Photo-catalytic H₂ evolution, structural effect and electron transfer mechanism based on four novel [2Fe₂S] model complexes by photochemical splitting water

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Abstract

Four novel [2Fe₂S] model complexes(**1-4**) had been synthesized and characterized by IR, ¹HNMR, elemental analysis and single crystal X-ray crystallography (for **2**). The key parameters affecting H₂ evolution of title compounds (**1-4**) were optimized by constructing homogeneous photo-catalytic system consisting of title sample (**1-4**) as catalyst, erythrosin B sodium salt (EBS²⁻) as photo-sensitizer(PS) and triethylamine(TEA) as sacrificial reagent in CH₃CN/H₂O solution under the irradiation of visible light. The maximum H₂ evolution was separately 211.4 ± 6.5 μmol (52.9 ± 1.6 TON vs. **4**), 199.4 ± 13.5 μmol (49.9 ± 3.4 TON vs. **1**), 124.8 ± 7.6 μmol (31.2 ± 1.9 TON

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vs. **3**) and $34.9 \pm 6.9 \mu\text{mol}$ (8.7 ± 1.7 TON vs. **2**) under the optimal conditions with catalyst of $2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, EBS²⁻ of $4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, TEA of 10% (v/v) and pH 12 in CH₃CN/H₂O (1/1, v/v) solution. Furthermore, the structural effect and mechanism of electron transfer in the present system was carefully discussed by fluorescence spectra and cyclic voltammetry (CV) measurements.

Key words: [2Fe2S] model complex; Photo-catalysis; H₂ evolution; Mechanism

1. Introduction

Nowadays, the increasing consumption of fossil fuel drives people to look for new alternative energy resource, such as solar energy and hydrogen energy (Baniasadi, et al., 2014). Conversion of solar energy into chemical fuel, particularly solar driven splitting of water into molecular H₂ and O₂, represents one of the important approaches to use of solar energy because of its potential applications in recycling utilization of renewable resource, reducing the consumption of fossil fuel and subsequent emissions of greenhouse gases (Gray, 2009; Ismail and Bahnemann, 2014; Nicolet, et al., 1999).

It's well known that in nature, the natural [FeFe]-hydrogenases (H₂ases) plays a very important role in releasing molecular hydrogen over the natural world (Peters, et al., 1998). The synthesis of photocatalyst with key active site of [FeFe]-H₂ases has developed into a hotspot research area at present. So far the researches on [FeFe]-H₂ases and its derivatives have been widely reported in the literature (Na, et al., 2008). However, most of photo-catalytic systems based on [2Fe2S] cluster-based photo-catalysts are still focused on employing noble metal as sensitizer (such as complex of Ru, Ir, Rh, Pd, Pt) (Peters, et al., 1998; Na, et al., 2008; Song, et al., 2009), and the relatively low catalytic activity and poor photo-stability have become the major challenges for scientific community (Song, et al., 2009; Streich, et al., 2010; Zhang, et al., 2010; Cao, et al., 2012; Li, et al.,

2013; Wang, et al., 2013). For instance, Song et al. reported a H₂ evolution of 0.31 TON (vs. catalyst) from the biomimetic catalyst (5-[(μ-SCH₂)₂NFe₂(CO)₆-phenyl]-10,15,20-triphenylporphyrin) in the photo-catalytic system comprising of EtSH as electron donor and CF₃COOH (TFA) as proton source in H₂O/CH₂Cl₂ solution by UV irradiation 500W Hg lamp (Streich, et al., 2010). In 2010, Hammarström et al. recorded a H₂ generation of 200 TON (vs. cat.) based on the photo-catalytic system consisting of [Fe₂(μ-Cl₂bdt)(CO)₆] (Cl₂bdt = 3,6-dichlorobenzene-1,2-dithiolate) as catalyst, [Ru(bpy)₃]²⁺ as PS and ascorbic acid as sacrifice reagent (SR) in DMF/H₂O (1/1, v/v) solution (Zhang, et al., 2010). Thereafter, Sun and coworkers also reported a higher H₂ generation of 466 TON from the system containing [{(μ-SCH₂)₂NCH₂C₆H₅}{Fe(CO)₃}{Fe(CO)₂P(Pyr)₃}] as catalyst, [Ir(ppy)₂(bpy)]⁺ as PS, and TEA as electron donor in acetone/water (9/1, v/v) solution (Cao, et al., 2012).

Until recently, Wu's team found a H₂ production system (TON = 505) based on CdTe quantum dots (QDs) as PS, a water-soluble [FeFe]-H₂ase mimic as catalyst, and ascorbic acid (H₂A) as proton source and sacrificial electron donor (Li, et al., 2013). Soon after, a water-soluble catalyst Fe₂S₂(CO)₆ was assembled on the surface of CdSe QDs using an interface-directed approach, and displayed a high TON of 8781 (vs. Fe₂S₂(CO)₆) in a mixture of aqueous/organic solvent under visible light irradiation (Wang, et al., 2013). Freshly, a high H₂ evolution of 27315 TON was also reported from a photo-catalytic system based on [FeFe]-H₂ase model complex and CdSe quantum dot in 8h of irradiation (Zheng, et al., 2015). Obviously, it was an admirable work in the field of photo-catalytic H₂ evolution utilizing solar energy, but CdTe and CdSe are known as poisonous compounds which limit their application.

