

## Short communication

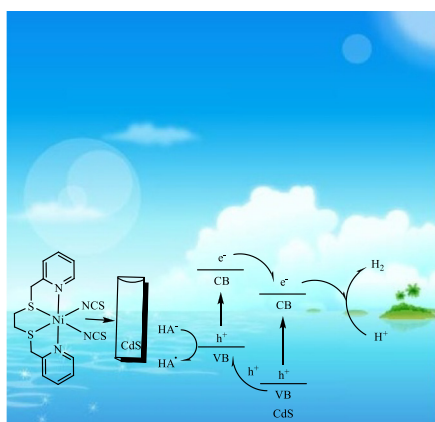
# A nickel(II) complex of *S,S'*-bis(2-pyridylmethyl)-1,2-thioethane, a cocatalyst for photochemical driven hydrogen evolution from water under visible light

Jia-Mei Lei, Su-Ping Luo, Shu-Zhong Zhan\*, Song-Ping Wu\*

College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China



## GRAPHICAL ABSTRACT



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## ABSTRACT

In the presence of KSCN, the reaction of *S,S'*-bis(2-pyridylmethyl)-1,2-thioethane (bpte) with NiCl<sub>2</sub> formed a new nickel(II) complex, [(bpte)Ni(SCN)<sub>2</sub>], a new cocatalyst for photochemical driven hydrogen production from water. Under photoirradiation with blue light ( $\lambda_{\text{max}} = 469 \text{ nm}$ ), together with CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid (H<sub>2</sub>A) as a sacrificial electron donor, the nickel complex acts as a catalyst for hydrogen evolution in heterogeneous environments. Under an optimal condition, this photocatalytic system achieved a turnover number (TON) of 23,800 mol H<sub>2</sub> per mol of catalyst (mol of cat<sup>-1</sup>) during 60 h irradiation. The highest apparent quantum yield (AQY) was ~32.1% at 420 nm.

## 1. Introduction

The rapid increase in the use of non-fossil energy sources is needed to solve the current environmental pollution. Hydrogen has attracted considerable attention as a secondary energy carrier. To get this

sustainable energy, lots of synthetic systems have been developed [1–3]. Among them, the photochemical driven H<sub>2</sub> evolution from water is an effective way [4,5]. To improve the efficiency of hydrogen evolution reaction (HER), the development of efficient and stable catalytic system established by abundant and cheap materials is a challenging

\* Corresponding authors.

E-mail addresses: [shzhzhan@scut.edu.cn](mailto:shzhzhan@scut.edu.cn) (S.-Z. Zhan), [chwsp@scut.edu.cn](mailto:chwsp@scut.edu.cn) (S.-P. Wu).

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work for solving this issue [6]. To design improved catalysts for this application, 3d metals and the related compounds are good choice. Compared to noble metals, such catalysts would be of special advantage for costs, abundance and toxicity. Thus, much efforts have made, and several nickel [7,8], cobalt [9,10] and iron [11] complexes have been developed as water reduction catalysts (WRC) in the photocatalytic systems for H<sub>2</sub> generation from water. However, this homogeneous system can't work for a long time due to the decomposition of molecular photosensitizer during irradiation [12]. To develop stable photocatalytic systems, inorganic compounds, such as CdS is selected as a photosensitizer. Moreover, the potential of its conduction band (CB) is more negative than the reduction potential of hydrogen proton (H<sup>+</sup>/H<sub>2</sub>), letting it more proper for H<sub>2</sub> generation [13]. It is apparent that transition metals capable of forming metal hydride intermediates are essential to the hydrogen evolution reaction mechanism [14,15]. So that, much effort has been made to prepare tetra- and pentadentate ligands and assembly coordinatively unsaturated complexes [16–19]. Considering that the ionic character of M–X (X = Cl<sup>−</sup> or SCN<sup>−</sup>) bond makes X<sup>−</sup> ion dissociate easily, leaving empty positions on the metal center, amenable to binding to H<sup>+</sup> or H<sub>2</sub>O for the formation of H<sub>2</sub>, a new nickel complex, [(bpte)Ni(SCN)<sub>2</sub>] has been synthesized in our lab. Combining CdS NRs as a photosensitizer, and ascorbic acid (H<sub>2</sub>A) as a sacrificial electron donor, this nickel complex acts as a new cocatalyst for H<sub>2</sub> production.

## 2. Results and discussion

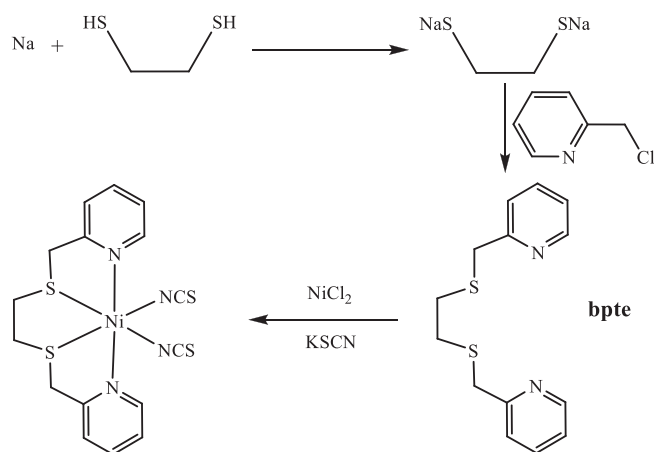
Physical measurements and crystal structure determination for this paper were listed in “Supplementary materials”. The CdS nanorods (CdS NRs) were prepared by using the known procedure [20].

