ORIGINAL PAPER



An artificial [FeFe]-hydrogenase mimic with organic chromophore-linked thiolate bridges for the photochemical production of hydrogen

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Received: 19 April 2016/Accepted: 30 May 2016 © Institute of Chemistry, Slovak Academy of Sciences 2016

Abstract An artificial [FeFe]-hydrogenase ([FeFe]-H₂ase) mimic 3II, consisting of dual organic chromophores covalently assembled to the [Fe₂S₂] active site, was constructed for light-driven hydrogen evolution. The structural conformation of synthetic photocatalyst was characterized crystallographically and spectroscopically. The photo-induced intramolecular electron transfer was evidently demonstrated by the combination of electrochemical, steady-state, and transient absorption spectroscopic studies. Finally, a remarkable activity was obtained in the present photocatalytic system, indicating the covalent incorporation of photosensitizer and catalytic center as a promising strategy to construct inexpensive, easily accessible [FeFe]-H₂ase model photocatalysts.

Keywords Hydrogenase · Enzyme mimic · Photocatalysis · Intramolecular electron transfer · Hydrogen evolution

Introduction

Hydrogen generation from solar energy represents a promising solution to produce a renewable, nonpolluting, sustainable fuel for looming global energy challenges. In this context, hydrogenases (H₂ases), a class of metalloenzymes catalyzing the reversible reduction of proton and oxidation of H₂, have attracted intensive attention (Tard and Pickett 2009; Lubitz et al. 2014). Among these distinct H_2 ases, the active site of [FeFe]- H_2 ase features a butterfly [Fe₂S₂] subunit coordinated by a cysteine-linked [Fe₄S₄] cluster, carbon monoxide, and cyanide ligands (Scheme 1). The two low-valent iron atoms are held together by a dithiolate bridge, and serve as the catalytic center for proton reduction (Adams and Stiefel 1998; Cammack 1999; Nicolet et al. 1999). On the other hand, the active site of [NiFe]- H_2 ase contains nickel and iron atoms, which are bridged by two cysteine residues (Scheme 1). The low-spin iron center is octahedrally coordinated by one CO and two CN⁻ ligands, while the other two cysteine residues are bound to the nickel in a terminal fashion (Lubitz et al. 2007).

Since the elucidation of the detailed picture of H₂ases, thousands of synthetic Fe/Ni and Fe/Fe thiolate complexes have been extensively investigated as the structural or functional models for both [NiFe]- and [FeFe]-H2ase active sites (Ogo et al. 2013; Rauchfuss 2015; Denny and Darensbourg 2015; Artero et al. 2015; Wombwell et al. 2015; Xu et al. 2015). On the aspect of converting solar energy into chemical fuel, the artificially photocatalytic systems consisting of photosensitizer (PS), $[Fe_2S_2]$ catalyst, sacrificial electron donor (D), and proton source have already accomplished the light-driven H₂ evolution with relatively high turnover numbers (TONs) (Lomoth and Ott 2009; Wang et al. 2012; Wu et al. 2014; Wang et al. 2015). However, the utilization of organometallic photosensitizers containing precious metals, such as Pt, Pd, Ru, Ir, Rh et al., or toxic quantum-confined semiconductors (QDs) resulted in undesirable resource and environmental impacts. The construction of a noble-metal-free and easily accessible photocatalyst still represents one of the greatest challenges.

Recently, we reported a photocatalytic $[FeFe]-H_2$ as mimic with organic photosensitizer covalently imbedded to

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Scheme 1 Schematic illustration of the active sites of biological [FeFe]-H₂ase (*left*), [NiFe]-H₂ase (*right*), and the artificial photocatalytic mimic (*middle*)



the $[Fe_2S_2]$ active site through an azadithiolate linker (Gao et al. 2014). With the aim of improving catalytic efficiency, a new compact, inexpensive $[FeFe]-H_2$ ase model photocatalyst (Scheme 1) with dual organic chromophores was constructed through molecular engineering. Herein, the synthesis and structural conformation of the artificial photocatalytic $[FeFe]-H_2$ ase mimic (coded as 3II) is presented. The desirable intramolecular electron transfer was evidently detected, and the photocatalytic activity of the molecular catalyst was demonstrated with a TON of 31.6 in the presence of proton source and sacrificial donor under light irradiation.

