



Calix[4]arene based dye-sensitized Pt@UiO-66-NH₂ metal-organic framework for efficient visible-light photocatalytic hydrogen production



Yi-Fan Chen^a, Li-Lin Tan^a, Jun-Min Liu^{a,*}, Su Qin^a, Zhi-Qiang Xie^a, Jian-Feng Huang^a, Yao-Wei Xu^a, Li-Min Xiao^b, Cheng-Yong Su^{a,*}

^a MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry, and School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, China

^b School of Computer Science and Engineering, Beihang University, Beijing, 100191, China

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ABSTRACT

A cone-calix[4]arene dye **Calix-3** with four D- π -A units has been utilized to sensitize Zr-containing metal-organic framework (MOF) embedded with Pt particles, denoted as Pt@UiO-66-NH₂, for photocatalytic H₂ production under visible light irradiation. The structures of UiO-66-NH₂, Pt-loadings, and dye-adsorbed amounts of these photocatalysts are optimized. Comparatively, **Calix-3**-sensitized Pt@UiO-66-NH₂ catalysts with 0.65 wt% of Pt loading and 15.7 $\mu\text{mol/g}$ of **Calix-3** dye amount exhibit much higher hydrogen production activity (1528 $\mu\text{mol g}^{-1} \text{h}^{-1}$ based on the mass of MOF or 236 $\text{mmol g}^{-1}_{[\text{Pt}]} \text{h}^{-1}$ based on Pt mass) than that sensitized by single D- π -A **M-3** dyes (516 $\mu\text{mol g}^{-1} \text{h}^{-1}$ or 24 $\text{mmol g}^{-1}_{[\text{Pt}]} \text{h}^{-1}$) under the similar photocatalytic conditions, and perform excellent stability during the long-term tests simultaneously. In view of the extremely low Pt loading, the activity based on Pt mass is one of the highest among all the reported MOF-based photocatalytic hydrogen production systems. The enhancement in hydrogen evolution efficiency and stability could be ascribed to lower tendency for aggregation, higher molar absorption coefficients, more efficient electron transfer, and better intrinsic and adsorbed stability of **Calix-3** dyes. This work provides useful insights for future design and synthesis of new functional dye sensitization MOF system for photocatalytic hydrogen production.

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1. Introduction

Hydrogen production from water splitting *via* photocatalysis, especially in the visible-light spectral region, attracts extensive attention owing to its clean and environmentally friendly use of solar energy. To date, various kinds of photocatalysts, including inorganic semiconducting materials, metal-incorporated zeolite, metal complexes, and other composite photocatalysts, have been discovered for hydrogen evolution reaction (HER) [1–5]. Among them, porous materials permit exposing active sites as much as possible to facilitate the accessibility of photogenerated electrons to substrates and suppress the undesired volume recombination between electrons and holes, making it promising for use as photocatalysts [6–8].

As a class of crystalline porous materials, metal-organic frameworks (MOFs) are assembled by metal clusters interconnected by multidentate organic linkers, which have shown semiconductor-like characters in photocatalysis [9–11]. The metal centers in MOFs can serve as “quantum dots” and the organic linkers as antenna to activate these metal clusters upon photoexcitation [12–14], therefore the short transport length of charge carriers can be achieved in MOFs. Moreover, water molecules can easily diffuse into the pores in MOFs, thus making MOFs as potential active photocatalysts in water reduction for hydrogen production [15]. In 2010, Garcia and co-workers used a highly stable Zr-containing MOFs of UiO-66 and UiO-66-NH₂ for water splitting under UV light irradiation, which opened the door for MOFs to photocatalytic water splitting [16]. Due to the versatile and tailorable structures, the utilization of solar energy by MOFs, especially in the visible region, could be desirable by selecting ligands or metal centers with visible-light response or post-modifying on the metal ions or the organic ligands [17–21]. For example, porphyrins are versatile functional molecules useful for light harvesting, so a mesoporous zirconium-porphyrin MOF based

* Corresponding authors.

E-mail addresses: liujunm@mail.sysu.edu.cn (J.-M. Liu), cesscy@mail.sysu.edu.cn (C.-Y. Su).

on tetrakis(4-carboxyphenyl)- porphyrin (H_2TCPP), was used for visible-light photocatalysis in the presence of triethanolamine as a sacrificial agent [22].

Given the merits of semiconductor-like MOFs further, another alternative promising strategy of integrating the two key components of the photosensitizer and the HER catalyst into MOFs has been adopted to enable light-driven proton reduction [23–25]. Notably, there have been several reports on photocatalysis by loading metal nanoparticles (NPs) into the cavities of a photosensitizing MOF, in which metal NPs act as effective electron acceptors to enable photocatalytic proton reduction with a high efficiency [8,26–28]. In addition, dye-sensitization has become a relatively mature technology for visible-light harvesting when it comes to semiconductor photocatalysts [29,30]. One of the great advantages of the dye sensitization system is ultrafast charge separation producing an electron and a hole at the dye-semiconductor interface, where the spatial charge separation achieved by the electron injection from dye-sensitizers into semiconductors dramatically suppresses the charge recombination of electrons and holes. The charge separation process is thus efficient enough to reach 100% quantum yield in the dye-sensitization system [15]. Nevertheless, the dye-sensitization system for photocatalytic water splitting still remains relatively less efficiency than other systems [31–33]. One of general concerns of dye-sensitization system is the lack of intrinsic stability of dye-sensitizers under photocatalytic reaction in water. Recently, a Rhodamine B sensitized MOF using Pt as a co-catalyst was used for water splitting under visible-light illumination [34], but the poor photostability of Rhodamine B dye makes it not suitable as an efficient photosensitizer [35]. The other factors affecting on the photoelectric conversion efficiency are aggregation of dye molecules on the surface, the co-existing species, and adsorbed stability which depends on the interactions between MOFs and dyes.

