## **Supporting Information**

# Photochemical water oxidation by cyclometalated iridium(III) complexes: A mechanistic insight

Sujay Mukhopadhyay, Roop Shikha Singh, Arnab Biswas and Daya Shankar Pandey\*

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005 (U.P.) India

#### Contents

1.	Experimental section	S2-S3
2.	<sup>1</sup> H NMR spectra of 1–3 after photochemical irradiation	S4
3.	Mass isotropic patterns of 1–3 along with simulated pattern	
4.	Cyclic Voltammograms of 2 and 3 in CH <sub>3</sub> CN	S6-S7
5.	UV/vis spectra of 2 and 3 and changes upon photochemical reaction	S7-S8
6.	GC spectra of air, control and after photochemical reaction of 1-3	S8-S10
7.	TON vs time plot of 1–3 for photochemical evolution of O <sub>2</sub>	S10
8.	First order kinetic plot for 1-3	S11
9.	TEM images of 2 and 3 after photochemical reaction	S12
10.	DLS plots for 1-3	S13
11.	XPS spectra for Ir-4f lines of 1-3	S13
12.	Plausible mechanism	S14
13.	Instrumental set up for two port photochemical reaction	S15
14.	Crystal data and selective bond lengths and angles for 1–2	S16-S17
15.	References	S18

#### **Experimental Section**

Reagents. The synthetic manipulations were performed under nitrogen atmosphere and solvents were dried and distilled prior to their use following literature procedures.<sup>1</sup> Hydrated iridium(III) trichloride, pentamethylcyclopentadiene, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-formyl methylbenzoate, tertiary butylaniline,  $[Ru(bpy)_3](ClO_4)_2,$ tetrabutylammonium perchlorate, were procured from Sigma Aldrich Chemical Co., India and sodium acetate anhydrous, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, CAN, were obtained from s. d. fine-chem. India,  $C_5Me_5$   $Ir(\mu$ -Cl)Cl $_2$  was synthesized and purified following literature procedures.<sup>2</sup>

General Methods. Electronic absorption spectra were acquired on a Shimadzu UV-1601. <sup>1</sup>H (300 MHz) NMR spectra at rt were obtained on a JEOL AL300 FT-NMR spectrometer using tetramethylsilane [Si(CH<sub>3</sub>)<sub>4</sub>] as an internal reference. Electrospray ionization mass spectrometric (ESI-MS) measurements were made on a THERMO Finningan LCQ Advantage Max ion trap mass spectrometer. Samples (10 µL) were dissolved in dichloromethane/acetonitrile (3:7, v/v) and introduced into the ESI source through a Finningan surveyor auto sampler. Mobile phase (MeOH/MeCN:H2O, 90:10) flowed at a rate of 250  $\mu$ L/min. The ion spray voltage was set at 5.3 KV, and capillary voltage at 34 V. The MS scan run up to 2.5 min and spectra print outs were averaged of over 10 scans. The electrochemical measurements under nitrogen atmosphere at rt were performed using a single compartment cell equipped with a glassy carbon working, platinum wire counter, and Ag/Ag<sup>+</sup> reference electrode on a CHI 620c electrochemical analyser. All the peaks were independently calibrated with respect to an internal Ferrocene/Ferrocenium (Fc/Fc<sup>+</sup>) redox couple under identical condition. The differential pressure measurements during water oxidation were recorded on a Testo make manometer in an operating range of 0.01–34.5 kPa and accuracy within 0.3%. The oxygen produced as a result of water oxidation was detected and quantified with a monitor gas line of nitrogen using an Agilent make GC (Model no 7890A). TEM images were captured on FEI Technai 20 U Twin Transmission Electron Microscope. The samples were loaded over lacy carbon coated copper TEM grids (300 mesh) dried under ambient conditions, and imaged. Dynamic light scattering (DLS) analyses were run in Horiba particle size analyzer SZ-100 instrument. XPS spectroscopy was performed on a multitechnique X-ray photoelectron spectroscopy with XPS-mapping capability Axis Ultra

instrument (small spot capabilities <15 microns). XPS peak fits were performed using XPSPeak (version 4.1) software.

**Synthesis**. Synthesis of the ligands and complexes has been performed following standard procedures reported earlier by us elsewhere.<sup>3</sup>

X-ray Structure Determination. Crystals suitable for X-ray single crystal analysis for 1 and 2 were obtained by slow diffusion of methanol over a dichloromethane solution of the complex. X-ray data on 1 and 2 were collected on a Bruker Kappa Apex-II diffractometer at RT with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at Department of Chemistry, Center for Advanced Studies, Guru Nanak Dev University, Amritsar, India. Structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares on  $F^2$  (SHELX 97).<sup>4</sup> All the non-H atoms were treated anisotropically. The H-atoms attached to carbon were included as fixed contribution and geometrically calculated and refined using SHELX riding model. Computer program PLATON was used for analyzing the interaction and stacking distances.<sup>5</sup> CCDC deposition Nos. 1018749, 1018750 (1 and 2) contain supplementary crystallographic data for this paper. The data can be had free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

**Electrochemical Measurements**. Electrochemical behavior of **1–3** have been investigated by cyclic voltammetry (CV) in pure acetonitrile using 1 mM solution in the potential range +1.5 to -2.0 V and scan rate 50 mVs<sup>-1</sup>. The measurements were performed at rt using tetrabutyl ammonium perchlorate [ $(n-Bu)_4N$ ]ClO<sub>4</sub> (0.1 M) as a supporting electrolyte. Redox potentials were referenced to the Fc/Fc<sup>+</sup> couple (0.1 V).