Experiment

General procedures

All organometallic reactions and operations were carried out under a dry, oxygen-free argon atmosphere with standard Schlenk techniques. All solvents were dried and distilled prior to use according to standard methods. Fe(CO)₅, LiEt₃BH, 4-methylbenzoic acid, and *o*-aminothiophenol were commercially available and used without further purification. The starting material $[(\mu-S)_2{Fe(CO)_3}_2]$ was prepared according to the literature method (Bogan et al. 1983).

¹H and ¹³C spectra were collected on a Bruker AVANCE II/400 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on JASCO FT/IR 430 spectrophotometer. HR-MS spectra determinations were made on a GCT-MS instrument (Micromass, England). UV–Vis spectra were measured on a PerkinElmer Lambda 35 spectrophotometer. Steady-state emission spectra were determined on JASCO FP-6500 spectrophotometer.

Electrochemical measurements were made with a BAS 100B electrochemical workstation at a scan rate of 100 mV s^{-1} . All voltammograms were obtained in a

conventional three-electrode cell under argon and at ambient temperature. The working electrode was a glassy carbon disc (diameter 3 mm) that was successively polished with 3 and 1 μ m diamond pastes and sonicated for 15 min prior to use. The reference electrode was a nonaqueous Ag/Ag⁺ electrode (0.01 mol L⁻¹ AgNO₃ and 0.1 mol L⁻¹ *n*-Bu₄NPF₆ in CH₃CN), and the counter electrode was a platinum wire. The potentials were reported versus ferrocene (Fc)/ferrocenium (Fc⁺) couple.

Nanosecond transient absorption measurements were manipulated on an LP-920 Laser flash photolysis setup (Edinburgh Instruments Ltd.). The excitation source was the unfocused third harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II); the probe light source was a pulse xenon lamp. The signals were detected by Edinburgh analytical instruments (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and computer.

Synthesis and characterization

Compound 1: 4-methylbenzoic acid (10.24 g, 75 mmol) was added portionwise to polyphosphoric acid (30 mL) at 100 °C until a smooth paste was obtained. *o*-aminothiophenol (9.36 g, 75 mmol) was added, and the reaction mixture was heated to 185 °C. After stirring at 185 °C for a further 30 min, the mixture was poured into vigorously stirred H₂O. The resulting solution was extracted with CH₂Cl₂, and washed by Na₂CO₃ aqueous solution and then deionized water. The concentrated residue was further purified on silica gel (CH₂Cl₂ as elute), providing 1 as white solid (7.91 g, 70%).

¹H NMR (400 MHz, CDCl₃): $\delta = 8.07$ (d, J = 8.0 Hz, 1H, NC₆H₄S), 7.99 (d, J = 8.0 Hz, 2H, C₆H₄), 7.90 (d, J = 8.0 Hz, 1H, NC₆H₄S), 7.50 (t, J = 7.6 Hz, 1H, NC₆. H₄S), 7.38 (t, J = 7.6 Hz, 1H, NC₆H₄S), 7.31 (d, J = 8.0 Hz, 2H, C₆H₄), 2.43 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.2$, 154.2, 141.4, 134.9, 131.0, 129.7, 127.5, 126.3, 125.0, 123.1, 121.6, 21.5 ppm; HR-MS (EI) : *m/z* calc. for [M⁺]: 225.0612; found: 225.0612.

