis of ligand, H₃L and complex, [Co₂(HL)₂(H₂O)₂](NO₃) **1**

3.2. Linear scan voltammetry

To study the electrochemical behavior of complex **1**, linear scan voltammetrys were measured in a neutral buffer (pH 7.0). As shown in Fig. 1, the potentials for reduction of complex **1** obtained by comparison with the back-ground, are the similar (ca. -1.60 V versus Ag/AgCl), indicating that no proton is lost during the initial reduction. The peak current strength increases continually with increasing complex **1** concentration

from 0.0 to 0.305 mM, and no turning point is found, demonstrating that complex **1** undergoes redox cycling during the electrochemical experiment.

3.3. Cyclic voltammetry

From Fig. 2, in DMF solution at a glassy carbon electrode, complex **1** displays two quasi-reversible redox couples at -0.66 and -1.40 V versus Ag/AgNO₃, which can be assigned to the couples of Co^{III/II} and Co^{II/I}, respectively. In an aqueous buffer, **1** exhibits two reduction peaks at -0.43 V and -1.42 V versus Ag/AgCl, which are assigned to the couples of Co^{III/II} and Co^{II/I}, respectively (Fig. S5a). In order to probe the nature of the reduction process, we investigated the pH dependence on the cathodic peak potential. As shown in Fig. S5b, the reduction waves are shifted to lower potentials with increasing pH values, which is consistent with a catalytic process [34].

3. 4. Electrocatalytic hydrogen evolution from acetic acid in DMF

As shown in Fig. S6, in the absence of complex **1**, the cyclic voltammogram of acetic acid exhibits no catalytic current at the potentials of the couples of Co^{II}/Co^I and Co^I/Co⁰, suggesting that proton reduction from acetic acid to H₂ occurs with Co^{III}/Co^{II} and Co^{II}/Co^I. Addition of the varying amounts of acetic acid triggers catalytic currents at potentials near the couples of Co^{III}/Co^{II} and Co^{II}/Co^I. Fig. 3 shows a systematic increase in i_{cat} near -0.75 and -1.55 V with increasing acid concentration from 0.0 to

0.51 mM. This result clearly indicates that hydrogen evolution electrocatalyzed by **1** indeed requires reductions of Co(III) to Co(II) and Co(II) to Co(I).

To test that the product of this reaction was hydrogen gas, CPE of a 0.15 μ M complex **1** containing 1.0 mM acetic acid was conducted in a double-compartment cell using a glassy carbon plate electrode. When an applied potential was -1.50 V versus Ag/AgNO₃, the maximum charge was only 18 mC during 2 min of electrolysis in absence of complex **1** (Fig. 4a). However, under the same conditions, the maximum charge reached 139 mC with addition of complex **1**, accompanying evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S7, ~0.060 mL of H₂ was produced over an electrolysis period of 1.5 h. And Fig. 4b shows the total charge of bulk electrolysis of complex **1** in the presence of acid. According to *Eq. (1)* [21], we calculated a TOF for complex **1** reaching a maximum of 125.4 moles of hydrogen per mole of catalyst per hour at an OP of 991.6 mV (Eq. S1).

$$\text{TOF} = \Delta C / (F \cdot n_1 \cdot n_2 \cdot t) \quad (1)$$

Where, F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H₂, n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis; ΔC is the charge from the catalyst solution minus the charge from solution without catalyst.

3.5. Electrocatalytic hydrogen evolution from aqueous buffer

From Fig. S8, a catalytic current is not apparent in the absence of complex **1** until a potential of -1.55 V versus Ag/AgCl is attained. With addition of complex **1**, the onset of catalytic current is observed at about -1.13 V versus Ag/AgCl, showing that the addition of complex **1** can efficiently reduce the potential.

