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Highly efficient photocatalytic hydrogen evolution from nickel quinolinethiolate complexes under visible light irradiation

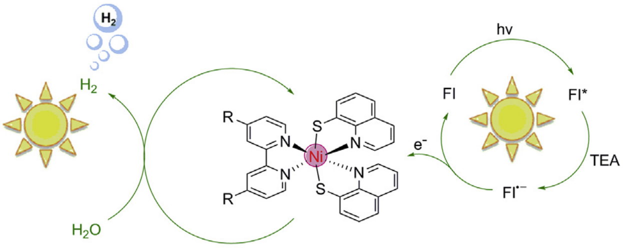
Heng Rao [a, b], Wen-Qian Yu [a, c], Hui-Qin Zheng [d], Julien Bonin [b, **], Yao-Ting Fan [a, *], Hong-Wei Hou [a]

[a] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450001, PR China
[b] Universite Paris Diderot, Sorbonne Paris Cite, Laboratoire d'Electrochimie Moleculaire, UMR 7591 CNRS, 15 rue Jean-Antoine de Baïf, F-75205, Paris Cedex 13, France
[c] School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, PR China
[d] Department of Chemistry, Henan Institute of Education, Zhengzhou, 450046, PR China

HIGHLIGHTS

- Two novel nickel quinolinethiolate complexes based photocatalysts (**1**, **2**) is reported.
- H_2 evolution activity of **1**, **2** reached 5923/7634 TON in the noble-metal-free system.
- A H_2 evolution mechanism of heterocoupling between Ni$-$H$^-$ and N$-$H$^+$ is proposed.
- The elaborate nickel photocatalysts are efficient and stable.

GRAPHICAL ABSTRACT



1: R=H, 2: R=CH_3

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ABSTRACT

Earth-abundant metal complexes have emerged as promising surrogates of platinum for catalyzing the hydrogen evolution reaction (HER). In this study, we report the design and synthesis of two novel nickel quinolinethiolate complexes, namely [Ni(Hqt)$_2$(4, 4′-Z-2, 2′-bpy)] (Hqt = 8-quinolinethiol, Z = $-$H [**1**] or $-CH_3$ [**2**], bpy = bipyridine). An efficient three-component photocatalytic homogeneous system for hydrogen generation working under visible light irradiation was constructed by using the target complexes as catalysts, triethylamine (TEA) as sacrificial electron donor and xanthene dyes as photosensitizer. We obtain turnover numbers (TON, *vs.* catalyst) for H_2 evolution of 5923/7634 under the optimal conditions with 5.0×10^{-6} M complex **1/2** respectively, 1.0×10^{-3} M fluorescein and 5% (v/v) TEA at pH 12.3 in EtOH/H_2O (1:1, v/v) mixture after 8 h irradiation ($\lambda > 420$ nm). We discuss the mechanism of H_2 evolution in the homogeneous photocatalytic system based on fluorescence spectrum and cyclic voltammetry data.

1. Introduction

Hydrogen energy is a target fuel resource compared with traditional fossil fuels for alleviating the increasing energy demand and for addressing environmental pollution issues [1]. Water splitting as a clean hydrogen source compared to hydrocarbons

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* Corresponding author.
** Corresponding author.
E-mail addresses: julien.bonin@univ-paris-diderot.fr (J. Bonin), yt.fan@zzu.edu.cn (Y.-T. Fan).

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steam reforming has received great attention during the past decades [2]. Inspired by natural photosynthesis in green plants and some bacteria, photocatalytic hydrogen evolution using solar energy is regarded as one of the most promising ways to solve these deteriorative energy and environment problems [3–5]. Presently, the challenge facing photocatalytic water splitting is to develop low-cost, highly efficient, environmentally benign and stable photocatalysts working under visible light, on large scales. In the past few years, great progress has been obtained in the field of visible-light-driven hydrogen evolution reaction (HER) by using molecular catalysts based on earth-abundant elements instead of noble-metal catalysts [6–9]. The [FeFe] and [NiFe] hydrogenase in nature is one of the most famous representatives [10]. Generally, they are more efficient than hetero- and homogeneous synthetic catalysts for hydrogen generation, but these enzymes are not ideal catalysts for large-scale application because they are usually sensitive to oxygen and difficult to be separated and purified. For this reason, functional complexes based on earth-abundant elements (e.g. Fe, Co, Ni, Mo) have been constructed to mimic the function of [Fe, Ni] hydrogenase active site for hydrogen evolution. Some of them even displayed a high efficiency and good robustness.

