



# A molecular precatalyst for water oxidation based on half-sandwich iridium fragment



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## ABSTRACT

A newly Ir-mediated complex constructed by treating  $[\text{Cp}^*\text{IrCl}_2]_2$  with an azo-compound [sodium (*E*)-4-((3-hydroxynaphthalen-2-yl)diazanyl)benzenesulfonate (HL)], was fully characterized by NMR, EA, TGA, IR and single crystal X-ray diffraction to reveal its molecular structure with mononuclear framework. Cyclic voltammetry (CV) was performed on detecting its electronic properties, affording potential application of catalyzing water oxidation to evolve oxygen. Moreover, the complex utilized as precatalyst of WOC was preformed under mild conditions, offering a high turnover frequency (TOF) which reached up to  $4692.1 \text{ M}^{-1} \text{ s}^{-1}$ . Meanwhile, the mechanism of water-oxidation reaction was elaborated in detail in this work.

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## 1. Introduction

Water-oxidation catalysts (WOCs) have been intensively and persistently developed recently, due to its a promising strategy for meeting energy crisis [1–5]. Among these WOCs, molecular catalysts for water oxidation (MWOCs) have taken advantages of aspects like stabilization of intermediates, resulting in lower kinetic barrier and higher efficiency [6–12]. Since the first homogeneous case was formed by Meyer's so-called "Blue Dimer" based on ruthenium [13], numerous analogues have been continuously designed and synthesized relying on three elements as privileged catalysts: manganese, ruthenium and iridium [14]. The initial MWOC based on iridium has been originated with Bernhard and co-workers in 2008 [15]. In this work, they have elaborated in detail that certain Ir(III)-based complexes, bearing unsubstituted or substituted 2-phenylpyridine ligands, were suitable to use as a catalyst precursors for water oxidation [15]. The iridium center retained two open sites in the compounds which could be bound by substrate water to give rise to activity for catalyzing water oxidation; and in contrast, a control experiment with  $[\text{Ir}(\text{ppy})(\text{bpy})]^+$  showed no activity, suggesting a key role for these open

coordination sites in binding and activation of substrate water [15]. In 2009, Crabtree and co-workers have initially used pentamethyl cyclopentadienyl ( $\text{Cp}^*$ ) as an organic linker to construct half-sandwich organometallic complexes as MWOCs, and activity of these compounds was induced by cerium(IV) or  $\text{NaIO}_4$  as sacrificial oxidant [16]. In this work, Crabtree and co-workers have distinctly described that iridium center bore the  $\text{Cp}^*$  ligand along with a LX-type bidentate chelate ligand, and one open site was available to bind to substrate water, showing activity of catalyst for water oxidation under alkaline conditions [16].

According to the observed kinetics of oxygen evolution, Crabtree and co-workers speculated that oxidation of the iridium(III) precatalysts to form a key iridium(V) species, which was sufficiently electron deficient to undergo nucleophilic, was attacked by substrate water to form the O–O bond [16–18]. The contribution of the  $\text{Cp}^*$  group stabilized the intermediate Ir(V) due to its own rich-electron characteristic, although  $\text{Cp}^*$  was extensively modified and lost from the sites that were active for water oxidation [19]. The possibility of ligand degradation in  $\text{Cp}^*\text{Ir}$  complexes under the presence of cerium(IV) or hydrogen peroxide as a chemical oxidant was confirmed by Macchioni and co-workers. In order to unambiguously prove that oxidation degradation of the  $\text{Cp}^*$  ligand and further formation of acetic and formic acids, the *in situ* NMR experiments was performed [20,21].

On the other hand, a suitable organic ligand utilized as a linker

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to construct WOCs plays an important role in the O<sub>2</sub>-evolution activity because it can stabilize the intermediate of the catalyst and improve catalytic efficiency [9]. As a general requirement, the robustness and inertness of organic linker is essential to construct a highly efficient homogeneous catalyst. In other word, the robustness is an important characteristic for homogeneous catalyst which is worth with evaluating in all cases but most particularly for water oxidation where harsh conditions are required and where the ligand incorporates a potentially oxidation-labile group [9]. Taking into this consideration, a useful candidate of the organic ligands needs to meet the follow requirements: 1) enough electronic donors to form a stable chelated complex with metal atoms; 2) rich-electron groups to offer large density of electron to stabilize the high-valence state of catalyst mediates; 3) conjugate co-planar system to facilitate electron transfer [22–24]. Among many candidates, azo-compounds are just meeting these requirements to construct a series of efficient WOCs [22–24].

In our previous work, a series of azo-ligands were employed successfully synthesizing WOCs based on half-sandwich Ru, Rh and Ir motifs [22–24], which had good redox properties and high activity of catalyzing water oxidation. Herein, a commercial azo-compound (Chart 1) was explored to construct a new precatalysis based on half-sandwich iridium motifs, which exhibited a good TOF of catalyzing water oxidation.

## 2. Experimental

### 2.1. General conditions

General, All solvents and reagents were of commercial grade. UV–vis spectra were collected using a Varian Cary 50 Bio UV–vis spectrometer with samples in a 1.0 cm quartz cuvette at pH 7.0. Elemental analyses were performed on an Elementar III Vario El analyzer. IR spectra was measured on a Nicolet Avatar-360 spectrophotometer (as KBr pellet). Cyclic voltammograms (CVs) were measured on Electrochemical Workstation (CHI660E). Oxygen pressure was tested by Transient Pressure Recorder (OM-CP-PRTRANS-1-30A). The crystal sample used for X-ray crystallography was obtained by diffusion of ether into the complex methanol solution at room temperature.