To further testify the catalytic activity of complex **1**, bulk electrolysis of a 0.15 μ M complex **1** were measured in 0.25 M buffer. From Fig. 5a (the total charge of bulk electrolysis of complex **1** in a 0.25 M buffer solution), when the applied potential is -1.55 V versus Ag/AgCl, the maximum charge reaches 2676 mC during 2 min of electrolysis, accompanying a large amount of gas bubble appeared, which was confirmed to be H₂ by GC analysis. The evolved H₂ was analyzed as H₂ by gas chromatography, Fig. S9a, which gave ~8.0 mL of H₂ over an electrolysis period of 1 h with a Faradaic efficiency of 91% for H₂ (Fig. S9b). A CPE experiment under the same potential without complex **1** only gave a charge of 155 mC (Fig. 5b), showing that this cobalt complex does serve an effective hydrogen production under such conditions. According to *Eq. (1)*, we also calculated a TOF for complex **1** reaching a maximum of 1301 moles of hydrogen per mole of catalyst per hour at an OP of 638 mV (*Eq. S2*). To the best of our knowledge, this value is significantly higher than some reported molecular catalysts based on cobalt complexes for electrochemical hydrogen production from neutral water. For example, a cobalt complex supported by N,N-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine that shows a TOF of 300 moles of H₂ per mole of catalyst per hour at an OP of 0.98 V [7], and a cobalt(II)

complex with N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene, Co(bpbH₂)Cl₂ (376 moles of hydrogen per mole of catalyst per hour at an OP of 687 mV) [35].

3.6. Investigation of the stability and durability of complex 1

In order to test whether **1** retains activity for water reduction over longer time periods, a 72 h CPE electrolysis of 0.15 μ M complex **1** at -1.45 V versus Ag/AgCl was conducted in a stirred 0.25 M buffer (pH 7.0). As shown in Fig. S10, a total of 6414 C is accumulated during the electrolysis. Complex **1** affords a charge build-up over time, with no substantial loss in activity over the course of 72 h, indicating this catalyst is stable and durable under weak basic or neutral conditions. After a 72 h electrolysis period, pH increases by 5.6 units (from 7.0 to 12.6), consistent with accumulation of OH⁻ by water reduction, $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. Noteworthy is that the original catalytic function can be recovered and repeated several times when the solution pH is adjusted back to the original 7.0.

3.7. Photocatalytic hydrogen evolution from aqueous buffer

To explore the photocatalytic hydrogen evolution in aqueous media, a much more attractive system for the sustainable generation of hydrogen, we chose ascorbic acid as electron donor and [Ru(bpy)₃]Cl₂ as photosensitizer to test photocatalytic activity of complex **1**. The capability of **1** to foster hydrogen evolution in light activated experiments were tested upon continuous visible irradiation (LED lamp, $\lambda = 469$ nm)

of 0.25 M buffer with varying pH values containing different concentrations of **1**, Ru(bpy)₃Cl₂ and ascorbic acid.

To confirm that hydrogen evolving activity by complex **1** is dependent on pH of medium, the activity of H₂ evolution by **1** was investigated in the pH range of 3.0–7.0. As shown in Fig. S11, the best pH for photocatalytic H₂ evolution by complex **1** (0.10 mM) is observed at pH 6.0, with a TON of 903 mol of H₂ (mol of cat)^{−1}. This result is different from the reported results that the best pH for photocatalytic H₂ evolution by photo-catalyst was observed at pH 4.0 [7,36].

To investigate the effect of the concentrations of sacrificial reagent and photosensitizer on the photo-catalytic efficiency, different photocatalytic systems were designed. For the photocatalytic system containing 0.12 M ascorbic acid and 0.10 mM complex **1**, the TON during 2 h photocatalysis increased with increasing the concentrations of Ru(bpy)₃Cl₂ until a saturation value of 673 mol of H₂ (mol of cat)^{−1} was reached at 0.70 mM. After that, the TON decreased when the concentration of Ru(bpy)₃Cl₂ was set to more (Fig. S12).