Copmplex 3II: A mixture of compound 1 (9 g, 40 mmol), NBS (7.12 g, 40 mmol), and azodiisobutyronitrile (0.65 g) was refluxed in anhydrous CCl₄ for 12 h. The mixture was cooled to room temperature, concentrated in vacuo, and the residue crystallized from cyclohexane yielding 8 g 1b as white solid. Super hydride LiEt₃BH (1 M solution in THF, 8 mL, 8 mmol) was added to a fresh prepared solution of $[(\mu-S)_2 \{Fe(CO)_3\}_2]$ (2) (1.38 g, 4 mmol) in THF (30 mL) at -78 °C by syringe over 30 min. 1b (2.42 g, 8 mmol) was added to the resulting dark-green solution. The mixture was stirred for 2 h at -78 °C, and then 1 h at room temperature. The solvent was removed on a rotary evaporator. The crude product was purified by column chromatography (silica, 10% dichloromethane in hexane as eluent) to give complex 3II (2.62 g, 85%) as a red solid.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.16$ (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.48 (m, 2H), 7.40 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 3.71(s, 2H), 3.30 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 208.3$, 167.4, 167.3, 141.7, 141.5, 135.1, 135.0, 133.3, 132.9, 130.0, 129.2, 128.1, 127.9, 126.4, 126.3, 125.4, 125.2, 123.3, 123.2, 121.7, 121.6, 42.6, 28.3 ppm; IR (CH₂Cl₂): $\tilde{\nu}/cm^{-1}$ 2044, 2016, 1994, 1959, 1916 (CO); HR-MS (ESI): m/z calc. for [M + H⁺]: 792.8981; found: 792.8976.

Crystal structure determination

Diffraction measurement of complex 3II was made on a SMART APEX II diffractometer. Data were collected at 298 K using graphite monochromatic Mo- K_{α} radiation ($\lambda = 0.71073$ Å) in the ω -2 θ scan mode. Data processing was accomplished with the SAINT processing program (Siemens Energy & Automation Inc. 1996). Intensity data were corrected for absorption by the SADABS program (Sheldrick 1996). The structures were solved by direct methods and refined by full-matrix least-squares techniques on F_{O}^{2} using the SHELXTL 97 crystallographic software package (Sheldrick 1997). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located using the geometric method, and their positions and thermal parameters were fixed during the structure refinement.

Crystallographic data of 3II: $C_{34}H_{20}Fe_2N_2O_6S_4$, $M_w = 792.46 \text{ g mol}^{-1}$, red block, size $0.33 \times 0.29 \times 0.11 \text{ mm}$, orthorhombic, space group *Pbca*, a = 12.8288(14), b = 16.8812 (17), c = 31.089 (3) Å, $\alpha = \beta = \gamma = 90.00^{\circ}$, V = 6732.8 (12) Å³, T = 298 (2) K, Z = 8, $\rho_{calcd.} = 1.564 \text{ g cm}^{-3}$, λ (Mo- K_{α}) = 0.71073 Å, μ (Mo- K_{α}) = 1.158 mm⁻¹, *F* (000) = 3216, 36569 reflections in h (-15/15), k (-20/20), l (-38/38), measured in the range $2.06^{\circ} \le \Theta \le 26.00^{\circ}$, completeness $\Theta_{\text{max}} =$ 99.9%, 6606 independent reflections, $R_{\text{int}} = 0.0628$, 4253 reflections with $F_{\text{o}} > 4\sigma$ (F_{o}), 433 parameters, 0 restraints, $R1_{\text{obs}} = 0.0431$, $wR_{\text{obs}}^2 = 0.0950$, $R1_{\text{all}} = 0.0828$, $wR_{\text{all}}^2 = 0.1073$, Goodness-of-fit on $F^2 = 1.014$, largest difference peak and hole: 0.356/-0.300 e Å⁻³.

Photocatalytic H₂ production

Photochemical hydrogen production was performed by irradiating an acetonitrile solution (10 mL) of 3II ($2.5 \times 10^{-4} \text{ mol } \text{L}^{-1}$) in the presence of acetic acid (0.01 mol L^{-1}) and ethanethiol (0.01 mol L^{-1}) with a 500 W Xe lamp in a Schlenk tube at 298 K (controlled by the cooling jacket). Prior to irradiation, the solution was freeze–pump–thaw degassed for three times and then warmed to room temperature under N₂. The gas phase of the photocatalytic system was analyzed on a GC 7890T instrument with a thermal conductivity detector, a 5 Å molecular sieve column (2 mm × 2 m), and with N₂ as carrying gas.