Herein, we used low-cost cone-calixarene-based dye (denoted as **Calix-3**, Scheme 1), which has been successfully synthesized and applied in dye-sensitized solar cells [36], as light absorbing antenna and demonstrate an active hydrogen production system over **Calix-3**-sensitized Zr-containing MOF UiO-66-NH₂ (denoted as Calix-3/Pt@UiO-66-NH₂). **Calix-3** was selected for durable photocatalytic H₂ production for the following reasons: (1) **Calix-3** has a cone conformation, which is beneficial to impede dye aggregation; (2) it has four light-harvesting units per molecule, which is not only favorable to achieve high molar extinction coefficients but also ensures more effective electron transfer between the dye and surrounding MOF; (3) it has four –COOH groups in one molecule

and thus it is expected that a strong hydrogen bonding, besides aromatic stacking and Van Der Waals interaction, exists between UiO-66-NH₂ and dyes, which would increase the stability of the dyes adsorbed on the MOF surface; and (4) it has high photostability and thermostability, which are vital for the photocatalytic water splitting. Furthermore, UiO-66-NH₂ as a stable MOF has been reported for photocatalytic hydrogen production and organic conversion [16,34]. The influences of structure of UiO-66-NH₂, Pt-loading, dye-adsorbed amount, and the comparison dye **M-3** on the photocatalytic hydrogen production were also investigated. The optimized photocatalytic hydrogen production rate of Calix-3/Pt@UiO-66-NH₂ with 0.65 wt% of Pt loading and 15.7 μmol/g of **Calix-3** dye amount was 1528 μmol g⁻¹ h⁻¹ based on the mass of MOF and 236 mmol g⁻¹ [Pt] h⁻¹ based on Pt mass, respectively, and the catalysts could be repeatedly utilized without substantial loss in hydrogen production activity.

2. Experiments

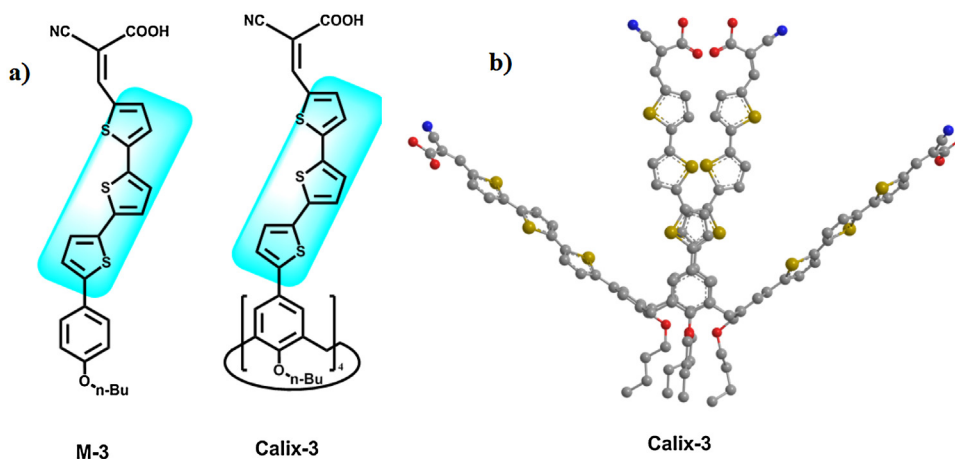
2.1. Preparation of photocatalysts

2.1.1. Synthesis of UiO-66-NH₂-1

All reagents were analytical grade and were used without further purification. UiO-66-NH₂-1 (Scheme 2a) was prepared following a modified procedure as described in literature [37]. In a typical synthetic process, a stainless steel vessel with Teflon liner containing ZrCl₄ (0.134 g, 0.575 mmol, pre-dissolved in 10 mL of DMF and 1 mL HCl) and 2-amino-1,4-benzenedicarboxylic acid (H₂BDC-NH₂, 0.125 g, 0.70 mmol, pre-dissolved in 5 mL of DMF) was heated at 80 °C overnight. The resulting yellow crystalline powder was filtered out, washed with DMF (3 × 30 mL) and MeOH (3 × 30 mL), and then dried in air at 90 °C.

2.1.2. Synthesis of UiO-66-NH₂-2

UiO-66-NH₂-2 (Scheme 2b) was prepared following a modified procedure as described in literature [38]. UiO-66-NH₂-2 was synthesized by adding solution mixtures of ZrCl₄ (0.106 g, 0.454 mmol) in 50 mL of *N,N*-dimethylformamide (DMF) and 2-amino-1,4-benzenedicarboxylic acid (H₂BDC-NH₂, 0.081 g, 0.454 mmol) in 30 mL of DMF. Each of the mixtures was sonicated to dissolve the respective components. The solutions were then sealed in a stainless steel vessel with Teflon liner and heated to 120 °C for 24 h. The resulting yellow crystalline powder was filtered out, washed with DMF (3 × 30 mL) and MeOH (3 × 30 mL), and then dried in air at 90 °C.



Scheme 1. a) structures of **Calix-3** and comparison dye **M-3** and b) the optimized structure of cone-calixarene-based dye **Calix-3**.

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