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Photocatalytic water oxidation mediated by iridium complexes

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ABSTRACT

The results of a systematic investigation on the photocatalytic water oxidation activity of eight Ir complexes are reported. In particular, $[\text{Cp}^*\text{IrL}_n]\text{X}_m$ [**1**, $\text{L}_n = (\text{H}_2\text{O})_3$, $\text{X}_m = (\text{NO}_3^-)_2$; **2**, $\text{L}_n = N$ -dimethylimidazolin-2-ylidene and $(\text{Cl}^-)_2$; **4**, $\text{L}_n = 1,1'$ -dimethyl-3,3'-ethylene-diimidazol-2,2'-diylidene and Cl^- , $\text{X}_m = \text{PF}_6^-$; **5**, $\text{L}_n = 2$ -phenylpyridine (ppy) and NO_3^- ; **6**, $\text{L}_n = 2$ -benzoylpyridine (bzpy) and NO_3^- ; **8**, $\text{L}_n = 2,2'$ -bipyridine (bpy) and Cl^-], $[\text{Ir}(\text{HEDTA})\text{Cl}]\text{Na}$ (**3**) and $[\text{Ir}(\text{ppy})_2(\text{OH}_2)_2]\text{OTf}$ (**7**), whose water oxidation activity driven by chemical oxidants was already proved, were tested as mediators (10 μM –100 μM) in photocatalytic experiments exploiting $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1 mM) as photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ (2.5 mM–30 mM) as electron acceptor, at pH 5.2 and pH 8 by $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$ and $\text{Na}_2\text{B}_4\text{O}_7$ buffers, respectively. All complexes showed to be competent catalysts for the photolytic water oxidation. Best performances were obtained with **2** at pH 5.2, where TOF > 2.5 min^{-1} , TON > 80 and quantum yield > 0.1. H/D kinetic isotopic effect was evaluated for **1**, **2** and **8** and related to their tendency to undergo oxidative transformation as deduced by ^1H NMR studies, using CH_3COOH as molecular probe.

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1. Introduction

The generation of solar fuels by means of a man-made photosynthetic apparatus [1] strongly relies on the development of an efficient water oxidation catalyst (WOC) [2–6]. Over the last years, iridium organometallic complexes have been successfully exploited as catalysts for WO driven by chemical sacrificial oxidants, such as a cerium(IV) ammonium nitrate (CAN) and sodium periodate [7–26]. They exhibit remarkable performances both in terms of turnover frequency (TOF) and turnover number (TON). The majority of them belong to the Cp^*IrL_n (Cp^* = pentamethylcyclopentadienyl anion) class, where the selection of L ligand is critical in determining the catalytic activity, stability and also the nature of the active species. As a matter of fact, it has been shown that, under the harsh catalytic conditions used, particularly with CAN, Cp^* undergoes a gradual oxidative transformation ultimately leading to its complete degradation into acetic acid, formic acid, etc. . . , in some cases [14,27,28,29–31]. The proper selection of L ligands is critical also to allow the heterogenization of Ir WOCs onto a proper support [32–34]. The latter

strategy appears particularly promising for integrating Ir WOCs into a device for the photosynthesis of solar fuels and has the advantages of minimizing the associative deactivation processes and maximizing the number of active sites. Similar advantages have been recently obtained by the exploitation of layered double hydroxides doped with iridium as WOCs [35].

In spite of so many studies on Ir organometallic WOCs in combination with chemical sacrificial oxidants, the photocatalytic oxidation of water mediated by iridium complexes has been much less explored [36–40]. The classical protocol to evaluate possible photocatalytic activity stems on combining $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, $\text{Na}_2\text{S}_2\text{O}_8$ as electron acceptor and a catalyst as illustrated in Scheme 1 [41].

Herein we report the results of a systematic investigation on the photocatalytic WO activity of eight well established Ir catalysts (Fig. 1), using differential manometry to quantify gas evolution, validated by the classic system of O_2 detection based on the Clark electrode. As described below, such methodology simplifies the experimental procedure since it avoids deoxygenating the solution before catalysis. Complex **4**, whose photocatalytic activity toward WO was previously investigated by Volpe et al. [36], was taken as reference for comparing the catalytic performance of other WOCs. More in-depth kinetic studies (pH, persulfate and catalyst concentration effects) were conducted for the most active WOCs (**1** and **2**) and for **8** bearing the robust bpy-ligand. Finally, the H/D kinetic