As stated above, although many researches have been made in the field of photo-catalytic hydrogen production, and most of H₂ evolution systems were still devoted to employing noble

metals as catalyst or PS (such as complex of Ru, Ir, Rh, Pd, Pt et al.) (Song, et al., 2009; Streich, et al., 2010; Zhang, et al., 2010; Cao, et al., 2012; Poddutoori, et al., 2011; Wang, et al., 2012; V. Artero, M. Fontecave, 2005; Capon, et al., 2009; Wang, et al., 2011; Lomoth and Ott, 2009; Wang and Sun, 2010) except for several quantum dots (CdSe, CdTe et al.) as PS (Li, et al., 2013; Wang, et al., 2013). However, the study on photo-catalytic hydrogen production based on [2Fe2S] complex as photo-catalyst and non-noble metal compound or cheap organic dyes as PS are still extremely rarely (Li, et al., 2008; Kluwer, et al., 2009; Samuel, et al., 2010; Orain, et al., 2014), the correlation between catalyst structure and hydrogen production activity in the photo-catalytic system was rarely uttered.

Taking into account above the factors, in this work, we synthesized four new [2Fe2S] cluster model compounds (**1-4**), and evaluated their H₂ generation activity in the constructed noble-metal-free ‘three components’ photo-catalytic system. The structural effect of title compounds on H₂ evolution and plausible H₂ generation mechanism was carefully discussed, respectively.

2. Experimental Section

2.1 Reagents and Instruments

All reactions and operations in this work were carried out under dry nitrogen atmosphere. Prior to use, all the solvents were dried and distilled according to the standard methods. Commercially available chemicals were reagent grade and used as received.

IR spectra were recorded in CDCl₃ on a Nicolet IR470 spectrophotometer (KBr disc). ¹H NMR spectra were carried out on a Bruker DRX (400 MHz) instrument. Elemental analysis was performed on a Carlo Erba 1160 elemental analyzer. UV-vis absorption spectra were obtained using a Hitachi U-2000 spectrophotometer (200-1100nm). The pH was determined by a JENCO 6071

model microcomputer pH-vision meter. CV experiments were conducted on a CHI630B electrochemical workstation. The fluorescence spectra were recorded in CH₃CN solution with a HITACHI F-4500 fluorescence spectrophotometer. The crystal structure of **2** was detected by X-ray diffraction analysis on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo KR radiation ($\lambda=0.71073 \text{ \AA}$) at 293K using the ω -2 θ scan mode. The structure of **2** was solved by direct methods and refined on F² against full-matrix least-squares methods using the SHELX-97 program package (Sheldrick, 1997). CCDC publication No. 978354 contains the supplementary crystallographic data for this paper. Details of crystal data and parameters of **2** for data collection and refinement are listed in Tab.1S.

2.2 Synthesis and characterization of target complexes 1-4

The synthesis routes of **1-4** were as shown in Scheme 1.

Scheme 1

Synthesis of complex 1: **1** was synthesized by refluxing the mixture of Fe₃(CO)₁₂ (0.9g, 1.8mmol) and 4-Hydroxy-2-mercapto-6-methylpyrimidine (**L**₁, 0.53g, 3.7mmol) in dry THF(20mL) under nitrogen atmosphere for 4h. The solution was cooled to room temperature and filtered, and then the solvent was evaporated to give a black solid product, the crude product was purified through a silica gel column (CH₂Cl₂/C₆H₁₄=5:1 as the eluent), low temperature recrystallization to give a purple red pure product 0.43g. Yield: 42.5%. Anal. Calcd for C₁₆H₁₀N₄O₈Fe₂S₂: C, 34.19%; H, 1.79%; N, 9.97%; Found: C, 34.56%; H, 1.92%; N, 9.17%; ¹HNMR (CDCl₃): 2.854(4H, -CH₂-), 2.007 (6H, -CH₃). IR: (CO): 2070cm⁻¹, 2039cm⁻¹, 1999cm⁻¹, (-C=O) 1645cm⁻¹.

Synthesis of complex 2: Both Fe₃(CO)₁₂ (1.8g, 3.6mmol) and dibenzyl disulfide (**L**₂, 0.94 g, 3.8mmol) was added to added to dry THF(20mL), the mixture was refluxed for 4h under nitrogen atmosphere. The following operation was handled as the synthesis of complex **1** to give a red

viscous pure product, and then the product was dissolved in a mixed solvent with CH₂Cl₂ and hexane (3:2, v/v). Red single crystals suitable for X-ray analysis were obtained after slowly evaporating solvent under a frozen condition of -20 °C. The crystals were manually selected and used for physical measurements. Details of crystal data and parameters for data collection and refinement are listed in Tab.1S. Details of crystal data and parameters for data collection and refinement are listed in Tab.1S. Yield: 1.5g (79.3% based on Fe). Anal.Calcd for C₂₀H₁₄O₆Fe₂S₂: C, 45.66%; H, 2.68%; Found: C, 47.21%; H, 2.86%; ¹HNMR (CDCl₃): 7.436(10H, Ph), 3.668(2H, -CH₂-), 3.259 (2H, -CH₂-), IR: CO: 2073cm⁻¹, 2036cm⁻¹, 1993cm⁻¹.

Synthesis of complex 3: Both Fe₃(CO)₁₂ (0.9g, 1.8mmol) and 2-Mercaptobenzimidazole (MBD) (0.57g, 3.8mmol) was added to dry THF(20mL), then the mixture was refluxed for 3h under nitrogen atmosphere. The following operation was handled as mentioned earlier to give a purple red pure product 0.76g. Yield: 67%. Anal.Calcd for C₂₀H₁₀N₄O₆Fe₂S₂: C, 41.55%; H, 1.74%; N, 9.69%; Found: C, 41.85%; H, 1.89; N, 9.83%; ¹HNMR (CDCl₃): δ 7.12-7.59(8H), 5.84(2H) ; IR: CO: 2073cm⁻¹, 2037cm⁻¹, 1994cm⁻¹.