### 2.1. General characterization for the nickel complex

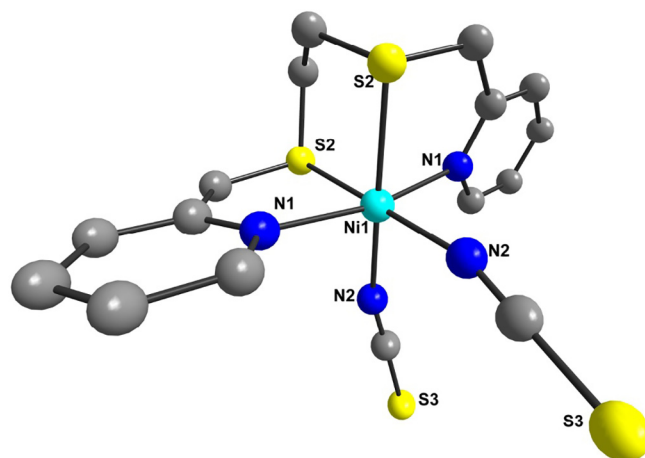
According to the reported procedure [21], S,S'-bis(2-pyridylmethyl)-1,2-thioethane (bpte) was prepared. The reaction of NiCl<sub>2</sub> with bpte and KSCN afforded a new nickel(II) complex, [(bpte)Ni(SCN)<sub>2</sub>] (Scheme 1) [22]. As shown in Fig. S1, the infrared band at 2085 cm<sup>−1</sup> can be assigned to the SCN stretching vibration.

As shown in Fig. 1, the nickel atom is six-coordinated by two nitrogen atoms and two sulfur atoms from the ligand (bpte), and two nitrogen atoms from SCN<sup>−</sup> ligands. The result is agreement with the ESI-MS analysis in methanol. According to Fig. S2, ESI-MS exhibited one peak at a mass-to-charge ratio (*m/z*) of 472.9503, which is attributed to [(bpte)Ni(SCN)<sub>2</sub>·Na]<sup>+</sup>.

To characterize photochemical behavior of the nickel complex, we first investigated its electrochemical performance in organic media,



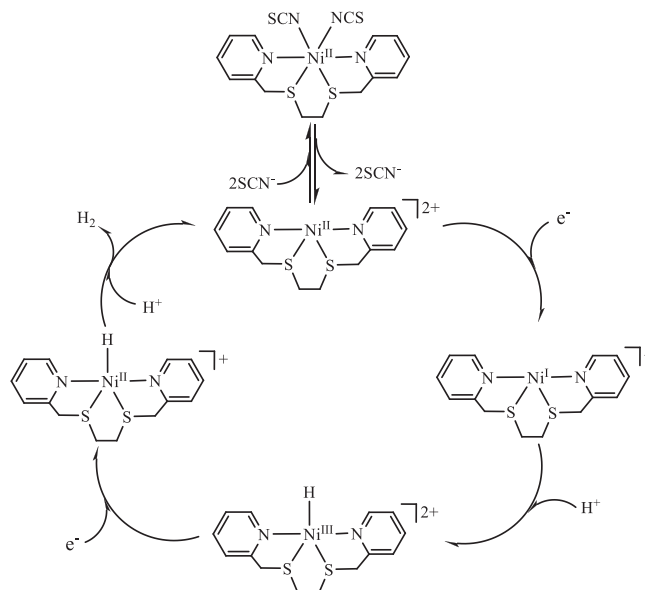
**Scheme 1.** Synthesis of the ligand, bpte and the nickel complex, [(bpte)Ni(SCN)<sub>2</sub>].



**Fig. 1.** Molecular structure of the nickel complex, [(bpte)Ni(SCN)<sub>2</sub>]. The selected bond lengths (Å): Ni1–N1, 2.115(3); Ni1–N2, 2.033(4); Ni1–S2, 2.4119(12). Symmetry transformations used to generate equivalent atoms:  $-x, y, 0.5 - z$ .

with the results shown in Fig. S3. The nickel complex displayed a quasi-reversible redox wave at  $-1.04$  V versus Ag/AgNO<sub>3</sub>, which is assigned to the Ni<sup>II/I</sup> couple. As shown in Fig. S3b, addition of varied contents of acetic acid from 0.0 to 2.33 mM resulted in a systematic increase in the voltammetric current emerging at  $-1.11$  V versus Ag/AgNO<sub>3</sub>, which is consistent with a catalytic process [23]. The results indicate that the reduction of Ni(II) to Ni(I) and protonation are responsible for H<sub>2</sub> generation. On the basis of these analyses and literature precedent [24,25], a catalytic cycle for proton reduction to be H<sub>2</sub> was put forward. As shown in Scheme 2, a one-electron reduction of the nickel complex afforded a nickel(I) species, [(bpte)Ni]<sup>+</sup>. Then the introduction of H<sup>+</sup> formed a Ni<sup>III</sup>-H species, [H-Ni<sup>III</sup>(bpte)]<sup>2+</sup>. Another one-electron reduction of the Ni<sup>III</sup>-H species led to the formation of a Ni<sup>II</sup>-H species, [H-Ni<sup>II</sup>(bpte)]<sup>+</sup>. Further introduction of H<sup>+</sup> to [H-Ni<sup>II</sup>(bpte)]<sup>+</sup> provided a H<sub>2</sub> molecule and the starting complex.

Next, electrochemical behaviors of the nickel complex were investigated in aqueous media. From Fig. S4, with decreasing pH values from 7.0 to 4.7, the strength of the reduction wave of the buffer solution with [(bpte)Ni(SCN)<sub>2</sub>] increased, and the onset of the catalytic wave



**Scheme 2.** Possible electrocatalytic mechanism for proton reduction to hydrogen by [(bpte)Ni(SCN)<sub>2</sub>].

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