### 2.2. The synthesis of complex 1

[Cp\*IrCl<sub>2</sub>]<sub>2</sub> (80.0 mg, 0.1 mmol) was dissolved in 8 mL of methanol at room temperature. Then, the solution was added into 4 equiv of AgOTf (103.0 mg, 0.4 mmol) in dark and stirred vigorously

over night. After then, the reaction solution was added to about 0.1 mmol (35.0 mg) of HL and kept vigorously stirring for 6 h, brown precipitate was collected by vacuum filtration in air. **1**, Yield, 61.3 mg, 87.4%.

Complex **1**: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 1.42 (s, 15H, CH<sub>3</sub>-Cp\*), 8.39 (d, *J* = 8.0 Hz, 2H, aromatic), 8.306 (s, 2H, aromatic), 8.17 (2, 1H, aromatic), 7.89 (m, 1H, aromatic), 7.84 (m, 1H, aromatic), 7.44 (m, 1H, aromatic), 7.26 (d, *J* = 8.0 Hz, 1H, aromatic). <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 8.99 (CH<sub>3</sub>-Cp\*), 80.07 (Cp\*), 95.39, 119.01, 119.97, 125.38, 126.17, 126.27, 127.32, 128.06, 129.24, 129.77, 133.83, 134.85, 151.36, 156.85 (aromatic groups). Elemental analysis calcd (%) for C<sub>27</sub>H<sub>29</sub>IrN<sub>2</sub>O<sub>6</sub>S: C, 46.21. H, 4.16. N, 3.99. Found: C, 46.18. H, 4.13. N, 3.92. IR(KBr, cm<sup>-1</sup>): 3446 (s), 2925 (w), 1732 (w), 1611(w), 1500 (w), 1364 (w), 1227 (m), 1174 (m), 1127(w), 1032 (s), 643(m).

### 2.3. Water oxidation

Ce<sup>IV</sup> salt and NaIO<sub>4</sub> various solutions of complex **1** were mixed to add into the PBS solution (pH = 11) in a 25 mL vial sealed seriously. Firstly, **1** was soluble in the methanol. 10 μL of methanol solution [Cp\*Ir] = 6.67 × 10<sup>-6</sup> M was mixed with 0.6 g Ce<sup>IV</sup> salt and NaIO<sub>4</sub> into PBS solution. Next, the complex was soluble in the acetonitrile and no catalyst was taken part in the reaction under same conditions.

### 2.4. X-ray crystal structure determinations

Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated MoKα radiation (λ = 0.71073 Å). All the data were collected at room temperature using the ω scan technique. The structure was solved by direct methods, using Fourier techniques, and refined on *F*<sup>2</sup> by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program [25]. A summary of the crystallographic data and selected experimental information were given in supporting information.

## 3. Results and discussion

### 3.1. Synthesis and characterization

According to our previous reports, the formation of this newly precatalyst of MWOCs accessed to employ [Cp\*IrCl<sub>2</sub>]<sub>2</sub> as raw material treated with 4 equiv of AgOTf (AgOTf: silver triflate) in methanol solution for 6 h in dark, and subsequently addition of the organic ligand HL was stoichiometric into the mixture with vigorously stirring for 6 h (Scheme 1). As a result, the brown product of complex **1** [Cp\*IrL(H<sub>2</sub>O)] was obtained and purified via recrystallization in high yield. The primary characterization of the complex was performed on by IR, EA and NMR to confirm its component and molecular structure, and Thermo Gravimetric Analyzer (TGA) was carried out on testing thermodynamic stability of complex **1** in air (Fig. s1).

In order to further confirm its specifically molecular structure, single crystal X-ray diffraction was performed on a suitable crystal which was obtained via diffusion of ether into methanol solution to determine its accurate structure. As Fig. 1 depicted, a three-leg-piano geometry of half-sandwich iridium motifs which is a standard binding mode of this analogues, is directly supported by two O atoms (from ligand and water molecule) and one N atom from azo groups. The distorted co-plane of this organic linker with the iridium atom shelters half-sphere of the coordinate center, and one open site is bond to substrate water molecule, facilitating from catalyzing water-oxidation reaction.

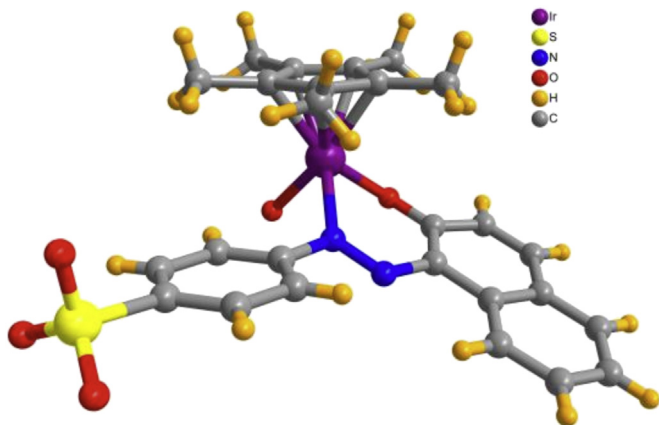


Chart 1. Schematic structure of HL.

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