Synthesis of complex 4: Fe₃(CO)₁₂ (0.9g, 1.8mmol) and 2-mercaptobenthiazole (MBT) (0.64 g, 3.8mmol) was added to added to dry THF(20mL), and the mixture was refluxed for 3h under nitrogen atmosphere. The following operation was handled as stated in the synthesis of complex 1 to give a purple black pure product 0.73g. Yield: 65.8%. Anal.Calcd for C₂₀H₁₀N₄O₆Fe₂S₄: C, 39.24%; H, 1.32%; N, 4.58%; Found: C, 40.53%; H, 1.44%; N, 4.75%; ¹HNMR (CDCl₃): δ 7.7-7.75(4H), 7.4 (4H), IR: CO: 2069cm⁻¹, 2030cm⁻¹, 1995cm⁻¹.

We also tried to cultivate single crystals of complexes (1, 3 and 4) by slowly evaporating solvent under frozen condition of -20 °C, to that end, different solvents had been examined in this study, including CH₂Cl₂, CHCl₃, hexane, cyclohexane, petroleum ether, toluene, methanol and so on.

Unfortunately, the single crystals of these complexes (**1**, **3** and **4**) were not obtained at the same temperature condition. However, their structures could be confirmed by IR and ¹HNMR data.

2.3 Photo-catalytic H₂ generation

Photo-catalytic reaction was carried out in a 60mL quartz glass photo-reactor with 20mL of CH₃CN/H₂O solution containing target compound as catalyst, xanthene dyes as PS and TEA as sacrificial reagent under nitrogen atmosphere with magnetic stirring. The mixture was treated under ultrasonication for 30 min. Then the solution was irradiated by a 300W Xe lamp with 420nm cut off filter. During the reaction, the condensed water was used to maintain the temperature at 25±1°C, and the H₂ generation was measured by Gas Chromatograph (GC, Agilent 4890D) equipped with a thermal conductivity detector (TCD) and a porapak Q stainless column. The temperatures of the injection port, the oven and the detector were 100°C, 80°C and 150°C, respectively. Nitrogen served as the carrier gas at a flow rate of 20mL/min. The total gas volume was measured by releasing the pressure in the bottles using displacement of saturated brine equipment.

3. Results and Discussion

3.1 UV-visible absorption spectra of 1-4

Fig.1

Fig. 1 shows UV-vis absorption spectra of complexes **1–4** in CH₃CN at room temperature, all of which exhibit intense absorption band at wavelengths below 375 nm. There were two strong high-energy absorption bands at near 200nm and 320nm separately for all of them. As shown in Fig.1, spectroscopic work on the diiron site, the intense absorption between 230 and 300 nm is attributed to π - π^* ligand-centred (LC) transitions, and moderate intensity at 300–400 nm is assigned to metal-to-ligand charge-transfer (MLCT) transitions(Cui, et al., 2012). There is much

weaker intensity in the visible region, which is likely to be MLCT transition in character.

3.2 Crystal Structure of **2**

The crystal structure of **2** is shown in Fig. 2, and the selected bond lengths and bond angles are listed in Tab. 2S.

Fig.2

As shown in Fig. 2 and Tab. 2S, the complex **2** crystallizes in the space group P-1(2), each of two irons (II) is surrounded by two sulfur bridging, one iron (II) and three carbonyl groups, respectively. The iron coordination polyhedral can be described as distorted octahedron with the three carbonyl groups in facial positions. The [2Fe2S] skeleton of **2** displays an “open butterfly” structure. The Fe(1)-Fe(2) bond of 2.5245(6) Å is slightly longer than that of the complex (μ-pdt) [Fe(CO)₃]₂ (2.510(11) Å) (Lyon, et al., 1999). On the other hand, the bond length of Fe1-S is 2.2588 Å and 2.2639 Å separately, and is close to that of the reported complex (μ-pdt)[Fe(CO)₃]₂ (2.249 Å-2.254 Å) from the literature (Lyon, et al., 1999), but obviously longer than that of Fe2-S (2.2583 Å and 2.2691 Å) in the present work. Meanwhile, the CO bond length is in the range from 1.131(4) to 1.153(4) Å, Fe-C bond length changes from 1.775 (4) to 1.817(4) Å, which is close to the reported values in the literature, such as 1.130-1.141 Å of C-O bond and 1.797-1.802 Å of Fe-C bond for complex (μ-pdt) [Fe(CO)₃]₂ (Lyon, et al., 2001).

3.3 Effects of key parameters on H₂ generation

3.3.1 Effect of PS species

In order to examine the effect of PS species on H₂ generation, herein, four xanthene dyes (Fig. 3(a)), namely eosin Y (EY²⁻), eosin B (EB²⁻), erythrosin B sodium salt (EBS²⁻) and rose bengal sodium salt (RBS²⁻), were used as PS. The changing trends of H₂ generation with PS species were depicted in Fig.3.

Fig.3

As shown in Fig.3b, when EBS²⁻, EY²⁻, RBS²⁻ and EB²⁻ was used as PS separately, the maximum H₂ evolution of the photo-catalytic hydrogen production system was recorded as 199.4 ± 13.5 μmol (49.9 ± 3.4 TON vs. **1**), 168.8 ± 7.6 μmol (42.2 ± 1.9 TON vs. **1**), 124.4 ± 12.4 μmol (31.1 ± 3.1 TON vs. **1**) and 10.4 ± 0.6 μmol (2.6 ± 0.2 TON vs. **1**), respectively. Obviously, the species of xanthene dyes significantly affected the H₂ evolution in the present system, among which, EBS²⁻ as PS displayed more activity of H₂ evolution than others. The difference could be attributed to the effects of heavy atom and concentration quenching (Rohatgi and Singhal, 1966). In addition, the low H₂ evolution activity for EB²⁻ might be related to the strong electron withdrawing group -NO₂ in EB²⁻ molecule, which was unfavorable for intra-molecular electron transfer (ET) from the ground state to the excited state. In this case, the electron-withdrawing effect of substituent in xanthene dyes molecule might seem to be a more important factor than that of heavy atom effect. Similar research was also reported by Arakawa (Abe, et al., 2000) and Eisenberg (Lazarides, et al., 2009), in which EY²⁻ usually displayed relatively high H₂ evolution activity.

