

Cite this: DOI: 10.1039/c1cc12200b

www.rsc.org/chemcomm

## COMMUNICATION

## A triad [FeFe] hydrogenase system for light-driven hydrogen evolution†

Hong-Yan Wang, Gang Si, Wei-Ning Cao, Wen-Guang Wang, Zhi-Jun Li, Feng Wang, Chen-Ho Tung and Li-Zhu Wu\*

Received 16th April 2011, Accepted 17th June 2011

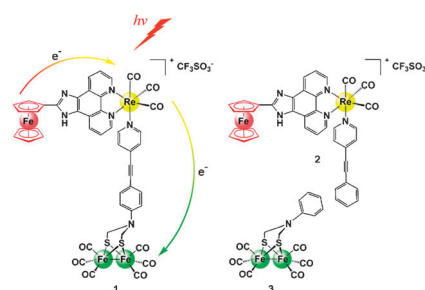
DOI: 10.1039/c1cc12200b

A novel molecular triad [FeFe]-H<sub>2</sub>ase **1**, and its model complexes **2** and **3** have been successfully constructed. The multistep PET and long-lived Fe(I)Fe(0) species were found to be responsible for the better performance of triad **1** than that of **2** with **3** for light-driven H<sub>2</sub> evolution.

Creation of molecular photocatalysts that promote the production of hydrogen (H<sub>2</sub>) from homogeneous solution is of tremendous potential significance in the sense of solar energy conversion.<sup>1</sup> Photosynthesis in nature provides a blueprint for the conversion of light to chemical energy by a chain of photoinduced electron transfer (PET) processes.<sup>2–7</sup> Hydrogenases (H<sub>2</sub>ases), enzymes in nature for H<sub>2</sub> evolution, can couple to the charge separation events and catalyze the reversible reduction of protons to H<sub>2</sub> with remarkable activity.<sup>3–5</sup> In an effort to develop artificial molecular systems, a number of covalently linked dyads using a butterfly Fe<sub>2</sub>S<sub>2</sub> subunit of [FeFe]-H<sub>2</sub>ases mimics for H<sub>2</sub> generation have been constructed.<sup>3–12</sup> However, the PET process from a sensitizer to a [FeFe]-H<sub>2</sub>ase mimic has been observed only in two cases.<sup>11,12</sup> The lack of PET is mainly due to the fact that the more negative potential of [FeFe]-H<sub>2</sub>ase mimics with respect to the excited state reduction potential of sensitizers renders the photoreduction of [FeFe]-H<sub>2</sub>ase mimics thermodynamically unfeasible, thus leading to the intramolecular photochemical H<sub>2</sub> production from these systems rather challenging.<sup>8–10</sup> Very recently, Wasielewski *et al.*<sup>11</sup> made use of naphthalene-monoimide as a promising ligand to reduce the negative reduction potentials and to stabilize the monoreduced [FeFe]-H<sub>2</sub>ase complexes. On the other hand, we designed three molecular dyads with rhenium(i) complexes,<sup>12</sup> possessing a more powerful redox potential, directly linked to one of the iron centers of [FeFe]-H<sub>2</sub>ase mimics. The combination of rhenium(i) complexes and porphyrins with the [FeFe] H<sub>2</sub>ases mimics was able to realize the PET from sensitizers to active sites of [FeFe]-H<sub>2</sub>ases, resulting in the formation of Fe(I)Fe(0) species that is crucial for their performance on light-driven H<sub>2</sub> production.

In this communication, we wish to report a rigid molecular triad **1**, for the first time, by using a ferrocene as the electron donor, a rhenium(i) complex as the chromophore and a [FeFe]-H<sub>2</sub>ase mimic as the catalyst (Scheme 1). Considering that an *N*-bridged adt [FeFe]-H<sub>2</sub>ase [ $\mu$ -adt = N(CH<sub>2</sub>S)<sub>2</sub>] complex could be reduced more easily than a *C*-bridged pdt model [ $\mu$ -pdt = C(CH<sub>2</sub>S)<sub>2</sub>],<sup>13</sup> the assembly of the electron donor, the chromophore and the active site of adt [FeFe]-H<sub>2</sub>ase is believed to provide a more powerful driving force for the PET process than those reported for dyads,<sup>11,12</sup> at the same time, the long distance and weak electronic coupling between the terminal donor and the catalytic center in triad **1** are expected to prevent charge recombination efficiently, which is reminiscent of the multistep PET employed as a key strategy to achieve long-lived charge separation in natural photosynthesis.<sup>1–7</sup>