As shown in Fig. S13, for the photocatalytic system containing 0.30 mM Ru(bpy)₃Cl₂ and 0.10 mM complex **1**, the TON used in 2 h increases with increasing the concentration of ascorbic acid until a saturation value of 306 mol of H₂ (mol of cat)^{−1} is reached at 0.15 M. To investigate the effect of concentration of complex **1** on H₂ production, photolysis was carried out at different concentrations of **1** ranging from 0.02 to 0.10 mM at pH 6.0. As shown in Fig. 6, **1** photocatalyzes H₂ production

with a TON of 1441 (air) or 1505 (Ar) mol of H₂ (mol of cat)⁻¹ at 0.10 mM **1**. From Fig. S14, when the concentration of **1** is lowered to 0.02 mM, the TON increases significantly to 4314 (air) or 4650 (Ar) mol of H₂ (mol of cat)⁻¹.

The value (4650 mol of H₂ (mol of cat)⁻¹) is significantly larger than some other reported molecular cobalt catalysts for photochemical hydrogen production. For example, cobalt complexes with pentadentate ligands [7,37] yielding a TON of 450 at 0.050 mM concentration and some of the cobalt complexes supported by neutral ligands [38,39] for which TONs up to ca. 2000 were measured at 20 μM concentration. In order to study oxygen effect on photocatalytic hydrogen evolution, photolysis were conducted under air and Ar, respectively. The amount of H₂ (0.230 mM) produced in the presence of air during the first two hours of irradiation is 86% of that produced when the H₂ evolution was conducted in Ar (0.267 mM), showing that O₂ does inhibit the evolution of H₂ (Fig. 6a).

To identify complex **1** is indeed responsible for the photocatalysis, two of the three components (ascorbic acid, [Ru(bpy)₃]Cl₂, or complex **1**) or CoCl₂·6H₂O were added to a reaction flask after cessation of the H₂ evolution to see if the H₂ production could be resumed. However, addition of any of the four components, in the same amount as used in the photocatalytic system, resulted in no significant amount of H₂ generation. As shown in Fig. S15, the photocatalytic system containing complex **1** and [Ru(bpy)₃]Cl₂ only provides 8.0 μmol H₂. And the addition of both ascorbic acid and [Ru(bpy)₃]Cl₂ led to a decrease in H₂ evolution (7.0 μmol). However, no

significant amount of H₂ was observed when both ascorbic acid and [Ru(bpy)₃]Cl₂ were added.

To assess possible mechanism of our photocatalytic system, the luminescence of the excited photosensitizer, [Ru(bpy)₃]²⁺, in aqueous buffer solution were measured as a function of both ascorbic acid and complex **1** concentration, respectively (Fig. 7). On the basis of the Stern-Volmer plot (Fig. 7 and Fig. S16), the quenching constant k_q , calculated using the equation $I_0/I = 1 + K_{sv}[Q] = 1 + k_q\tau_0[Q]$, is $6.47 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for complex **1**, which is at the diffusion-controlled limit. The Stern–Volmer analysis of the reductive quenching by ascorbic acid provides a quenching rate constant of $12.03 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 7 and Fig. S17), indicating that reductive quenching by the ascorbic acid donor dominates over oxidative quenching by **1**. This is different from previous findings [40,41] that the rate constant for oxidative quenching is higher than that of reductive quenching. On the basis of literature precedent [40,42,43] and above analyses, we propose the catalytic cycle depicted in Scheme 2 for the generation of hydrogen from water by complex **1**. The excited state of tris(2,2'-bipyridine)ruthenium(II) *Ru(bpy)₃²⁺ reacts with ascorbic acid ion, HA⁻ to afford the reducing ion, Ru(bpy)₃⁺ (Eqs 2 and 3). Then the Ru(bpy)₃⁺ reduces the cobalt complex, [Co₂(HL)₂(H₂O)₂](NO₃) **1**, which in turn reacts with H₃O⁺ to form an unstable hydride (Eqs 4 and 5). Further reaction with H₃O⁺ gives H₂ (Eq. 6). More detailed mechanistic studies are under investigation.

