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Efficient electrocatalytic and photocatalytic hydrogen evolution using a linear trimeric thiolato complex of nickel

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ABSTRACT

Increasing interest has been paid to the development of earth-abundant metal complexes as promising surrogates of noble-metal platinum and biological catalysts hydrogenases for catalyzing the hydrogen evolution reaction. In this study, we report on a molecular H₂-evolving catalyst based on a linear trimeric thiolato complex of nickel Ni₃(L^{N2S2})₂ (L^{N2S2} = N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylenediaminato). Electrochemical studies showed that the trinuclear nickel complex Ni₃(L^{N2S2})₂ can electrocatalyze hydrogen evolution from weakly acidic solutions with remarkable turnover frequencies (3495 s⁻¹ at -1.98 V and 715 s⁻¹ at -1.58 V vs SCE). An efficient noble-metal-free homogeneous photocatalytic system for hydrogen generation from water working under visible light irradiation was further constructed by using the target nickel complex as photocatalyst, fluorescein (Fl) as photosensitizer (PS), and triethylamine (TEA) as sacrificial electron donor. Our studies showed that Ni₃(L^{N2S2})₂ can be used in purely aqueous solution and gave a turnover number (TON, vs catalyst) for H₂ evolution of 790, corresponding to a TOF 60 h⁻¹. The results show that multinuclear nickel(II) complexes are a promising new direction for molecular catalysts for the electro- and photoreduction of protons.

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Introduction

Hydrogen energy is a promising fuel resource for the future compared with traditional fossil fuels. Water splitting into hydrogen source with visible light is one of the most promising scenarios for sustainable energy supply. In this arena, hydrogenases, biological catalysts for reduction of protons to hydrogen, operate reversibly in weakly acidic, aqueous solutions at turnover frequencies in excess of 1000 s⁻¹ with very

low overpotentials. In spite of the efficiency of hydrogenases, their translations for industrial application have been proven difficult due to its large size and instability. Thus, considerable research has focused on the molecular catalysts [1–6]. The molecular catalytic systems can provide a large degree of tunability toward the optimization of this reductive half-reaction. An efficient homogenous molecular system for photochemical reduction of protons to H₂ generally requires three basic components [1–3]: i.e., a photosensitizer (PS), a

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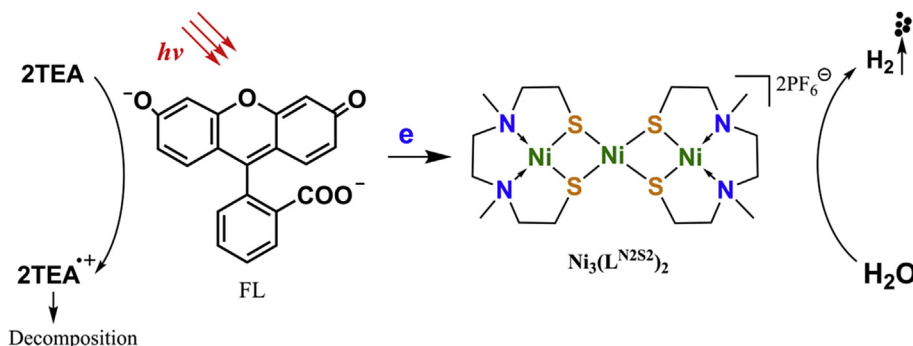
molecular H₂-evolving catalyst, and a sacrificial electron donor.