The active site of adt [FeFe]-H<sub>2</sub>ase was firstly synthesized by the Sonogashira reaction of an iodophenyl-substituted [FeFe]-H<sub>2</sub>ase complex with pyridylacetylene, which has been shown an effective protocol to prepare arylacetylene-functionalized adt mimics of [FeFe]-H<sub>2</sub>ases.<sup>14</sup> A single crystal of a 3-pyridyl-substituted [FeFe]-H<sub>2</sub>ase mimic shows that the two iron atoms and the two sulfur atoms form a butterfly conformation with an Fe–Fe bond length of 2.5018 Å (see ESI†). As expected, the linear and rigid triple bond offers excellent control over the distance between the functional pyridine group and the active site of [FeFe]-H<sub>2</sub>ase. The pyridyl group, as a convenient site, was further coupled with a ferrocene-appended rhenium(i) complex in a refluxing THF solution to afford triad **1** in a yield of 70%. For comparison, model complexes **2** and **3** were also prepared by a similar method. All of the complexes were well characterized by IR and <sup>1</sup>H NMR spectroscopy, MS spectrometry, and satisfactory elemental analyses (see ESI†).

Scheme 1 Molecular structures of triad **1** and model complexes **2** and **3**.

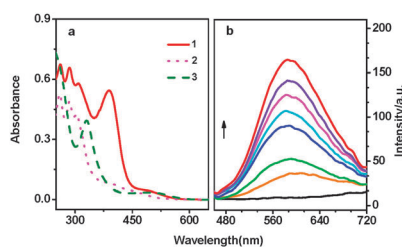
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & Graduate University, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: lzwu@mail.ipc.ac.cn

† Electronic supplementary information (ESI) available: Details for synthesis, crystal structure, electrochemical and spectroscopic studies. CCDC 823956. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12200b

To evaluate whether the ferrocene moiety could act as a suitable donor to build an efficient triad system based on a [FeFe]-H<sub>2</sub>ases mimic, the electrochemical properties of triad **1** as well as model complexes **2** and **3** were studied by cyclic voltammetry in CH<sub>3</sub>CN (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as an electrolyte) under an argon atmosphere (see ESI†). Triad **1** exhibits a reversible oxidation process at +0.17 V and an irreversible oxidation process at a peak potential of *ca.* +1.03 V in CH<sub>3</sub>CN. The former is ascribed to the redox process of Fc<sup>+1/0</sup> on the ferrocene subunit, and the latter is tentatively assigned to the Re<sup>II/I</sup> oxidation.<sup>15,16</sup> It is clear that the ferrocene group in triad **1** is reduction-active and capable of acting as an effective electron donor. On the other hand, triad **1** displays a quasi-reversible reduction process at -1.49 V in CH<sub>3</sub>CN, consistent with that of complex **3** at -1.57 V, and can be therefore attributed to the one-electron reduction of the [Fe<sup>I</sup>Fe<sup>I</sup>] + e<sup>-</sup> → [Fe<sup>I</sup>Fe<sup>0</sup>] process, while the irreversible oxidative potential at +0.54 V is originated from the [Fe<sup>I</sup>Fe<sup>I</sup>] → [Fe<sup>I</sup>Fe<sup>II</sup>] + e<sup>-</sup> one-electron oxidative process. As compared to C-bridged all-carbonyl ptd diiron complexes (0.82 V and -1.66 V *vs.* Fc/Fc<sup>+</sup>),<sup>13</sup> the N-bridged adt [FeFe]-H<sub>2</sub>ases models are more easily oxidized or reduced.

Fig. 1a shows UV-vis absorption spectra of complexes **1–3** in CH<sub>3</sub>CN, all of which exhibit intense absorption bands at wavelengths below 380 nm. Significantly, triad **1** exhibits a broad and intense band in the region of 350–600 nm, while model complex **2** does not show such a band. With reference to spectroscopic work on rhenium(i) complexes,<sup>15,16</sup> the two absorption bands at <350 nm and >400 nm for complex **2** are ascribed to the intraligand (IL) and the dπ(Re) → π\*(N–N) <sup>1</sup>MLCT state, respectively. The incorporation of a ferrocene group into the rhenium(i) complex caused almost no change in the characteristic absorption of the <sup>1</sup>MLCT state, implying no significant electronic interaction between the ferrocene donor and the rhenium(i) chromophore in complex **2** in the ground state. Complex **3**, on the other hand, displays the respective absorption bands of [FeFe]-H<sub>2</sub>ases mimics at 300–400 nm and 450–600 nm,<sup>17</sup> analogous to that observed in triad **1**. The similarity of the typical infrared absorption of coordinated CO around the Fe–Fe metal core in **1** and **3** (see ESI†) indicates that the ferrocene-appended rhenium(i) complex has no much electronic interaction with the active site of the [FeFe]-H<sub>2</sub>ase mimic either in the ground state.