Scheme 2 The possible photocatalytic mechanism for proton reduction by complex **1**

4. Conclusion

In summary, a water soluble cobalt complex **1**, which is easy to be obtained, can catalyze water reduction to form dihydrogen. Electrochemical studies show that complex **1** is a highly active molecular electrocatalyst for water reduction with a TOF of 1301 moles of hydrogen per mole of catalyst per hour at an OP of 638 mV (pH 7.0). Complex **1** in an aqueous buffer (pH 6.0) under air, together with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and ascorbic acid as a sacrificial electron donor, in the presence of blue light ($\lambda_{\text{max}} = 469 \text{ nm}$) produces dihydrogen with $4314 \text{ mol of H}_2 (\text{mol of cat})^{-1}$. These results may offer a new method for the design of effective cobalt-based molecular catalysts for hydrogen production in purely aqueous media.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 20971045 and 21271073).

References

- [1] Walter MG, Warren EL, McKone JR, Boettcher SW, Mi QX, Santori EA, et al. Solar water splitting cells. *Chem Rev* 2010; 110: 6446-73.
- [2] Chen HM, Chen CK, Liu RS, Zhang L, Zhang JJ, Wilkinson DP. Nano-architecture and material designs for water splitting photoelectrodes. *Chem Soc Rev* 2012; 41: 5654-71.
- [3] Cook TR, Dogutan DK, Reece SY, Surendranath Y, Teets TS, Nocera DG. Solar energy supply and storage for the legacy and nonlegacy worlds. *Chem Rev* 2010; 110: 6474-6502.
- [4] Suntivich J, May KJ, Gasteiger HA, Goodenough JB, Shao-Horn YA. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* 2011; 334: 1383-85.
- [5] Cao J, Fu LZ, Zhou LL, Zhan SZ, Electrochemical-driven hydrogen evolution from acetic acid and water catalyzed by a mixed-valent $\text{Co}^{\text{II}}\text{-Co}^{\text{I}}$ complex with high turnover frequency. *J Power Sources* 2015; 279: 107-113.
- [6] Sun Y, Bigi JP, Piro NA, Tang ML, Long JR, Chang CJ. Molecular cobalt pentapyridine catalysts for generating hydrogen from water. *J Am Chem Soc* 2011; 133: 9212-15

- [7] Singh WM, Baine T, Kudo S, Tian S, Ma XAN, et al. Electrocatalytic and photocatalytic hydrogen production in aqueous solution by a molecular cobalt complex. *Angew Chem Int Ed* 2012; 51: 5941-44.
- [8] Stubbert BD, Peters JC, Gray HB. Rapid water reduction to H₂ catalyzed by a cobalt bis(iminopyridine) complex. *J Am Chem Soc* 2011; 133: 18070–73.
- [9] Cao JP, Fu LZ, Zhou LL, Zhan SZ. Electrochemical-driven hydrogen evolution from acetic acid and water catalyzed by a mixed-valent Co^{II}-Co^I complex with high turnover frequency. *J Power Sources* 2015; 279: 107-113.
- [10] Fu LZ, Zhou LL, Tang LZ, Zhang YX, Zhan SZ. Electrochemical and photochemical-driven hydrogen evolution catalyzed by a dinuclear Co^{II}-Co^{II} complex. *J Power Sources* 2015; 280: 453-458.
- [11] Carroll ME, Barton BE, Rauchfuss TB, Carroll PJ. Synthetic models for the active site of the [FeFe]-hydrogenase: Catalytic proton reduction and the structure of the doubly protonated intermediate. *J Am Chem Soc* 2012; 134: 18843–52.
- [12] Quentel F, Passard G, Gloaguen F. Electrochemical hydrogen production in aqueous micellar solution by a diiron benzenedithiolate complex relevant to [FeFe] hydrogenases. *Energy Environ Sci* 2012; 5: 7757-61.
- [13] Nguyen AD, Rail MD, Shanmugam M, Fettinger JC, Berben LA. Electrocatalytic hydrogen evolution from water by a series of iron carbonyl clusters. *Inorg Chem* 2013; 52: 12847-54.