In particular, Ni-based catalysts have demonstrated excellent catalytic activity and received much research attention. DuBois and co-workers recently developed a series of mononuclear nickel (II) complexes with amine diphosphine ligands for electrochemical hydrogen generation [11–14]. One of these catalysts was also utilized for photocatalytic hydrogen evolution with a turnover number (TON) up to 2700 when $Ru(bpy)_3^{2+}$ is used as the photosensitizer (PS) and ascorbic acid as the sacrificial electron donor [15]. Besides the bidentate PP ligand, SS or SN ligands were also reported, inspired by the NiFe dithiolate active sites. In 2011, Eisenberg and co-workers reported the nickel complex $[Ni(pyS)_3]^-$ (pyS = pyridine-2-thiolate) having an impressive photocatalytic activity for H_2 evolution in a homogeneous system with fluorescein (FI) as the PS and TEA as the sacrificial electron donor in alkaline ethanol/water (1:1, v/v) [16]. Over 5500 turnovers relative to catalyst and a TOF of higher than 250 mol H_2 per mole catalyst per hour were obtained after 40 h. The same authors reported a series of Ni thiolate complexes for robust photocatalytic and electrocatalytic hydrogen production from water and their photocatalytic activities were greatly improved [17,18]. In 2014, Roberts observed that the films electrodeposited onto glassy carbon electrodes from acidic acetonitrile solution of $[Bu_4N][Ni(bdt)_2]$ (bdt = 1,2-benzenedithiolate) were active toward electrocatalytic hydrogen production at potentials 0.2–0.4 V more positive than untreated electrodes [19]. Finally, Lau and co-workers recently reported several Ni(II) complexes bearing tetradentate macrocyclic N_4, N_3S, and N_3P ligands for both photocatalytic and electrocatalytic hydrogen evolution [20]. These research findings inspired us to explore the low-cost and noble-metal-free homogeneous systems based on Ni catalysts containing S ligand for hydrogen evolution. These catalysts moreover exhibited redox processes that might occur on the metal as well as on the ligand, making such systems potential charge reservoirs in multi-electron processes [21].

8-quinolinethiol is a non-toxic and heterocyclic chelating ligand with interesting extraction properties commonly used in analytical chemistry. The presence of the sulfur atom may also constitutes a good compound for spectral investigation of n-n* electronic transition. Besides, it has also been widely used to prepare functional material with different purposes, such as magnetic, electrical, photoluminescence or electroluminescence properties [22–24]. However, there has been no report to our knowledge on photocatalytic water reduction based on metal quinolinethiolate complexes so far. The presence of N and S atoms in the molecule provides favorable conditions to be coordinated with transition metals. More importantly, the ligand sites corresponding to N and S donors are available for protonation, thus allowing these systems the ability to assemble the two protons and two electrons required to produce H_2 from step-wise proton-electron transfers. Actually, in many cases, quinolate-type ligand emits from a quinolate-based intraligand charge-transfer (ILCT) singlet or triplet excited state. This ILCT state is formed when the highest occupied molecular orbital (HOMO) is localized on thiolate/phenolate ring and the lowest unoccupied molecular orbital (LUMO) is localized on the pyridyl ring of the quinoline ligand [25,26]. Furthermore, chromophore quinoline-8-thiol has an intense absorption band in the visible region and emits in the deep-red spectral region from the quinolate-centered triplet intraligand charge-transfer excited state [27].

On the basis of the previous considerations, we have investigated the photocatalytic hydrogen evolution by using Ni(Hqt) 2(4,4′-Z-2,2′-bpy)](Hqt = 8-quinolinethiol, Z = −H [**1**], $-CH_3$ [**2**], bpy = bipyridine) under alkaline conditions. Commonly available organic dyes (Scheme 1) were used as PS for light harvesting and TEA as the effective electron donor. Careful optimization of the overall system led to high performances in terms of catalytic turnover numbers (TON). Electrochemical analysis demonstrated the proton reducing ability of the Ni complexes, justifying their use as water reduction catalysts. Quenching studies further elucidated the catalytic mechanism observed in this water reduction system.

2. Experimental section

2.1. Reagents and instrumentation

All reagents were of analytical grade and were used without further purification. Gas chromatography was realized with an Agilent 4890D equipped with a Porapak Q stainless steel column and a thermal conductivity detector (TCD). Temperature of the injection port, the oven and the detector were 100 °C, 80 °C and 150 °C, respectively. Nitrogen was the carrier gas at a flow rate of 20 $mL\ min^{-1}$. IR spectra were recorded in the region of 400–4000 cm^{-1} on a Shimadzu IR 435 spectrophotometer with pressed KBr pellets. ^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz). Mass spectra were performed on a Bruker Esquire 3000 mass spectrometers. The pH value was determined by a PHS-25 pH meter. The fluorescence spectra were recorded in 8:1:1 DMF/EtOH/H_2O (v/v/v) with a Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) experiments were conducted on a CHI 630B electrochemical workstation equipped with a glassy carbon working electrode, a Pt auxiliary electrode, and a standard calomel electrode (SCE) as the reference electrode, and achieved a 8:1:1 DMF/EtOH/H_2O (v/v/v) mixture containing 0.1 M $TBAPF_6$ under N_2 atmosphere.

2.2. Synthesis and characterization

The synthetic route of following-mentioned compounds is presented in Scheme S1.

2.2.1. 8-Quinolinesulfonyl chloride

This complex was prepared according to the literature [28]. Quinoline (2.19 g, 0.017 mol) was added slowly to the chlorosulfonic acid (19.8 g, 0.170 mol) while stirring in an ice bath. The reaction mixture was heated to 130–140 °C for 6 h. After cooled to room temperature with continuous stirring, the mixture was gradually poured on crushed ice. The precipitate was filtered off and washed with ice water for three times. After dried in vacuum, the solid was collected and recrystallized from a dichloromethane/ether mixture to yield a light yellow crystalline solid (3.20 g,