Since triad **1** and complex **2** incorporated a redox-sensitive ferrocenyl group, spectroscopic changes are expected with the addition of an oxidant. Triad **1** and complex **2** show no emission in solution at room temperature. Upon addition of

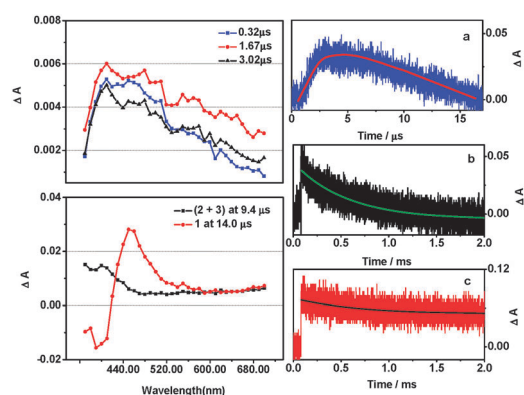


**Fig. 1** (a) UV-vis absorption spectra of triad **1**, **2** and **3** ( $3 \times 10^{-5}$  M); (b) emission spectra of **2** with the addition of Fe(ClO<sub>4</sub>)<sub>3</sub>; 0 eq., 0.25 eq., 0.35 eq., 0.46 eq., 0.60 eq., 0.75 eq., 0.90 eq., 1.00 eq. in CH<sub>3</sub>CN.

Fe(ClO<sub>4</sub>)<sub>3</sub> into the solution, the emission of **2** was enhanced dramatically with a maximum at 590 nm (Fig. 1b), similar in energy to the reported <sup>3</sup>MLCT of rhenium(i) complexes,<sup>15,16</sup> while its absorption in the low-energy region remained unchanged. The results further confirm that there is no much interaction between the rhenium(i) chromophore and the ferrocene donor in complex **2** in the ground state, but such interaction does occur in the excited state. The oxidation of the ferrocene by Fe(ClO<sub>4</sub>)<sub>3</sub> in complex **2** restored the emission capability of the rhenium(i) chromophore by preventing the PET process from the ferrocene donor to the rhenium(i) chromophore. In sharp contrast, with the titration of Fe(ClO<sub>4</sub>)<sub>3</sub> into the solution of triad **1**, not much spectral change could be detected under the same condition. Clearly, the intramolecular quenching of the revived rhenium(i) chromophore by the active site of [FeFe]-H<sub>2</sub>ase in triad **1** operates.

Combining electrochemical and spectroscopic studies, we estimated the free-energy change ( $\Delta G^\circ$ ) of the PET process in triad **1**. According to the determined oxidation potential  $E_{\text{ox}}$  of the ferrocene group, reduction potential  $E_{\text{red}}$  of the [FeFe]-H<sub>2</sub>ase active site, and the excited state energy  $E_{0-0}$  of the rhenium(i) chromophore, which was read from the cross-point (485 nm, 2.56 eV) of the excitation spectrum and the revived emission of complex **2** by the Fe(ClO<sub>4</sub>)<sub>3</sub> oxidant (see ESI†), the free-energy change ( $\Delta G^\circ$ ) was calculated as -0.90 eV for triad **1**, and -0.80 eV for **2** with **3**, respectively. The results indicate that the PET in the designed systems is exothermic. The greater driving force of triad **1** than that of **2** with **3** for the PET processes is expected to make more contributions to light-driven H<sub>2</sub> generation.