3.3.2 Effect of the CH₃CN/H₂O ratio

The volume ratio of CH₃CN/H₂O (v/v) is also important factor to affect H₂ generation in the photocatalytic system. Herein, it was investigated and the result was illustrated in Fig.4.

Fig.4

As shown in Fig.4, the H₂ evolution gradually increased with increasing the ratio of CH₃CN/H₂O (v/v) in the range from 1:2 to 1:1, the maximum H₂ evolution of 199.4 ± 13.5 μmol (49.9 ± 3.4 TON vs. **1**) appeared in 1:1 ratio of CH₃CN to H₂O (v/v) at 4.0h of irradiation. And then the H₂ evolution decreased with the ratio of CH₃CN/H₂O (v/v) changing from 1:1 to 2: 1, the maximum H₂ evolution was only 162.2 ± 16.4 μmol (40.6 ± 4.1 TON vs. **1**) and 58.6 ± 7.8 μmol

(14.7 ± 2.0 TON vs.1) at 2:1 and 1: 2 ratio of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v), respectively. That is, the ratio of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v) deviated from 1:1, the H_2 evolution was drastically reduced as reported in the literature (Cline, et al., 2008). The result showed that the volume ratio of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ significantly affected the H_2 generation in the present system because the properties of solvent, such as polarity, dielectric constant and diffusion coefficient, significantly affected photo-catalytic reaction (Wang, et al., 2013). Therefore, the reasonable control for the ratio of $\text{CH}_3\text{CN} / \text{H}_2\text{O}$ (v/v) was also an effective strategy to improve the H_2 generation.

3.3.3 Effect of TEA concentration

Previously, it was found that TEA was a more effective sacrificial reagent (SR) than other several (such as TEOA, EDTA and CH_3COOH) in the photo-catalytic system. Thus, the effect of TEA concentration on H_2 evolution was further discussed and the result was illustrated in Fig.5.

Fig.5

As can be seen from Fig.5, the H_2 generation gradually increased with the increase of TEA concentration in the range from 5% to 10%, and then decreased with the further increase of TEA concentration from 10% to 15%, the maximum H_2 generation of $199.4 \pm 13.5 \mu\text{mol}$ (49.9 ± 3.4 TON vs. 1) appeared at 10% TEA with 4h irradiation. However, when the TEA concentration deviated from the optimal value, the H_2 generation decreased sharply, e.g. only $138.2 \pm 5.2 \mu\text{mol}$ (34.6 ± 1.3 TON vs. 1) and $119.8 \pm 13 \mu\text{mol}$ (40.0 ± 3.2 TON vs.1) H_2 was observed when the concentration of TEA was 15% and 5% in 4h irradiation, respectively. The reason was most likely related to faster reductive quenching of excited-state PS ($^3\text{EBS}^{2-}$) that led to a more rapid rate of transferring the second electron from the decomposing TEA^+ radical cation, which was formed by oxidizing TEA through photo-generated holes(h^+) on EBS^{2-} , to the ground state catalyst, and then TEA^+ quickly released a proton to give a neutral alkyl radical, namely $\text{Et}_2\text{N}\dot{\text{C}}\text{HCH}_3$, as described in the literature

(McCormick, et al., 2010), afterward, $\text{Et}_2\text{N}\dot{\text{C}}\text{HCH}_3$ radical quickly dimerized or became $\text{CH}_2=\text{CHNEt}_2$ and TEA because TEA was usually involved in the reductive quenching of excited-state PS ($^3\text{EBS}^{2-}$), this was also consistent with the early reports (DeLaive, et al., 1980; Probst, et al., 2009). The result suggested that the TEA concentration should be controlled in a reasonable range for more H_2 evolution in the present system.

3.4 Effect of medium pH

The pH level significantly affects the interaction of PS and catalyst, the state of PS and TEA as well as the subsequent driving force for H_2 evolution in the photo-catalytic system. Fig.6 depicts that the variable trend of H_2 generation with the pH in the range from 9 to 13.

Fig.6

As shown in Fig.6, the H_2 evolution significantly increased with the solution pH value adjusted from 9 to 12, the maximum H_2 evolution of $199.4 \pm 13.5 \mu\text{mol}$ (49.9 ± 3.4 TON vs. 1) occurred at pH 12. However, when the solution pH value increased to 13, only trace amounts of hydrogen could be observed at pH 13.

The phenomenon could be expected because it might cause protonation of TEA at lower pH value, which led to the partial loss of its electron donor ability. Likewise, it was not favorable for the formation of hydride intermediate species ($\eta^2\text{-H}_2$) $\text{Fe}^{\text{II}}\text{-Fe}^{\text{I}}$ at higher pH value. The result was also consistent with those of the earlier work (Lazarides, et al., 2009; Zheng, et al., 2014; Xie, et al., 2012). The present work suggested that H_2 evolution activity of the title catalysts(1-4) could be significantly improved by proper control of the solution pH value, but it would be inhibited by lower or higher pH values (pH <12 or >12) in the present system.

3.5 Effect of catalyst structure

To the best of our knowledge, the catalyst structure is also a vitally important factor to affect H_2

evolution except for the factors as above mentioned. Hence, the H₂ generation experiments of the title samples with various structures (**1-4**) were further arranged and the results were listed in Fig.7.