Among the homogeneous H₂-evolving catalysts, molecular species based on earth-abundant nickel centers have demonstrated excellent catalytic activity and received much research attention [4–6]. It is noted that these nickel-based molecular catalysts often are mononuclear nickel catalysts [1–6], and multinuclear nickel complexes remain unexplored [7–9]. Furthermore, in these reported homogeneous H₂-evolving systems, most of nickel complexes usually operate in mixtures of organic solvents and water owing to their poor solubility and aqueous activity [1–6]. The search for efficient nickel-based molecular catalysts that can function in purely aqueous solution still remains a great challenge [10,11]. As part of our attempts to model the active site of the Ni-containing hydrogenases and construct multinuclear nickel-thiolato species, in this work, we report that a trinuclear nickel complex (Ni₃(L^{N2S2})₂) can serve as an efficient visible light-driven molecular catalyst in a noble-metal-free artificial photocatalytic system for H₂ evolution in combination with fluorescein (FL) as photosensitizer (PS) and triethylamine (TEA) as sacrificial electron donor (Scheme 1). The catalyst gives over 790 turnovers (TON) with an initial TOF of 60 h⁻¹. In addition, Ni₃(L^{N2S2})₂ can also electrocatalyze hydrogen evolution from weakly acidic solutions with remarkable turnover frequencies (3495 s⁻¹ at -1.98 V and 715 s⁻¹ at -1.58 V vs SCE).

Experimental Section

Materials and general methods

All chemical reagents in the syntheses were of analytical grade and used without further purification, unless otherwise indicated. Water was purified using Milli-Q system. Triethylamine (TEA) and all solvents were dried by standard literature methods [12]. The elemental analyses (C, H, and N contents) were determined on a Vario EL III analyzer. Ni was analyzed on a PLASMA-SPEC ICP atomic emission spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were obtained using a Thermo Scientific Lumina fluorescence spectrophotometer.



Scheme 1 – Photocatalytic hydrogen evolution system using Ni₃(L^{N2S2})₂ as molecular photocatalyst, FL as PS and TEA as sacrificial electron donor.

Synthetic procedures

Synthesis of ligand H₂L^{N2S2} (L^{N2S2} = N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylenediaminato). The synthesis of the ligand H₂L^{N2S2} was synthesized by the published procedures [13]. A solution of N,N-dimethyl-1,3-ethanediamine (4.68 g, 53.2 mmol) in 5 mL benzene was placed in Schlenk reaction tube and the temperature was raised to 40 °C. Propylene sulfide (8.2 mL, 111.64 mmol) in 5 mL benzene was then added dropwise, the temperature was raised to 80 °C. The mixture was stirred overnight at 80 °C. The oily product was washed with 4 × 10 mL of distilled water in a 125 mL separatory funnel. The ligand H₂L^{N2S2} solution was then dried over MgSO₄ and gravity filtered into a tarred 25 mL round-bottom flask. The benzene was removed to yield a colorless viscous liquid (6.76 g, 24.13 mmol, 45% yield). ¹H NMR (500 MHz, d⁶-DMSO): δ (ppm) = 2.4–2.8 (m, 8H), 2.2 (s, 6H), 2.1 (s, 2H).

Synthesis of Ni₃(L^{N2S2})₂. The synthesis of the Ni₃(L^{N2S2})₂ was synthesized by referencing the modified procedures [14]. A solution of 200 mg (1.0 mmol) of H₂L^{N2S2} in 5 mL of ethanol was added to a stirred solution (10 mL) of 488 mg of Ni(PF₆)₂ (1.4 mmol). The solution was stirred for 6 h. After the solvent was removed in vacuum, the dark red microcrystalline product was separated. Recrystallization from MeCN yielded of pure product. Anal. Calcd for C₁₆H₃₆N₄S₄P₂F₁₂Ni₃·3H₂O: C, 20.60; H, 4.54; N, 6.01; Ni, 18.88. Found: C, 20.11; H, 4.31; N, 5.88; Ni, 18.06. Λ_m(MeOH): 181 cm⁻¹ mol⁻¹ Ω⁻¹.

Electrochemical measurement in the presence of acetic acid

Electrochemical measurement were performed with a CHI Instrument model 650E electrochemical analyzer using a glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) reference electrode at a scan rate of 200 mV s⁻¹. A sample solution containing 1.0 mM Ni₃(L^{N2S2})₂ and 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte in dry MeCN was prepared. To the solution was added using a microsyringe an aliquot of acetic acid, and then the mixture was purged well with nitrogen gas before measurement. Controlled potential coulometry was done in an electrolytic cell with a glassy-carbon working electrode, SCE reference electrode, and a platinum wire counter electrode.

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