The PET process in **1** was further evidenced by a flash photolysis investigation at room temperature. Fig. 2 displays the time-resolved absorption spectra of triad **1**, complexes **2** and **2** with **3**, respectively, in CH<sub>3</sub>CN solution. Upon laser excitation of triad **1** using 355 nm light, a strong transient absorption throughout the near-UV and visible region with a maximum at 440 nm emerged immediately, while complex **2** displayed totally different curves from that of **1**, but similar to the behavior of a dyad system containing a cyclometallated platinum(ii) complex and a ferrocene donor, a typical PET case for long-lived charge separation.<sup>18</sup> From the kinetics



**Fig. 2** Left: transient absorption spectra of **2** (top), triad **1** (red line) and **2** with **3** (black line) (bottom); right: the kinetic trace at (a) 400 nm for **2**; (b) 400 nm for **2** with **3**; (c) 440 nm for triad **1** in CH<sub>3</sub>CN ( $3 \times 10^{-5}$  M) following excitation with 355 nm laser pulses.

probed at 400 nm, a fast rise phase followed by a slow decay suggests that the PET led to the formation and the disappearance of the charge-separated state in complex **2**. The rise grows quickly with the forward ET rate constant ( $k_{\text{ET}}$ ) of  $1.09 \times 10^6 \text{ s}^{-1}$ , and the back CR rate ( $k_{\text{CR}}$ ) derived from the decay phase is  $1.75 \times 10^5 \text{ s}^{-1}$  (5.7  $\mu\text{s}$ ) at room temperature. When [FeFe]-H<sub>2</sub>ase mimic **3** was introduced into the solution of complex **2**, the absorptions were immediately replaced by a series of new absorptions with characteristic absorptions at 400 nm. The generated new absorptions were much weaker but their shape was quite similar to that of triad **1**, both of which are in line with the Fe(i)Fe(0) species formed by the reduction of [FeFe]-H<sub>2</sub>ases models.<sup>12,16,19,20</sup> In comparison to that of **2** with **3**, the red-shifted absorption for triad **1** is possibly due to the different electronic effect for the covalent-linked triad **1** and [FeFe]-H<sub>2</sub>ase model **3**. Evidently, triad **1** yielded much more Fe(i)Fe(0) species than the combined **2** and **3** under the same concentration. The decay of Fe(i)Fe(0) absorption could be described by a monoexponential function with a lifetime of 708  $\mu\text{s}$  for **2** with **3**, and > 2 ms for triad **1** (no decay was seen within an instrument limitation of 2 ms), respectively. Prolonged irradiation of triad **1** and **2** with **3** in the CH<sub>3</sub>CN solution led to no permanent change, indicating that the Fe(i)Fe(0) species formed by the PET was quite stable. If we assume the generated new absorptions originated from the Fe(i)Fe(0) species of a reduced [FeFe] H<sub>2</sub>ases mimic alone, the rate ( $k_{\text{CR}}$ ) for the back electron transfer was determined to be  $< 0.50 \times 10^2 \text{ s}^{-1}$  (> 2 ms) and  $1.41 \times 10^3 \text{ s}^{-1}$  (708  $\mu\text{s}$ ) for triad **1** and **2** with **3**, respectively.

The photochemical H<sub>2</sub> evolution experiment was performed in degassed CH<sub>3</sub>CN solution at room temperature, where ascorbic acid (H<sub>2</sub>A) served as a proton source and a sacrificial electron donor, respectively. The time-dependence shows that the amount of H<sub>2</sub> evolution increased in the first 60 min, and then slowed down the rate of H<sub>2</sub> evolution (see ESI<sup>†</sup>), similar to the reported [FeFe]-H<sub>2</sub>ases dyads.<sup>11,12</sup> The generated H<sub>2</sub> was collected and analyzed by GC with methane as an internal standard. Irrespective of H<sub>2</sub> dissolution in the solvent, with irradiation for 1.5 hour, the amount of H<sub>2</sub> and its turnover number (TON) reach 15.7  $\mu\text{L}$  and 0.35 for triad **1**, and 1.8  $\mu\text{L}$  and 0.04 for **2** with **3**, respectively. Control experiments indicated that the absence of any of the components yielded unobservable amount of H<sub>2</sub> (see ESI<sup>†</sup>). Despite the fact that the light-driven reaction is not catalytic, the combination of the ferrocene donor, the rhenium(i) chromophore and the active site of a [FeFe]-H<sub>2</sub>ase mimic was found crucial in improving the efficiency of light-driven H<sub>2</sub> production. The difference in the H<sub>2</sub> evolution efficiency for triad **1**, and **2** with **3** implies that the assembly of an electron donor, a chromophore and a [FeFe]-H<sub>2</sub>ase catalyst to build up a multistep PET chain is a promising strategy for H<sub>2</sub> evolution.