Results and discussion

Compound 1 was prepared in a high yield from 4-methylbenzoic acid and *o*-aminothiophenol (Palmer et al. 1971) as a starting material and reference to investigate the photo-induced electron transfer process. $[(\mu-S)_2$. {Fe(CO)₃}₂]²⁻ dianion, freshly derived from $[(\mu-S)_2$. {Fe(CO)₃}₂] in tetrahydrofuran (THF), was treated with the halogenated product of 1 at -78 °C to generate the target complex 3II in a reasonable yield (as depicted in Scheme 2). The solids of 1 and 3II were stable in air and very soluble in various solvents. Their structural identities were fully characterized by a combination of ¹H, ¹³C NMR, IR spectroscopies, and mass spectrometry.

The molecular structure of 3II (Fig. 1, crystal data in Table 1), was determined by X-ray crystallography. In agreement with previously reported diiron thiolate complexes (Heinekey 2009; Tard and Pickett 2009), 3II exhibited the $[Fe_2S_2]$ core with butterfly conformation. The Fe-Fe bond length [2.5198 (7) Å] of 3II was slightly longer than those of its azadithiolate derivatives (Darensbourg et al. 2003; Georgakaki et al. 2003; Tard et al. 2005; Tard and Pickett 2009; Gloaguen and Rauchfuss 2009), still within the expected range (Nicolet et al. 2001). Unlike diiron bidentate dithiolates $[(\mu-S)_2R{Fe(CO)_3}_2]$, the $[Fe_2S_2]$ core of complexes $[(\mu-SR)_2[Fe(CO)_3]_2]$ usually showed three possible stereoisomers with regard to the orientations of S-R bonds (Fig. 2). Only two isomers had been observed, isolated, and identified as anti and syn_{eq} (Seyferth and Henderson 1981; Seyferth et al. 1986). The syn_{ax} isomer fell into the absent type in [(μ -



Scheme 2 Synthetic procedures of reference compound 1 and artificial mimic 3II



Fig. 1 Molecular structure of 3II (ellipsoids at 30% probability level). The hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (deg) for complex 3II

| Bond lengths | | Bond angles | |
|---------------|-------------|---------------------|-------------|
| Fe (1)–Fe (2) | 2.5198 (7) | Fe (1)–S (1)–Fe (2) | 67.52 (3) |
| Fe (1)–S (1) | 2.2638 (10) | Fe (1)-S (2)-Fe (2) | 68.00 (3) |
| Fe (1)–S (2) | 2.2529 (10) | C (1)-Fe (1)-Fe (2) | 150.49 (11) |
| Fe (2)–S(1) | 2.2704 (10) | C (6)-Fe (2)-Fe (1) | 150.35 (14) |
| Fe (2)–S (2) | 2.2530 (9) | C (1)-Fe (1)-S (1) | 104.71 (11) |
| Fe (1)–C (1) | 1.812 (4) | C (1)–Fe (1)–S (2) | 101.52 (11) |
| Fe (1)–C (2) | 1.790 (4) | C (6)–Fe (2)–S (1) | 107.23 (14) |
| Fe (1)–C (3) | 1.776 (4) | C (6)–Fe (2)–S (2) | 99.59 (14) |
| Fe (2)–C (4) | 1.783 (4) | Fe (1)-S (1)-C (7) | 113.71 (11) |
| Fe (2)–C (5) | 1.779 (4) | Fe (2)-S (1)-C (7) | 111.97 (12) |
| Fe (2)–C (6) | 1.786 (4) | Fe (1)-S (2)-C (21) | 115.54 (13) |
| S (1)–C (7) | 1.845 (3) | Fe (2)-S (2)-C (21) | 114.28 (11) |
| S (2)–C (21) | 1.826 (3) | S (1)–C (7)–C (8) | 113.2 (2) |
| S (1)···S (2) | 2.9069 (12) | S (2)–C (21)–C (22) | 112.0 (2) |
| | | Dihedral* | 78.5 |