- [14] Helm ML, Stewart MP, Bullock RM, DuBois MR, DuBois DL, A synthetic nickel electrocatalyst with a turnover frequency above 100,000 s⁻¹ for H₂ production. *Science* 2011; 333: 863–66.
- [15] Cao JP, Fang T, Fu LZ, Zhou LL, Zhan SZ. A nickel molecular electro-catalyst for generating hydrogen from acetic acid or water. *Int J Hydrogen Energy* 2014; 39: 10980-86
- [16] Cao JP, Fang T, Wang ZQ, Ren YW, Zhan SZ. A dinuclear triazenido-copper complex: a new molecular electro-catalyst for generating hydrogen from acetic acid or water. *J Mol Catal A Chem* 2014; 391: 191–197.
- [17] Cao JP, Fang T, Fu LZ, Zhou LL, Zhan SZ. First mononuclear copper(II) electro-catalyst for catalyzing hydrogen evolution from acetic acid and water. *Int J Hydrogen Energy* 2014; 39: 13972-78.
- [18] Zhou LL, Fang T, Cao JP, Zhu Z, Su X, Zhan SZ. A dinuclear copper(II) electrocatalyst both water reduction and oxidation. *J Power Sources* 2015; 273: 298-304.
- [19] Fang T, Lu HX, Zhao JX, Zhan SZ, Lv QY A new copper(I)–triazenido electro-catalyst for catalyzing hydrogen evolution from acetic acid and water. *J Mol Catal A Chem* 2015; 396: 304-309.
- [20] Karunadasa HI, Chang CJ, Long JR. A molecular molybdenum-oxo catalyst for generating hydrogen from water. *Nature* 2010; 464: 1329-33.

- [21] Cao JP, Fang T, Zhou LL, Fu LZ, Zhan SZ. A molecular molybdenum electrocatalyst for generating hydrogen from acetic acid or water. *J Power Sources* 2014; 272: 169-175
- [22] Cao JP, Fang T, Zhou LL, Fu LZ, Zhan SZ. A molecular molybdenum–schiff base electro-catalyst for generating hydrogen from acetic acid or water. *Electrochimica Acta* 2014; 147: 129-135
- [23] Heyduk AF, Nocera DG. Hydrogen produced from hydrohalic acid solutions by a two-electron mixed-valence photocatalyst. *Science* 2001; 293: 1639-41.
- [24] Esswein AJ, Nocera DG. Hydrogen production by molecular photocatalysis. *Chem Rev* 2007; 107: 4022-47.
- [25] Sun Y, Bigi JP, Piro NA, Tang ML, Long JR, Chang CJ. Molecular cobalt pentapyridine catalysts for generating hydrogen from water. *J Am Chem Soc* 2011; 133: 9212-15.
- [26] Sun Y, Sun J, Long JR, Yang P, Chang JC. Photocatalytic generation of hydrogen from water using a cobalt pentapyridine complex in combination with molecular and semiconductor nanowire photosensitizers. *Chem Sci* 2013; 4: 118–124.
- [27] Bigi JP, Hanna TE, Harman WH, Chang A, Chang CJ. Electrocatalytic reduction of protons to hydrogen by a water-compatible cobalt polypyridylplatform. *Chem Commun* 2010; 46: 958–60.

