Journal of Catalysis 325 (2015) 118–127

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Molecular engineering of photosensitizers for fast and stable photocatalytic hydrogen generation

Danni Xu [a], Qianqian Chu [b], Zhuangzhi Wu [c], Qingyun Chen [d], Sheng-Qiang Fan [a,*], Guan-Jun Yang [b,*], Baizeng Fang [e,*]

[a] Department of Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[b] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[c] School of Materials Science and Engineering, Central South University, Changsha 410083, PR China
[d] State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[e] Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC V6T 1Z3, Canada

ARTICLE INFO

Article history:
Received 25 November 2014
Revised 26 February 2015
Accepted 27 February 2015
Available online 29 March 2015

Keywords:
Hydrogen
Iridium
Photosensitizer
Formyl group
Photochemistry

ABSTRACT

A family of iridium(III) complexes with a general structure, $[Ir(C\hat{}N)_2(N\hat{}N)]PF_6$ (C^N is cyclometalating ligand and N^N is bipyridyl ligand), was synthesized and explored as photosensitizers (PSs) for photocatalytic hydrogen generation using a three-component system containing an electron donor, triethylamine (TEA), a colloidal platinum catalyst and water. The introduction of a novel fluorinated C^N ligand, 2-(2,4-difluorophenyl)-4-methylquinoline, leads to much faster electron transfer from TEA to the excited-state Ir-PSs, as confirmed from Stern–Volmer measurements. In combination with the employment of various N^N ligands attached with surface-adsorbing groups including vinyl, formyl, cyano, and pyridyl, the photocatalytic hydrogen-generation duration is significantly extended. This might be related to the fast quenching of the reduced state (Ir-PS$^-$) resulting from the enhanced interaction between the Ir-PSs and the Pt catalyst. In photocatalytic reactions at relatively low Ir-PS concentrations, turnover numbers of over 10,000 for hydrogen generation can be attained using the formyl Ir-PS.

1. Introduction

Hydrogen is an extremely environment friendly fuel as when it burns it releases only water vapor into the atmosphere, and thus has a great deal of applications such as in fuel cells and batteries [1–7]. Various strategies have been explored to generate hydrogen cleanly and efficiently [8–12]. Conversion of solar energy into chemical energy through light-driven water splitting can generate environmentally benign oxygen and hydrogen, providing a carbon-free fuel with the highest energy output relative to molecular weight [13,14]. The major task in this field is to develop robust and highly efficient photocatalytic materials. So far, two important categories of materials, inorganic semiconductor nanocrystals and transition metal complexes, have been intensively investigated as either photosensitizers (PSs) or photocatalysts for photocatalytic hydrogen generation [13,14]. The metal complexes generally consist of a transition metal center and surrounding inorganic or organic ligands. This specific structure can normally form unique metal-to-ligand charge transfer (MLCT) transitions, giving long triplet excited-state lifetimes, which is critical to the charge separation and transfer process [15,16]. Furthermore, the versatile choices of metal ions and ligands allow the photonic and electronic properties to be tuned at molecular levels. A number of metal complexes with Ru(II) [17], Zn(II) [18–20], Pt(II) [21], Re(I) [22] or Ir(III) [23–32] centers were reported to be active PSs for hydrogen generation. The Ir(III) complexes with a heteroleptic structure, $[Ir(C\hat{}N)_2(N\hat{}N)]PF_6$ (C^N is cyclometalating ligand and N^N is bipyridyl ligand), have been attracting intensive attention since the first report by Bernhard et al. [23] due to their ordered electronic structure. Specifically, the highest occupied molecular orbitals (HOMOs) are located predominately on the Ir(III) metal center and two C^N ligands, while the lowest unoccupied molecular orbitals (LUMOs) are mainly located on the N^N ligand [29]. This means that the HOMO and LUMO in an Ir-PS molecule are spatially separated. In a three-component hydrogen-generation reaction containing an Ir-PS, an electron donor (e.g., triethylamine (TEA)), and a catalyst (e.g., colloidal platinum) (Fig. 1), the photoreaction follows a reductive-quenching pathway with the light excitation (Ir-PS + $h\nu \rightarrow$ Ir-PS*), the quenching of the excited state by TEA (Ir-PS* + TEA $\rightarrow$ Ir-PS$^-$ + TEA$^+$), and the quenching of the reduced

---

* Corresponding authors. Fax: +86 29 82663914.
E-mail addresses: fsq@mail.xjtu.edu.cn (S.-Q. Fan), ygj@mail.xjtu.edu.cn (G.-J. Yang), bfang@chbe.ubc.ca (B. Fang).

http://dx.doi.org/10.1016/j.jcat.2015.02.020
0021-9517/© 2015 Elsevier Inc. All rights reserved.