* Defined by the intersection of the two [SFe2] planes

 SR_{2} {Fe(CO)₃}] cases due to steric repulsion, which could be overcome in the linked thiolates [(μ -edt/pdt/adt){Fe (CO)₃}] (edt = ethanedithiolate; pdt = propanedithiolate;



Fig. 2 Orientational stereoisomers of $[Fe_2S_2]$ core in $[(\mu-SR)_2$ {Fe(CO)₃}₂] complexes

adt = azadithiolate). In the solid state of 3II, the two S–R bonds (S1–C7, S2–C21) resided in the apical and equatorial positions of thiolate bridges, respectively. The molecule took an anti conformation. Accordingly, the Fe_{avg}–S–C angles were 112.8° for the apical C7 atom and 114.9° for the equatorial C21 atom.

Likewise, the atoms of the phenylbenzo[d]thiazole moieties in 3II molecule were almost coplanar, and the dihedral angle between the two planes was 3.7°. The average value (ca. 2.26 Å) of Fe-S bond lengths in 3II exhibited no significant difference related to the corresponding those in reported diiron thiolates (Tard and Pickett 2009). Meanwhile, the Fe-S bonds with sulfur atom bonded to the axial carbon atom were 0.01-0.02 Å longer than the other two Fe-S bonds within the anti-isomer. The C-Fe-Fe angles composed by the apical CO ligands and the Fe-Fe bonds were almost identical [<C1-Fe1- $Fe2 = 150.49(11)^{\circ}$, <C6-Fe2-Fe1 = 150.35 (14)°], suggestive of less steric encumbrance from the upwards apical and outwards equatorial substitutes. It was noteworthy that the distance of S1...S2 [2.9069 (12) Å] and the dihedral angle between the planes defined by Fe1-S1-Fe2 and Fe1-S2–Fe2 (78.5°) were somewhat enlarged as compared with previously reported models with bridged dithiolate ligands (Tard and Pickett 2009).

The proton NMR spectrum provided information as to the nature of configuration of 3II in solution. The CDCl₃ solution of 3II displayed two distinct categories of the methylene resonances at 3.23 and 3.71 ppm with essentially equal intensities (Fig. 3), suggesting that the two signals originated from one species in different positions (King 1962). Likewise, two groups of resonances assigned to the phenylbenzo[*d*]thiazole substitutes fell into the range defined by aromatic protons with a similar pattern as that of the above-mentioned methylene. Unlike previously reported results (Zhong et al. 2008; Crouthers et al. 2015), no signals arising from the syn_{eq} isomer of 3II and other impurities could be detected during the NMR measurement. The observations strongly suggested that in solution, the anti-isomer of 3II was thermodynamically favored and always predominated.

Complex 3II displayed five infrared bands in the \tilde{v} (CO) stretching region (1916–2044 cm⁻¹), which obviously shifted to lower frequencies as compared with those of the precursor compound 2 (2073, 2037, and 1998 cm⁻¹). The observations reflected a relatively enhanced electron accumulation on iron atoms, which led to a stronger backbonding from the iron atoms to CO and red-shifts of the \tilde{v} (CO) frequencies. On the other hand, the more electron rich iron atoms simultaneously elongated the Fe–Fe bond length in complex 3II (vide supra).

The photophysical properties of artificial mimic 3II, together with the multi-component references, were investigated to give a primary insight into the intramolecular electron transfer process. Complex 3II exhibited an intense absorption band peaking at ca. 315 nm with a shoulder at ca. 330 nm and weak absorption band in the region of 400-500 nm (Fig. 4). The maximal absorption band was attributed to $\pi - \pi^*$ excitation within the organic chromophore. The low-energy shoulder at ca. 330 nm and the broad absorption in visible region were similar to the characteristic bands of previously reported [FeFe]-H₂ase mimics (Eilers et al. 2007). The states responsible for the near-UV absorption featured σ - σ * and d- σ * character (Goy et al. 2013), and dominated the photophysical and photochemical properties of 3II. Excitation at the maximal absorptions of 3II, 1, and the multi-component reference system consisting of equimolar 1 and 2 resulted in fluorescence emission bands in analogously visible region. The emission intensity of 3II was strongly quenched with a quenching efficiency of 93% relative to that of 1. Under the same conditions, the addition of equimolar 2 to the solution of 1 caused an extremely low quenching efficiency of 8%. The results strongly suggested that the intermolecular collision process and quenching rarely operated (Baskaran et al. 2005). The remarkably decreased intensity of the fluorescence band of 3II mainly arose from the intramolecular oxidative process with electron from the excited phenylbenzo[*d*]thiazole moiety to [Fe₂S₂] unit in 3II.