In summary, a novel triad system **1** containing a ferrocene electron donor, a rhenium(i) chromophore and an adt [FeFe]-H<sub>2</sub>ase mimic has been successfully constructed. Electrochemical and spectroscopic studies show that the rigid molecular

triad **1** enables the multistep PET from the electron donor to the active site of [FeFe]-H<sub>2</sub>ase to occur efficiently with the formation of the long-lived Fe(i)Fe(0) state that can further react with a proton for H<sub>2</sub> production. The better performance for triad **1** than **2** with **3** indicates that the multistep PET and long-lived Fe(i)Fe(0) species are important for photochemical H<sub>2</sub> evolution. Because two electrons are required to produce each molecule of H<sub>2</sub>, the regeneration of the molecular photocatalyst in the entire catalytic reaction is being actively performed to improve both stability and efficiency of the triad for H<sub>2</sub> evolution.

We are grateful for financial support from Solar Energy Initiative of the Knowledge Innovation Program of the Chinese Academy of Sciences (KGCXZ-YW-389), the National Natural Science Foundation of China (Nos. 20732007, 21090343 and 50973125), the Ministry of Science and Technology of China (Nos. G2007CB808004 and 2009CB22008), and the Bureau for Basic Research of the Chinese Academy of Sciences.

## Notes and references

- 1 A. J. Esswein and D. G. Nocera, *Chem. Rev.*, 2007, **107**, 4022.
- 2 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890.
- 3 A. Magnuson, M. Anderlund, O. Johansson, P. Lindblad, R. Lomoth, T. Polivka, S. Ott, K. Stensjö, S. Styring, V. Sundström and L. Hammarström, *Acc. Chem. Res.*, 2009, **42**, 1899.
- 4 M. T. Olsen, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 2010, **132**, 17733.
- 5 R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2004, **126**, 12004.
- 6 C. E. Lubner, P. Knörzer, P. J. N. Silva, K. A. Vincent, T. Happe, D. A. Bryant and J. H. Golbeck, *Biochemistry*, 2010, **49**, 10264.
- 7 M. Klwuer, R. Kapre, F. Hartl, M. Lutz, A. L. Spek, A. M. Brouwer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 10460.
- 8 S. Ott, M. Kritikos, B. Åkermark and L. Sun, *Angew. Chem., Int. Ed.*, 2003, **42**, 3285.
- 9 L.-C. Song, M.-Y. Tang, F.-H. Su and Q.-M. Hu, *Angew. Chem., Int. Ed.*, 2006, **45**, 1130.
- 10 J. Ekström, M. Abrahamsson, C. Olson, J. Bergquist, F. B. Kaynak, L. Eriksson, L. Sun, H. C. Becker, B. Åkermark, L. Hammarström and S. Ott, *Dalton Trans.*, 2006, 4599.
- 11 A. P. S. Samuel, D. T. Co, C. L. Stern and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2010, **132**, 8813.
- 12 W.-G. Wang, F. Wang, H.-Y. Wang, G. Si, C.-H. Tung and L.-Z. Wu, *Chem.-Asian J.*, 2010, **8**, 1796.
- 13 J.-F. Capon, F. Gloaguen, F. Y. Petillon, P. Schollhammer and J. Talarmin, *Coord. Chem. Rev.*, 2009, **253**, 1476.
- 14 G. Si, W.-G. Wang, H.-Y. Wang, C.-H. Tung and L.-Z. Wu, *Inorg. Chem.*, 2008, **47**, 8101.
- 15 K. S. Schanze, D. B. MacQueen, T. A. Perkins and L. A. Cabana, *Coord. Chem. Rev.*, 1993, **122**, 63.
- 16 H.-Y. Wang, W.-G. Wang, G. Si, F. Wang, C.-H. Tung and L.-Z. Wu, *Langmuir*, 2010, **26**, 9766.
- 17 G. Eilers, L. Schwartz, M. Stein, G. Zampella, L. D. Gioia, S. Ott and R. Lomoth, *Chem.-Eur. J.*, 2007, **13**, 7075.
- 18 J. Ding, K. Feng, C. H. Tung and L. Z. Wu, *J. Phys. Chem. C*, 2011, **115**, 833.
- 19 S. J. Borg, T. Behrsing, S. P. Best, M. Razavet, X. Liu and C. J. Pickett, *J. Am. Chem. Soc.*, 2004, **126**, 16988.
- 20 Y. Na, M. Wang, J. Pan, P. Zhang, B. Åkermark and L. Sun, *Inorg. Chem.*, 2008, **47**, 2805.