Fig.7

As shown in Fig.7, the H₂ generation of the four samples (**1-4**) displayed a similar developing trend, the maximum H₂ generation of $211.4 \pm 6.5 \mu\text{mol}$ (52.9 ± 1.6 TON vs. **4**) appeared at 4h of irradiation, the next one was $199.4 \pm 13.5 \mu\text{mol}$ (49.9 ± 3.4 TON vs. **1**), the third one was $124.8 \pm 7.6 \mu\text{mol}$ (31.2 ± 1.9 TON vs. **3**) and the last one was $34.9 \pm 6.9 \mu\text{mol}$ (8.7 ± 1.7 TON vs. **2**). The results revealed that the H₂ generation activity of **1-4** was as follows: **4**>**1**>**3**>**2**. Among them, complex **4** showed higher H₂ generation activity than other ones. The reason could be attributed to the different proton capturing sites among them, which was conducive to forming hydrogen-producing species ($\eta^2\text{-H}_2\text{-Fe}^{\text{II}}\text{Fe}^{\text{I}}$) (Wang, et al., 2005). We noticed that there were four proton capture sites in the structure of **4** and **1** (two N and two S for **4**, four N for **1**), and only two proton capture sites could be observed in the structure of **3** (two N), but no proton capture site was found in the structure of **2**. Usually, the more proton capture sites are conducive to the formation of hydrogen-producing species ($\eta^2\text{-H}_2\text{-Fe}^{\text{II}}\text{Fe}^{\text{I}}$) (Wang, et al., 2005). As stated above, the H₂ generation activity of these samples (**1-4**) was better than records in the literatures (Song, et al., 2009; Streich, et al., 2010; Cao, et al., 2012; Zheng, et al., 2015; Poddutoori, et al., 2011). However, it was far less than some photo-catalytic systems containing CdTe/CdSe quantum dots (QDs) (Wang, et al., 2013), but the latter was considered to be poisonous.

3.6 The stability of photo-catalytic system

We observed that the H₂ generation stopped in the present system after 4h irradiation. To explore the causes of deactivation for the present system, the following experiments were further arranged. After the H₂ generation was ceased, the extra **1** (4 μmol), EBS²⁻ (8 μmol), and integrating **1**

(4 μ mol) with EBS²⁻ (8 μ mol) was added to the photo-catalytic system after H₂ generation ceased, respectively. The H₂ generation was displayed in the Fig.8.

Fig.8

As shown in Fig.8a, as might be expected, after the H₂ generation ceasing, when an extra **1** (4 μ mol) and EBS²⁻ (8 μ mol) was further added to the inactive system, respectively, only small amount H₂ about 58 μ mol (added **1**) and 104.2 μ mol (added EBS²⁻) was observed in the next 4h irradiation. The results indicated that the deactivation of photo-catalytic system was mainly attributed to the photo-degradation of EBS²⁻, then again, there was also a slight link with the degradation of complex **1**. Interestingly, when an extra **1** (4 μ mol) and EBS²⁻ (8 μ mol) were simultaneously added to the inactive system, a higher added H₂ evolution of 143.6 μ mol was also recorded, implying that there was a cooperative action between EBS²⁻ and **1** in the present system. The deduction was further confirmed by the change of absorption spectra of EBS²⁻ with irradiation time (Fig.8b). It can be seen from Fig.8b, the absorption peak intensity of EBS²⁻ was blue-shifted from 524nm to about 504nm after 0.5h irradiation, implying loss of iodine ions in the dye EBS²⁻ through the photo-catalytic process. Furthermore, the corresponding absorption peak intensity was weakened dramatically with the increase of irradiation time, e.g., only a very weak absorption peak was observed after 3.5h of irradiation, indicating that the EBS²⁻ dye was almost completely degraded in the photo-catalytic process.

4 Possible electron-transfer processes and hydrogen generation mechanism

To shed light on the possible electron-transfer (ET) processes and H₂ generation mechanism in the present system, the fluorescence spectra of EBS²⁻, reductive quenching of EBS²⁻ by TEA, oxidative quenching of EBS²⁻ by **1-4** and electrochemical properties of catalyst (**1-4**) were carefully investigated in CH₃CN under N₂ atmosphere by CV.

4.1 Fluorescence quenching

The fluorescence emission of EBS²⁻, the reductive quenching of EBS²⁻ by TEA and the oxidative quenching of EBS²⁻ by **1-4** were displayed in Fig.9.

Fig.9

Expectedly, when TEA was added to the solution of EBS²⁻, the fluorescence emission intensity of singlet excited state (¹*EBS²⁻) remained unchanged, indicating that it was not feasible for the direct ET from TEA to ¹*EBS²⁻ in the photo-induced H₂ evolution system. This evidence reinforced the view that the reduction quenching via the ³*EBS²⁻ species, which was produced by inter-system crossing (ISC) of ¹*EBS²⁻ species. The result was also consistent with the earlier reports in the literature (Lazarides, et al., 2009). However, the fluorescence intensity of EBS²⁻ was decreased dramatically with adding excess of catalyst (**1-4**) to the EBS²⁻ solution, and then was quenched up to ca. 61.3%, 60.0%, 78.7% and 88.9% while 15 equiv of **1**, 100 equiv of **2** and 4.5 equiv of **3** as well as 3 equiv of **4** was added to the above system, respectively. In addition, the quenching constant (k_q) was also determined by the Stern-Volmer equation (Eq.1) in all cases (Vincze, et al.,1999).

$$I_0 / I = 1 + k_q \tau_0 [Q] \quad (1)$$

where I_0 is the initial fluorescence emission intensity in the absence of quencher, I is the corresponding value in the presence of quencher, τ_0 is the excited-state lifetime in the absence of quencher (for EBS²⁻, τ_0 = 75ps) (Matczuk, et al., 1995), k_q is the bimolecular quenching rate constant, and $[Q]$ is the molar concentration of quencher.