- [28] King AE, Surendranath Y, Piro NA, Bigi JP, Long JR, Chang JC. A mechanistic study of proton reduction catalyzed by a pentapyridine cobalt complex: evidence for involvement of an anation-based pathway. *Chem. Sci* 2013; 4: 1578–87.
- [29] Fu LZ, Tang LZ, Zhang YX, Liang QN, Fang C, Zhan SZ. Hydrogen evolution catalyzed by a water-soluble cobalt(II) complex with picolinic acid ions. *Int J Hydrogen Energy* 2016; 41: 249-254.
- [30] Vennampalli M, Liang G, Katta L, Webster CE, Zhao X. Electronic effects on a mononuclear Co complex with a pentadentate ligand for catalytic H₂ evolution. *Inorg Chem* 2014, 53, 10094-10100.
- [31] Deponti E, Natali M. Photocatalytic hydrogen evolution with ruthenium polypyridine sensitizers: unveiling the key factors to improve efficiencies. *Dalton Trans* 2016; 45: 9136-47.
- [32] Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, Von Zelewsky A. Ru(II) polypyridine complexes: photophysics, photochemistry, eletrochemistry, and chemiluminescence. *Coord Chem Rev* 1988; 84: 85-277.
- [33] M.-J. Niu, D.-W. Sun, H.-H. Li, Z.-Q. Cao, S.-N. Wang, J.-M. Dou. Di-, tri-, and tetranuclear cobalt, copper, and manganese complexes bridged by μ -hydroxyl groups of tetradentate Schiff base ligands: structures, magnetic properties, and antitumor activities. *J Coord Chem* 2014; 67: 81-95.

- [34] Nicholson RS, Shain I. Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems. *Anal Chem* 1964; 36: 706-723.
- [35] Wang ZQ, Tang LZ, Zhang YX, Zhan SZ, Ye JS. Electrochemical-driven water splitting catalyzed by a water-soluble cobalt(II) complex supported by N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene with high turnover frequency. *J Power Sources* 2015; 287: 50-57.
- [36] Xie J, Zhou Q, Li C, Wang W, Hou Y, Zhang B, Wang X. An unexpected role of the monodentate ligand in photocatalytic hydrogen production of the pentadentate ligand-based cobalt complexes. *Chem Commun* 2014; 50: 6520-22.
- [37] Shan B, Baine T, Ma XAN, Zhao X, Schmehl XRH, Mechanistic details for cobalt catalyzed photochemical hydrogen production in aqueous solution: Efficiencies of the photochemical and non-photochemical steps. *Inorg Chem* 2013; 52: 4853-59.
- [38] Nippe M, Khnayzer RS, Panetier JA, Zee DZ, Olaiya BS, Head-Gordon M, et al. Catalytic proton reduction with transition metal complexes of the redox-active ligand bpy2PYMe. *Chem Sci* 2013; 4: 3934-45.
- [39] Khnayzer RS, Thoi VS, Nippe M, King AE, Jurss JW, El Roz KA, et al. Towards a comprehensive understanding of visible-light photogeneration of hydrogen from water using cobalt(II) polypyridyl catalysts. *Energy Environ Sci* 2014; 7: 1477-88.

- [40] Shan B, Baine T, Ma XAN, Zhao X, Schmehl RH. Mechanistic details for cobalt catalyzed photochemical hydrogen production in aqueous solution: Efficiencies of the photochemical and non-photochemical steps. *Inorg Chem* 2013; 52: 4853-59.
- [41] McNamara WR, Han Z, Alperin PJ, Brennessel WW, Holland PL, Eisenberg R. A cobalt–dithiolene complex for the photocatalytic and electrocatalytic reduction of protons. *J Am Chem Soc* 2011; 133: 15368–71.
- [42] Krishnan CV, Sutin N. Homogeneous catalysis of the photoreduction of water by visible light. 2. Mediation by a tris(2,2'-bipyridine)ruthenium(II)-cobalt(II) bipyridine system. *J Am Chem Soc* 1981; 103: 2141-42.
- [43] Brown GM, Brunschwig BS, Creutz C, Endicott JF, Sutin N. Homogeneous catalysis of the photoreduction of water by visible light. Mediation by a tris(2,2'-bipyridine)ruthenium(II)-cobalt(II) macrocycle system. *J Am Chem Soc* 1979; 101: 1298-1300.