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Iron–iron hydrogenase active subunit covalently linking to organic chromophore for light-driven hydrogen evolution

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ABSTRACT

The first photocatalytic [FeFe]-hydrogenase ([FeFe]-H_2ase) mimic **3** with noble-metal-free benzothiazole as donating photosensitizer had been successfully constructed *via* an easily accessible approach, and fully characterized by various spectroscopic and X-ray crystallographic techniques. Steady-state spectroscopy and electrochemistry revealed the evidences indicating that the photo-induced electron transfer occurred in **3**. The reduced [Fe^IFe^0] species was further confirmed by laser flash photolysis and considered to be responsible for the light-driven H_2 evolution. As a result, the photocatalytic system consisting of the photocatalyst **3** and the sacrificial electron donor in the presence of proton source indeed produced H_2 with a turnover number (TON) of 24.2 under light irradiation. The TON indicated a remarkably photocatalytic efficiency for an [FeFe]-H_2ase mimic assembled by the covalent combination of a photosensitizer to the catalytic center. The results demonstrated the tremendous potential of present synthetic strategy for the construction of compact, inexpensive, easily accessible [FeFe]-H_2ase model complexes as photocatalysts.

Introduction

Increasing energy demands and climate concerns have led to greater focus on renewable energy sources and sustainable development [1,2]. Hydrogen has the potential to be an ideal energy carrier and the utilization of sunlight to generate it represents a promising technology that can replace fossil fuels in the generation of mass energy [3,4]. Millions of years ago, nature provided a blueprint for the conversion of solar energy to chemical form, H_2, in which a class of metalloenzymes termed hydrogenases (H_2ases) catalyze the reversible reduction of proton and oxidation of hydrogen [5,6]. Among the distinct H_2ases, [FeFe]-H_2ase is the most efficient catalyst with turnover frequency as high as 1000 s^{-1} under mild conditions [7]. Extensive spectroscopic, crystallographic and theoretical studies have provided a detailed picture of the active site for [FeFe]-H_2ase, the so-called H-cluster (Scheme 1a). The H-cluster contains a butterfly [Fe_2S_2] subunit with one of its iron

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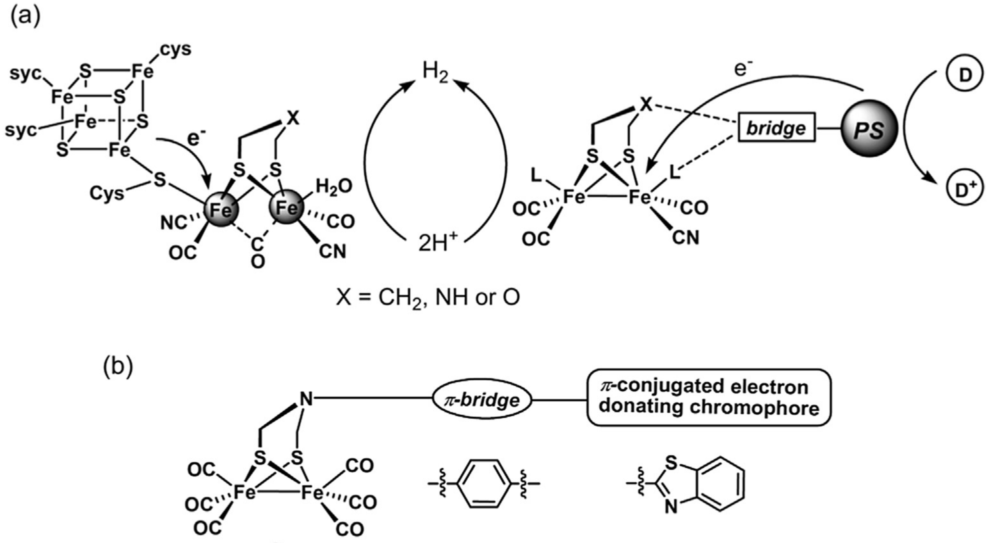
atoms linked to a cubic [Fe_4S_4] cluster through the sulfur atom of an L-cysteinyl ligand [8–10]. The two low-valent iron atoms are coordinated by biologically unusual CO and CN^- ligands and held together by a dithiolate bridge. The catalytic steps occur at the [Fe_2S_2] subunit and the [Fe_4S_4] cluster transfers electron to and from the active site.