According to Eq. 1, k_{q1} - k_{q4} was calculated to be $6.7 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ for **1**, $1.0 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ for **2**, $5.5 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$ for **3**, and $1.8 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$ for **4**, respectively. The larger quenching rate constant

suggested that all complexes gave fast quenching rates, and the ET from $^1\text{EBS}^{2-}$ to **1-4** could occur in the photolytic system. The deduction had also been proved by CV as described later (see 4.2).

4.2 Electrochemical properties of 1-4

In general, the reduction potential of target sample significantly affects H_2 evolution activity and the electron transfer (ET) process in the photolysis system. Thus the electrochemical behavior of **1-4** in CH_3CN was carefully investigated under N_2 atmosphere by CV, and the results were described in Fig.10 and Tab.1.

Fig. 10

As shown in Fig.10, these samples exhibited two irreversible reduction peaks at -0.80V / -1.91V for **1**, -0.70V/-1.42V for **2**, -0.50/-1.19V for **3** and -1.11/-1.46V for **4**, respectively. Analogously, one irreversible oxidation peak was also found at +2.35V for **1**, +1.9V for **2**, 2.21V for **3** and +2.26V for **4**, respectively. The first and second reduction peaks of compound (**1-4**) could be assigned to one-electron processes from $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{I}}\text{Fe}^0$ and $\text{Fe}^{\text{I}}\text{Fe}^0$ to Fe^0Fe^0 , respectively. Whereas the oxidation peak of **1-4** was due to one-electron oxidation processes from $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ couple, respectively. Notably, the first reduction peak for **1-4** was more positive than that of $(\mu\text{-pdt})[\text{Fe}(\text{CO})_3]_2$ obtained by Darensbourg and co-workers(Chong, et al.,2003), the result indicated that $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ species had a stronger electron-accepting ability in these complexes(**1-4**), which was conducive to accept electrons from PS and then transfer them to proton for H_2 production.

Tab. 1

Accordingly, based on the determined oxidation potential (E_{ox}) of EBS^{2-} , the reduction potential (E_{red}) of **1-4** and the excited state energy (E_{00}) of EY^{2-} read from the cross-point (at 542nm, 2.29eV) by emission and excitation spectra of EBS^{2-} (Fig. 9a), the free energy change ($\Delta G^\ominus$) of the

photocatalytic system could be estimated by the Rehm-Weller equation (Eq.2) (D. Rehm, A. Weller, 1970).

$$\Delta G^{\ominus} = E_{ox} - E_{red} - E_{00} \quad (2)$$

Where $\Delta G^{\ominus}$ is the free energy change of the photoinduced electron transfer between EBS^{2-} and catalyst, E_{ox} is the oxidation potential of EBS^{2-} , E_{red} is the reduction potential of catalyst, E_{00} is the excited state energy of EBS^{2-} .

According to Eq.2, the free energy of the first ET from between $^1\text{EBS}^{2-}$ and $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ was calculated to be -0.61eV, -0.71eV, -0.91eV and -0.30eV for **1-4**, respectively, indicating that the first ET from excited-state of $^1\text{EBS}^{2-}$ to $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ of **1-4** was all thermodynamically feasible because the calculated free energy was negative value. However, the second ET from $^1\text{EBS}^{2-}$ to $\text{Fe}^{\text{I}}\text{Fe}^0$ was thermodynamically unfeasible for **1**, **2** and **4**, but it was thermodynamically feasible for **3**. In the present system, the anticipated first ET took place successfully from EBS^{2-} to produce $\text{Fe}^{\text{I}}\text{Fe}^0$ species that could further react with a proton to generate H_2 . However, we was uncertain whether the H_2 production was determined by the first ET or the second ET in the system because the one-electron processes might be occurred either from $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{I}}\text{Fe}^0$ or from $\text{Fe}^{\text{I}}\text{Fe}^0$ to Fe^0Fe^0 species. Inspired by electrocatalysis mechanism for H_2 evolution, the electrochemical behaviors of **1-4** in the presence of HAc were run to prove the formation of intermediates $\text{H-Fe}^{\text{II}}\text{Fe}^{\text{I}}$, the results were presented in Fig.11.

Fig.11

As shown in Fig.11, the first reduction peak current of **1-4** increased slightly linearly with a negative shifted about 0.11V for **1**, 0.2 V for **2**, 0.35 V for **3** and 0.13V for **4** with increase of HAc concentration ranging from 0mM to 10mM for **1-3** or 0mM to 12mM for **4**, which was the characteristic of electrochemical catalytic reduction. The result was consistent with the previous

reports in the literatures (Song, et al., 2005; Song, et al., 2012; Capon, et al., 2005). However, the second reduction peak current increased remarkably for **1-4** with increase of HAc concentration. The reduction events implied that the title catalysts (**1-4**) could be reduced from $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{I}}\text{Fe}^0$ species that was further coupled with two protons to release molecule H_2 by the second ET.

The combination of electrochemical and thermodynamic properties for **1-4** suggested that the catalytic process for **1**, **2** and **4** was likely to undergo an E process (electron-transfer process) to C process (Chemical reaction process, here presented a proton-transfer process), followed by the second E process and C process, which was known simply as ECEC electrochemical mechanism (Scheme 2A) (Mejia-Rodriguez, et.al., 2004), but the catalytic process of **3** was more likely to undergo an EECC mechanism (Scheme 2B).