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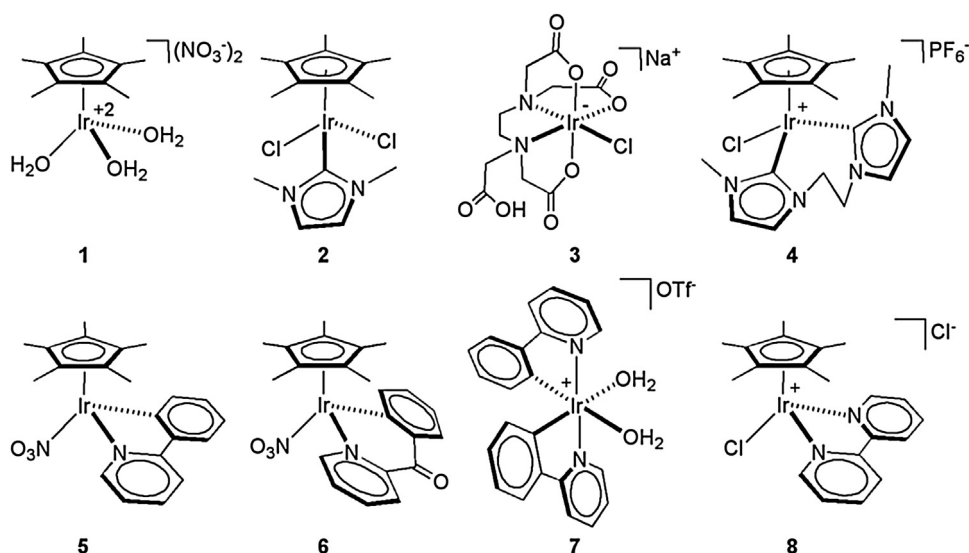
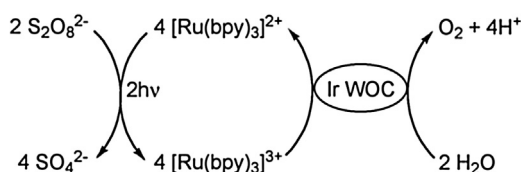


Fig. 1. Complexes exploited as water oxidation catalysts in this study.



Scheme 1. Simplified scheme showing the operation of the three-component system for photocatalytic water oxidation [41].

isotopic effect (KIE) and the oxidative transformation of catalysts were studied for **1**, **2** and **8**.

2. Experimental section

2.1. Materials

Compounds **1**[42], **2**[12], **3**[15], **4**[36], **5**[43], **6**[10], **7**[7] and **8**[44] were synthesized according to the literature. All solvents and reagents were purchased from commercial sources and used as received. ^1H NMR spectra were recorded on a Bruker Avance III HD spectrometer equipped with a Smart probe, operating at 400.13 MHz. The 50 mM buffer at pH = 5.2 was prepared by dissolving Na_2SiF_6 (2.35 g, 12.49 mmol) and NaHCO_3 (1.05 g, 12.49 mmol) in water (500 mL, Milli-Q Ultrapure). The solution was stirred for 48 h and then filtered throughout a Corning 0.20 μm filter to reach the final pH of 5.2 at 298 K. The 50 mM borate buffer was prepared by dissolving $\text{Na}_2\text{B}_4\text{O}_7$ (5.03 g, 24.99 mmol) in water (500 mL, Milli-Q Ultrapure), adding some drops of HCl (3 M) to reach a final pH of 8 at 298 K. Since complexes **4**, **5** and **6** exhibited a limited solubility in water, they were solubilized adding 3% (**4**), 2.5% and 7.5% (**5**) and 2.5% (**6**) in volume of acetonitrile, respectively.

2.2. Photocatalytic water oxidation experiments

Compounds **1–8** were tested as WOCs using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (1 mM) as photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ (2.5–30 mM) as electron acceptor (Scheme 1). Evolved O_2 was monitored by using either a differential manometer or a Clark electrode.

2.2.1. Manometric experiments

Manometric measurements were performed using two homemade-jacketed glass reactors coupled to a Testo 521-1

manometer. The moles of evolved O_2 were evaluated from the observed pressure difference (ΔP) through the state equation of ideal gases, after having measured the reactor volume by the slope of the ΔP versus number of moles trends derived by adding known quantities of gas. In a typical experiment, 5 mL of the aqueous buffer at pH 5.2, containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (1 mM), $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) and catalyst (100 μM), were loaded into one reactor. The other reactor was filled by 5 mL of the buffer solution and used as reference cell. Both reactors were equipped with a side arm for the connection to the manometer and with a septum to seal them. The two cells, maintained at constant temperature (298 K), under constant magnetic stirring, were not deoxygenated. Data acquisition was started, whereas the photocatalytic experiment was initiated only after having achieved a steady baseline (for details see paragraph 2.2.4). Gas evolution was monitored during the reaction by measuring the differential pressure between the two cells. TOF values were calculated from the linear trend of the TON vs time plots, assuming that molecular oxygen is the only produced gas. Errors in TOF and TON were estimated by the standard deviations of those values in experiments (2–4) conducted under exactly the same experimental conditions. Errors are not indicated in the tables along the paper when a single experiment was carried out.

Manometric experiments in deuterated water were performed analogously. $\text{NaHCO}_3/\text{Na}_2\text{SiF}_6$ 50 mM buffer solution was obtained by dissolving the proper amount of salts in D_2O . The pD was adjusted from 5.4 to 4.8 by adding a few drops of fuming HCl 37%. pD 4.8 corresponds to pH 5.2 according to the equation $\text{pH} = \text{pD} + 0.4$ [45]. Catalytic experiments were performed using concentrations of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $\text{Na}_2\text{S}_2\text{O}_8$ and catalyst equal to 1 mM, 5 mM and 100 μM , respectively. All the other conditions were those chosen for the experiments in H_2O . KIE was calculated by the ratio of TOF values in H_2O and D_2O .

2.2.2. Detection of oxygen by Clark electrode

The amount of oxygen produced in the first part of the photocatalytic experiments was determined also by a Clark oxygen electrode (Hanna, model HI 4421). Before starting each experiment, the gas permeable membrane was replaced to ensure a high-quality response. The electrode, secured in a Teflon tube, was inserted into a tight-fitting jacketed glass reaction vessel. The system was kept at a constant temperature of 298 K. In a typical experiment, 39 mL of the aqueous buffer solution, containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (1 mM),

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