Under an argon atmosphere, the acetonitrile solution of complex 3II with 0.05 mol L^{-1} *n*-Bu₄NPF₆ as supporting electrolyte displayed quasi-reversible and electrochemically irreversible reductions at -1.54 and -2.11 V, respectively (Fig. 5a). The former, in line with those of various all-CO diiron models bearing different thiolate bridges (Capon et al. 2009; Felton et al. 2009), could be assigned to the redox process of [Fe^IFe^I] to [Fe^IFe⁰], and demonstrated to be one-electron reduction process by bulk electrolysis. A comparison of the reduction potentials of 3II with that of reference 1 indicated that the $[Fe_2S_2]$ species accepted an electron more readily than the organic chromophore. Likewise, the irreversible oxidation event of [Fe^IFe^I] to [Fe^IFe^{II}] for 3II occurred at 0.47 V vs. Fc/Fc⁺. It was noticeable that the current intensity ratio of the oxidation and primary reduction peaks was 1.3. Therefore, the oxidation event of 3II could be assumed to be a combined result of two overlapping processes of [Fe^IFe^I] to [Fe¹Fe¹¹] and the oxidation of organic chromophore. Based on the determined oxidation potential E_{ox} of chromophore, reduction potential E_{red} of $[Fe_2S_2]$ active site, and the excited state energy E_{00} of chromophore, which was estimated from the intersection between the absorption and emission spectra of compound 1, the free-energy change for the photo-induced electron transfer in 3II was calculated to be -1.72 eV by the Rehm–Weller equation (Rehm and Weller 1970). The electron transfer process from the excited chromophore to $[Fe_2S_2]$ centre in the artificial mimic 3II was demonstrated to be exothermic and thermodynamically feasible.



Fig. 3 ¹H NMR spectrum of complex 3II in CDCl₃





Fig. 5 a Cyclic voltammograms of complex 3II and reference compound 1 in CH₃CN solution (0.05 mol L⁻¹ n-Bu₄NPF₆). The scan rate is 100 mV s⁻¹. b Dependence of current heights of electrocatalytic waves for 3II at -2.11 V on the concentration of HOAc

The behavior of electrochemical proton reduction for 3II was studied by cyclic voltammograms in the presence of HOAc. Upon the addition of HOAc, the primary reduction wave (-1.54 V) of 3II showed little variation, whereas the second redox peak (-2.11 V) exhibited a significant electrocatalytic response. The current height of the second redox event for 3II gradually increased and the potential was shifted to a relatively more negative value with sequential increments of HOAc concentration. Meanwhile, the current height change displayed a good linear dependence on the concentrations of added acid (Fig. 5b). All these electrochemical behaviors featured an electrocatalytic proton reduction process (Chong et al. 2003; Capon et al. 2009; Felton et al. 2009). Gas chromatography (GC) analysis demonstrated that molecular hydrogen was produced during above electrolysis, further confirming the electrocatalytic process.

The photochemical H_2 evolution was performed by irradiating the artificial mimic 3II in the presence of ethanethiol as sacrificial electron donor and acetic acid as proton source in degassed acetonitrile solution. Irradiation of the catalytic system with a 500 W Xe lamp led to immediate production of hydrogen, which was collected and determined by gas chromatography (GC) analysis with methane as the internal standard. Control experiments suggested that the presence of all of the catalyst 3II, sacrificial electron donor EtSH, and HOAc was essential for the photocatalytic H₂ production. The amount of generated H₂ increased steadily in the first 2 h, with a turnover frequency (TOF) of 19.7 h⁻¹ for the initial 1 h. Prolonged irradiation might result in the decomposition of photocatalyst, then the rate of H₂ evolution slowed down gradually, similar to the other reported artificial photosynthetic systems (Kluwer et al. 2009; Wang et al. 2010). With four hours of irradiation, the total amount of evolved H₂ had reached 79 mmol, defining a turnover number (TON) of 31.6 based on photocatalyst 3II (Fig. 6a).