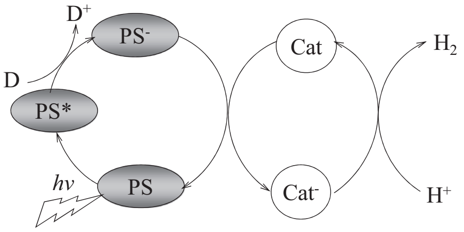

Fig. 1. Schematic diagram of reductive-quenching photocatalytic hydrogen generation. D stands for electron donor, PS for photosensitizer, and Cat for catalyst.

state by Pt catalyst [Ir-PS$^-$ + Pt(H$^+$) → Ir-PS + Pt + 1/2H$_2$] [29]. In this regard, the quenching of Ir-PS* by TEA is greatly influenced by the HOMO-locating C^N ligands, while the quenching of Ir-PS$^-$ by catalyst is mainly determined by the LUMO-locating N^N ligand. The effect of the C^N ligands on the quenching of Ir-PS* by TEA was investigated by Lo et al. [30] through Stern–Volmer measurements. The results showed that the widely used phenylpyridine Ir-PS (**PS7**, Fig. 2) presented much faster quenching rate of the excited state by TEA than a phenylquinoline Ir-PS (**PS6**, Fig. 2), despite the better light absorption of the latter [30]. The effect of the N^N ligand has also been examined [26,27,31,32], showing that the introduction of surface-adsorbing groups, such as vinyl (—CH=CH_2) [26,32], formyl (—CHO) [31], and pyridyl ($\text{—C}_6\text{H}_4\text{N}$) [27], to the bipyridyl ligand resulted in improved interactions between Pt catalyst and Ir-PSs, and thus fast quenching of the Ir-PS$^-$. In the Ir-PS$^-$ state, an electron populates on the antibonding orbital, which induces the N^N ligand to dissociate readily from the Ir metal center [29]. The fast quenching of Ir-PS$^-$ by the improved Pt/Ir-PS interactions is thus a way to increase the stability of the Ir-PS molecules, and accordingly the duration of the hydrogen-generation reactions.

For a highly efficient PS, it is critical to simultaneously meet the requirements of broad light absorption and fast electron transfers from the electron donor to the PS and from the PS to the catalyst. This is certainly a challenge in the molecular manipulation. In this study, a successful example of Ir-PS is exhibited in the fulfillment of the above three key aspects. First, phenylquinoline was used as the C^N ligand parent structure for stronger light absorption of its Ir-PSs than the phenylpyridine counterpart [30]. Secondly, fluorination on the phenylquinoline ligand was adopted to alter the electrochemical properties for fast quenching of Ir-PS* by TEA. Thirdly, various N^N ligands attached with different surface-adsorbing groups including vinyl (—CH=CH_2), formyl (—CHO), cyano (—C≡N), and pyridyl ($\text{—C}_6\text{H}_4\text{N}$) were employed to enhance the quenching rate of Ir-PS$^-$ by the Pt catalyst [26,27,31,32]. With these strategies, a family of new Ir-PSs (Fig. 2) were synthesized and examined as PSs for photocatalytic hydrogen generation.

2. Experimental section

2.1. Synthesis

All chemical reagents were used as received unless otherwise noted. Anhydrous dichloromethane was obtained from distillation over CaH_2. Nuclear magnetic resonance (**NMR**) spectra were recorded on 400 MHz spectrometer, and chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. N^N ligand **L1** was purchased from Aldrich, while **L2** [32], **L3** [31], and **L4** [33] were synthesized following the reported procedures. The cyclometalating ligand **1** and the final Ir(III) complexes **PS1**–**PS5** were synthesized according to a protocol shown in Scheme 1.