Scheme 2

According to the above statement, we speculated the possible mechanism of H_2 evolution in the present system as follows: the EBS^{2-} was excited to $^1\text{EBS}^{2-}$ upon irradiation of visible light, and then to a triplet excited state $^3\text{EBS}^{2-}$ via intersystem crossing (ISC), thereafter $^3\text{EBS}^{2-}$ accepted an electron from TEA to form EBS^{3-} . On the other hand, the excited $^3\text{EBS}^{2-}$ was quenched by TEA to form EBS^{3-} and a radical cation $\text{TEA}^{\cdot+}$. In this case, the ET was occurred from $^3\text{EBS}^{2-}$ to $[\text{Fe}_2\text{S}]$ center (**path I**). The present work had confirmed that $[\text{Fe}_2\text{S}_2](\text{Fe}^0\text{Fe}^{\text{I}})$ intermediate could be first formed by ET from $^1\text{EBS}^{2-}$ to target catalyst, and then underwent an ECEC (for **1**, **2** and **4**) or EECC (for **3**) process to form the $\text{H}_2\text{-Fe}_2\text{S}_2$ ($\eta^2\text{-H}_2\text{-Fe}^{\text{II}}\text{Fe}^{\text{I}}$) species (**path II**), which possessed a sufficient hydride character that could be protonated again in order to give H_2 and regenerate the $\text{Fe}_2\text{S}_2(\text{Fe}^{\text{I}}\text{Fe}^{\text{I}})$ species (Na, et al., 2006). Interestingly, the present system did not need adding any extra proton source, the proton reduced by the title catalyst was only from TEA and water.

5 Conclusions

Four new [2Fe2S] cluster model compounds (**1-4**) had been synthesized and characterized, their H₂ evolution activity had been evaluated based solely on a constructed non-noble metal photo-catalytic system, and the sequence of H₂ evolution activity was as follows: **4**>**1**>**3**>**2**, indicating the influence of catalyst structure on H₂ evolution was notable. The compound **4** displayed a higher H₂ evolution of 211.4 ± 6.5 μmol (52.9 ± 1.6 TON vs. **4**) than that of compounds **1-3**. The deactivation of photo-catalytic system was mainly due to the photo-degradation of EBS²⁻ and was also linked with the degradation of the title compounds. In the photo-catalytic process, firstly the excited ¹*EBS²⁻ transported an electron to catalyst to form the intermediate Fe⁰Fe^I, following an ECEC (for **1**, **2** and **4**) or EECC (for **3**) process to form the important H₂-Fe₂S₂ (η²-H₂-Fe^{II}Fe^I) species which could release H₂ and regenerate Fe^IFe^I species. The working principle had been suggested that the title compound **4** could be used as a potential candidate as photo-catalyst to photo-induce H₂ evolution utilizing solar energy in spite of the H₂ evolution activity was not high enough in this stage.

Acknowledgments

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Supplementary data

CCDC978354 contains the supplementary crystallographic data for **2**. Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **2** in CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Organomet. Chem. **691**, 5045–5051.

Dear Prof. Editor,

Thanks a lot for your time and the reviewers' comments for our manuscript (Manuscript ID: **SE-D-15-01024R1**) entitled " **Photo-catalytic H₂ evolution, structural effect and electron transfer mechanism based on four novel [2Fe2S] model complexes by photochemical splitting water**".

According to the attached referee's comments, the issues raised in the comments have been carefully revised by point to point and the detail is attached in the appendix. In addition, some minor bugs in the original Ms. are also found and corrected in the revised Ms. To facilitate the reader understand, the cultivation method of single crystal for compound **2** is added to Section 2.2 in the revised version. Although we also tried to cultivate single crystals of complexes (**1**, **3** and **4**) by slowly evaporating solvent under frozen condition of -20 °C, to that end, different solvents had been examined in this study, including CH₂Cl₂, CHCl₃, hexane, cyclohexane, petroleum ether, toluene, methanol and so on. Unfortunately, the single crystals of these complexes (**1**, **3** and **4**) were not obtained at the same temperature condition. However, their structures could be confirmed by IR and ¹HNMR data.

In order to facilitate the reading for editor, we highlight the changes made on the manuscript itself in yellow. The details are clearly set out in an appendix. Please find the statement and the detailed changes made according to the referee's comments.

If there is still any questions concerning the submitted draft, please do not hesitate to phone or email to me. (E-mail: yt.fan@zzu.edu.cn ; Fax: +86-(0)371-67766017).

Thank you very much for your assistance.

Sincerely yours,

Prof. Yao-Ting Fan

Feb.25, 2016

Graphical Abstract

We have constructed a homogeneous photo-catalytic system using [2Fe₂S] model complexes **1-4** as biomimetic photo-catalysts, EBS²⁻ as PS and TEA as sacrificial reagent in CH₃CN/H₂O (v/v, 1/1) solution under the visible light irradiation. The H₂ evolution performance and mechanism of target complexes **1-4** were evaluated. The result suggested that the different structures of [2Fe₂S] simulate complexes affect on H₂ evolution performance and mechanism, the maximum H₂ evolution was 211.4 ± 6.5 μmol (52.9 ± 1.6 TON vs. **4**). The H₂ generation mechanism might be able to firstly form an intermediate Fe⁰Fe^I by electron transferring from ¹*EBS²⁻ to [2Fe₂S] center, and then underwent an ECEC (for **1**, **2** and **4**) or EECC (for **3**) process to form the important H₂-Fe₂S₂ (η²-H₂-Fe^{II}Fe^I) species of H₂ production. The result indicated the target complexes are potential candidates as photo-catalysts for H₂ generation.