The readily accessible diiron dithiolate complexes bear the structural similarities to H-cluster, which encouraged the chemists to prepare synthetic models for the active site of [FeFe]-H_2ase [11–15]. A variety of the model complexes have been demonstrated to be catalysts for proton reduction under electrochemical conditions [16–18]. In order to further simulate the successful photosynthesis in nature for solar energy conversion, the efforts to construct artificial photosynthetic systems for H_2 generation have been performed. In 2003, Sun, Ott and co-workers represented the first attempt to construct a supramolecular photocatalyst with ruthenium (Ru) photosensitizer (PS) linked to [Fe_2S_2] mimic [19]. Afterward, scientists developed a series of PS–[Fe_2S_2] dyads and triads bearing Ru or prophyrin PS assembled to the [Fe_2S_2] active site *via* either covalent bond or noncovalent coordination [20–26]. However, the more negative reduction potential of [Fe_2S_2] moiety with respect to the excited state potential of Ru PS made the photo-reduction of [Fe_2S_2] catalytic center thermodynamically unfeasible. In the meantime, Wu, Sun, Chen et al.. selected rhenium (Re), platinum (Pt) and iridium (Ir) complexes as PS and several molecular dyads and a triad had been constructed [27–33]. The photochemical H_2 evolutions based on these mimics in homogenous solution were investigated. The important elements (i. the electron transfer from the photo-excited PS to [Fe_2S_2] catalytic center, ii. the generation of photo-reduced [Fe^IFe^0] species) for H_2 evolution arising from light irradiation had been demonstrated. In addition, other path-breaking strategies, *i.e.*, multi-component intermolecular systems [34–41], self-assembling/host-guest biomimetic systems in aqueous solution [24,42–45], quantum dots/semiconductor PS systems [46–50], also had been applied to complete the state-of-the-art photocatalytic systems for H_2 production. All these efforts provided significant insights into the field of light-driven H_2 production and satisfied the construction of artificial photosynthetic system.

On the other hand, the metal-free organic chromophores, which function as light harvesters, have been widely employed in the photochemical field. As compared to the metal complexes PS, the organic chromophores feature the following advantages: (1) the diversity of molecular structures as well as the facile synthesis and purification at lower cost, (2) higher molar extinction coefficients due to the intramolecular $\pi-\pi^*$ transitions, (3) no concerns about resource limitations and environmental impacts because of the lack of noble metals such as Ru, Re, Ir and Pt et al. However, to the best of our knowledge, there is as yet no report on the assembly consisting of an absolutely metal-free organic chromophore in combination with [Fe_2S_2] model complex in the field of artificial photosynthetic [FeFe]-H_2ase mimic. The H_2 production by utilizing inexpensive photocatalysts and light still represents one of the greatest challenges.

In this contribution, we firstly present an easily accessible approach with noble-metal-free organic chromophore (benzothiazole) as photosensitizer covalently linked to [Fe_2S_2] active cluster through an aromatic π-bridge to form photocatalytic [FeFe]-H_2ase mimic (Scheme 1). Benzothiazole derivatives have been known to exhibit excellent electro-optical properties, and be potentially important electron donors [51].Tunable photophysical properties originate from the $\pi-\pi^*$ transition in these heterocyclic compounds with electron-rich sulfur and nitrogen heteroatoms. The π-bridge is extended to conjugated aromatic unit, and the skeleton of this π-bridge is maintained basically planar. The planarity is commonly regarded as a positive structural factor in enhancing the molecular fluorescent properties for light-driven electron and/or energy transfer, which is closely related to the key step required for the photo-induced H_2 production. A simple and



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Scheme 1 – Schematic representations of (a) active site of natural [FeFe]-H_2ase and synthetic strategies of molecular assemblies for light-driven H_2 production, (b) photocatalytic [FeFe]-H_2ase mimic 3.