2.1.1. Synthesis of ligand 1

A mixture containing 2-chloro-4-methylquinoline (2.03 g, 11.3 mmol), 2,4-difluorophenyl boronic acid (2.66 g, 16.9 mmol), sodium carbonate (2.12 g), toluene (30 mL), ethanol (10 mL), and water (10 mL) was placed in a 100 mL of round-bottom flask. The mixture was deoxygenated before and after the addition of tetrakis(triphenylphosphine)palladium(0) (910 mg, 0.79 mmol). The mixture was refluxed at 110 °C for 16 h under argon. After cooled, water (30 mL) was added and the two layers were formed and separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL). All the organic portions were combined, washed with brine (30 mL), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed *in vacuo*. The oil was purified by column chromatography over silica using ethyl acetate/hexane (1:20) as eluent to give **1** (2.83 g, 98%) as colorless gum-like solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 6.94 (m, 1H), 7.04 (m, 1H), 7.58 (t, J = 8.3, 1H), 7.69 (d, J = 2.1, 1H), 7.73 (d, J = 8.4, 1H), 8.20–8.00 (m, 3H). m/z [ESI$^+$]: 256.1 ([M + H]$^+$). Anal. Cal. For $C_{16}H_{11}F_2N$: C, 75.3; H, 4.3; N, 5.5. Found: C, 75.7; H, 4.4; N, 5.7.

2.1.2. Synthesis of iridium dimer

A mixture of 2-(2,4-difluorophenyl)-4-methylquinoline (0.58 g, 2.28 mmol), iridium chloride hydrate (385 mg, 0.95 mmol), 2-ethoxyethanol (30 mL), and water (10 mL) was heated under argon at 130 °C for 16 h. The mixture was allowed to cool to room temperature, and then water (100 mL) was added to the reaction mixture. The resulted precipitate was collected by filtration, washed with water (250 mL), methanol (100 mL), and diethyl ether (250 mL), and dried to give the iridium dimer as a reddish powder (0.55 g, 87%), which was used without further purification in the next step.

2.1.3. Synthesis of **PS1**

A mixture of the iridium dimer (147 mg, 0.10 mmol), 4,4′-dimethyl-2,2′-bipyridyl (38 mg, 0.21 mmol), dichloromethane (20 mL), and methanol (6 mL) was heated under argon at 55 °C for 16 h. The mixture was allowed to cool to room temperature, and dichloromethane was removed under reduced pressure. A solution of KPF_6 (239 mg, 1.30 mmol) in 7 mL of water was added to the mixture. The formed orange precipitate was then filtered and washed subsequently with distilled water (250 mL), methanol (50 mL) and diethyl ether (250 mL). The precipitate was recrystallized by vapor diffusion of diethyl ether to dichloromethane solution to give **PS1** as an orange solid (130 mg, 63%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.40 (s, 6H), 2.88 (s, 6H), 6.01 (dd, J = 8.6 & 2.4, 2H), 7.02–7.13 (m, 4H), 7.26 (d, J = 8.8, 2H), 7.48 (dt, J = 7.9 & 0.7, 2H), 7.53 (d, J = 5.9, 2H), 8.01 (dd, J = 8.3 & 1.1, 2H), 8.12 (d, J = 6.2, 2H), 8.27 (s, 2H), 8.43 (d, J = 2.0, 2H). HRMS (ESI): m/z for $[C_{44}H_{32}F_4IrN_4]^+$: 885.2187; found: 885.2193. Anal. Cal. For $C_{47}H_{40}F_{10}IrN_4P0.1CH_2Cl_2$: C, 52.3; H, 3.7; N, 5.2. Found: C, 51.9; H, 3.6; N, 5.1.

2.1.4. Synthesis of **PS2**

A mixture of the iridium dimer (74 mg, 0.05 mmol), 5-(4-vinylphenyl)-2,2′-bipyridine [32] (26 mg, 0.10 mmol), dichloromethane (20 mL), and methanol (6 mL) was heated under argon at 55 °C for 16 h. The mixture was allowed to cool to room temperature, and dichloromethane was removed under reduced pressure. A solution of KPF_6 (239 mg, 1.30 mmol) in 7 mL of water was added to the mixture. The formed orange precipitates were then filtered and washed subsequently with distilled water (250 mL), methanol (50 mL), and diethyl ether (250 mL). The precipitate was recrystallized by vapor diffusion of diethyl ether to dichloromethane solution to give **PS2** as an orange solid (82 mg, 74%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.84 (s, 3H), 2.90 (s, 3H), 5.41 (d, J = 11.4,