Figure Captions

Scheme 1 The synthesis of complexes **1-4**

Scheme 2 Proposed photochemical proton reduction processes catalyzed by the biomimetic [2Fe2S] complexes

Fig.1 UV-visible absorption spectra of complexes **1-4** (1×10^{-4} M) in CH₃CN

Fig.2 The molecular structure of **2** with 30% probability level ellipsoids, hydrogen atoms are omitted for clarity

Fig.3 (a) The structures of PS; (b) Effect of the species of PS on H₂ generation, H₂ generation condition: **1** (2.0×10^{-4} mol·L⁻¹) and PS (4.0×10^{-4} mol·L⁻¹) in CH₃CN/H₂O (1/1, v/v) solution in 4h irradiation

Fig.4 Effect of volume ratio of CH₃CN/H₂O (v/v) on H₂ generation, H₂ generation condition: **1** (2.0×10^{-4} M) and EBS²⁻ (4.0×10^{-4} M) in 4h irradiation

Fig.5 Effect of TEA concentration on H₂ generation, H₂ generation condition: **1** (2.0×10^{-4} M) and EBS²⁻ (4.0×10^{-4} M) in CH₃CN/H₂O (1/1, v/v) solution in 4h irradiation

Fig.6 Effect of pH level on H₂ generation, H₂ generation condition: **1** (2.0×10^{-4} mol·L⁻¹), EBS²⁻ (4.0×10^{-4} mol·L⁻¹) and TEA (10%, v/v) in CH₃CN/H₂O (1/1, v/v) in 4h irradiation

Fig.7 H₂ generation performance of **1-4**, H₂ generation conditions: complex sample (2.0×10^{-4} M), EBS²⁻ (4.0×10^{-4} M) and TEA (10%, v/v), in CH₃CN/H₂O (1/1, v/v) in 4h irradiation

Fig.8 (a) Comparison of H₂ generation before and after adding extra **1** (4 μmol), EBS²⁻ (8 μmol) and integrating **1** (4 μmol) with EBS²⁻ (8 μmol), respectively, H₂ generation condition: EBS²⁻ (4.0×10^{-4} M), complex **1** (2.0×10^{-4} M), TEA (10%), pH (12.0) in CH₃CN/H₂O (1/1, v/v), irradiation of 4h; (b) Change of absorption spectra with irradiation time in a photo-catalytic system containing EBS²⁻ (4.0×10^{-4} M), complex **1** (4.0×10^{-4} M), 10% TEA and pH 12.0

Fig.9 (a) Excitation and emission spectra of EBS²⁻; (b)-(e) Oxidative quenching of EBS²⁻ (1×10^{-5} M) in CH₃CN/H₂O (v/v, 1/1) with a varied concentration of **1-4** from 0 to 3.0×10^{-4} M, 2.0×10^{-3} M, 9.0×10^{-5} M and 6×10^{-5} M, respectively; Inset: the corresponding Stern-Volmer plot of $[I_0/I-1]$ *verse* concentration of quencher

Fig.10 CV grams of EBS²⁻ (a) and **1-4** (b-e) with sample concentration of 1×10^{-3} mol·L⁻¹ in 0.05 mol·L⁻¹ n-Bu₄NPF₆/CH₃CN solution at a scan rate of 100 mV/s; working electrode: glassy carbon, auxiliary electrode: Pt wire, reference electrode: Ag/AgCl

Fig.11 CV grams of complex **1-4** (1×10^{-3} mol·L⁻¹) in the presence of HAc (0-12 mM) in 0.05 mol·L⁻¹ n-Bu₄NPF₆/CH₃CN at a scan rate of 100 mV/s; a) for **1**; b) for **2**; c) for **3** and d) for **4**

Scheme 1

Scheme 2

Fig.1

Fig.2

EBS²⁻: X=H, Y=Z=I; EY²⁻: X=H, Y=Z=Br
 RBS²⁻: X=Cl, Y=Z=I; EB²⁻: X=Br, Y=H, Z=-NO₂

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

Fig.11

Table

Tab. 1 Reduction potentials of EBS²⁻ and **1-4** in CH₃CN

Tab. 1

Compounds	E_{pc} (V) (Fe ^I Fe ^I /Fe ^I Fe ⁰)	E_{pc} (V) (Fe ⁰ Fe ^I /Fe ⁰ Fe ⁰)	E_{pa} (V) (Fe ^I Fe ^{II} / Fe ^I Fe ^I)	E_{pa} (V) (EBS ²⁻ /EBS ⁻)	$\Delta G_1^{\ominus 1)}$	$\Delta G_2^{\ominus 2)}$	Ref.
EBS²⁻	—	—	—	0.88	—	—	This work
1	-0.80	-1.91	2.35	—	-0.61	0.5	This work
2	-0.7	-1.42	0.73	—	-0.71	0.01	This work
3	-0.50	-1.19	2.21	—	-0.91	-0.22	This work
4	-1.11	-1.46	2.26	—	-0.30	0.05	This work
(μ-pdt)[Fe(CO) ₃] ₂	-1.34	-1.95	1.14	—	—	—	Chong, et al.,2003

Note: 1) The free energy of the initial ET from ¹*EBS²⁻ to Fe^I Fe^I unit was calculated from the equation

$\Delta G_1^{\ominus} = E_{ox} - E_{pc}(\text{Fe}^I\text{Fe}^I/\text{Fe}^I\text{Fe}^0) - E_{00}$; 2) The free energy of the second ET from ¹*EBS²⁻ to Fe^IFe⁰ unit was

calculated from the equation $\Delta G_2^{\ominus} = E_{ox} - E_{pc}(\text{Fe}^0\text{Fe}^I/\text{Fe}^0\text{Fe}^0) - E_{00}$