To further confirm the intramolecular electron transfer process in artificial mimic 3II during H_2 evolution, timeresolved absorption investigations were performed using the nanosecond flash photolysis technique (Fig. 6b). Laser excitation by 355 nm light resulted in an immediate formation of the excited state of compound 1, which was characterized by an absorption band at ca. 460 nm and





Fig. 6 a Time dependence of H_2 evolution from the artificial mimic 3II ($2.5 \times 10^{-4} \text{ mol } \text{L}^{-1}$ in CH₃CN solution consisting of EtSH (0.01 mol L^{-1}) and HOAc (0.01 mol L^{-1}), and **b** transient absorption

significantly quenched by oxygen. On the basis of these results, the transient was proposed to be due to the triplet excited state of 1 (Iijima et al. 2010; Yang et al. 2012). In contrast, 3II displayed a transient absorption spectrum with totally different profile as compared with that of 1 throughout the near-UV and visible region. The new spectral features, such as absorptions at ca. 410, 580 nm. indicated a newly generated species. According to the spectroelectrochemical studies of one-electron reduced states of similar diiron thiolate complexes (Borg et al. 2004; Na et al. 2007), the transient peaks at 410 and 580 nm could be ascribed to the absorption of $[Fe^{I}Fe^{0}]$ species of 3II. In addition, the formation of [Fe^IFe⁰] intermediate had been demonstrated as one of the most crucial processes in either electro- or photochemical H_2 evolution catalyzed by [Fe₂S₂] mimic complexes (Capon et al. 2009). In our case, all evidences indicated that the generation of [Fe^IFe⁰] species in artificial mimic 3II originated from the effectively intramolecular electron transfer from the photoexcited organic chromophore to the $[Fe_2S_2]$ active site, because energy transfer would not result in any new absorptions in the measuring spectral window (Wolpher et al. 2003). The photochemical H_2 evolution was closely related to the photo-induced electron transfer, and the molecular photocatalyst 3II had achieved a promising efficiency for light-driven H₂ production.

Conclusions

In summary, artificial H_2 as mimic 3II was prepared by covalently embedding of dual organic chromophores to the $[Fe_2S_2]$ active site. Solid-state X-ray diffraction analysis and solution NMR spectroscopic studies found the two chromophore moieties in anti-configurations. Electrochemical and spectroscopic results revealed the

spectra of 1 ($5 \times 10^{-5} \text{ mol } \text{L}^{-1}$, 0.15 µs: *dotted line*) and 3II ($5 \times 10^{-5} \text{ mol } \text{L}^{-1}$, 0.2 µs: *solid line*) upon laser pulse by 355 nm light in an acetonitrile solution under argon atmosphere

thermodynamical feasibility of photo-induced intramolecular electron transfer and the resulted luminescence quenching in mimic 3II. The subsequently reduced [Fe^IFe⁰] species generating from the efficiently intramolecular electron transfer was evidently detected by laser flash photolysis. In the presence of sacrificial electron donor and proton source, the photocatalyst 3II exhibited catalytic activities for light-driven H₂ evolution in homogeneous solution. A remarkable TON of 31.6 was obtained for such a simple and compact hydrogenase mimic after four hours of irradiation. In view of the facile modifications based on the present molecule platform, improved performance of such [FeFe]-H₂ase model photocatalyst could be expected. Further investigations are now in progress.

Acknowledgements We are grateful to the National Natural Science Foundation of China (Nos. 21201022, 61106050, and 61473132), The Specialized Research Fund for the Doctoral Program of Higher Education (New Teachers, No. 20122216120001), and the Scientific and Technological Development Project of Jilin Province (No. 20150311086YY) for financial support.

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