Absorbance studies. Electronic absorption spectra of 1–3 were measured in acetonitrile and in 9:1 water: acetonitrile (c, 10  $\mu$ M) at rt. UV/vis experiment have also been performed at rt using an aqueous solution of [Ru(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (**PS**) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (**SO**) and adding 1–3 in acetonitrile.

Sample preparation for DLS. Photochemical reaction mixture containing 25  $\mu$ M 1–3 together with 500  $\mu$ M [Ru(bpy)<sub>3</sub>]<sub>2</sub> and 2500  $\mu$ M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, pH 7.2 at 25 °C were first filtered using a 0.22  $\mu$ m filter paper from Millipore in dark. Then irradiated continuously for 15 min and analyzed for any nanoparticle formation by DLS.



Figure S1: <sup>1</sup>H NMR spectra of recovered products of 1 (a), 2 (b), 3 (c) after photochemical reaction with PS and SO in  $CH_3CN:H_2O$  1:9 solution.



**Figure S2**: (a) Mass spectral plot showing isotopic distribution of **1** (a), **2** (b), **3** (c) calculated theoretically along with their simulation found.



Figure S3: Cyclic voltammogram of (a) 2 and (b) 3 in pure acetonitrile solvent.



**Figure S4**: Cyclic voltammogram of (a) **2** and (b) **3** in acetonitrile solvent after addition of  $300 \mu$ L water.



Figure S5: Zoom cyclic voltammogram (reduction waves) of (a) 2 and (b) 3 in acetonitrile solvent after addition of 300  $\mu$ L water.



Figure S6: UV/vis spectral pattern of 1 - 3 in pure acetonitrile and 1:9 acetonitrile:water.



**Figure S7**: (a) UV/vis spectra of  $[Ru(bipy)_3]^{2+} + Na_2S_2O_8 + 2$ , inset showing the tiny peak at 762 nm. (b) UV/vis spectra of  $[Ru(bipy)_3]^{2+} + Na_2S_2O_8 + 3$ .



Figure S8: GC spectra of (a) air and (b) control for chemical water oxidation by CAN



**Figure S9**: GC spectra of (a) CAN + 1, (b) CAN + 2, (c) CAN + 3.



**Figure S10**: GC spectra of (a) air and (b) control for photochemical water oxidation.



Figure S11: GC spectra of  $[Ru(bipy)_3]^{2+} + Na_2S_2O_8 + (a)$  1, (b) 2, (c) 3 after photochemical irradiation.



Figure S12: TON for  $O_2$  generation vs time (min) for (a) 1, (b) 2, (c) 3, for photochemical water oxidation.



Figure S13. First order kinetic plot for the photochemical water oxidation reaction of 1, 2, 3.



Figure S14: TEM image of 2 after photocatalytic reaction with RuBp and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.



Figure S15: TEM image of 3 after photocatalytic reaction with RuBp and  $Na_2S_2O_8$ .



**Figure S16**. (a) DLS spectra of catalysts **1**, **2**, and **3**, after 15 minutes of photochemical reaction; (b) DLS spectra of catalysts **1**, **2**, and **3**, after 24 h of photochemical reaction. (c) DLS spectra after applying vacuum pressure for 15 minutes.



Figure S17. XPS spectra for Ir-4f lines for 1 (a), 2 (b), 3 (c).



**Figure S18**: Plausible mechanism for the catalytic cycle of photochemical water oxidation process.



Figure S19: Instrumental set up used for photochemical water oxidation. (a) Two port sensing method for observing differential pressure increase in the reaction vial (right) with

respect to reference vial (left) by a manometer. (b) and (c) LED irradiation of the samples. (d) Manometer reading after 5 minutes.

1 2 **Crystal parameters** C<sub>29</sub>H<sub>35</sub>ClIrNO<sub>2</sub> C<sub>28</sub>H<sub>32</sub>ClIrN<sub>2</sub> empirical formula formula weight 657.25 624.23 crystal system Triclinic Triclinic P -1 space group P -1 a (A°) 8.578(3) 8.423(17) b (A°) 11.680(4) 11.622(2) c (A°) 14.133(5) 13.821(3) 100.173(6) 98.609(17)  $\alpha$  (deg)  $\beta$  (deg) 98.743(17) 98.473(5) 101.874(16) 99.561(7) γ (deg) V (A° <sup>3</sup>) 1345.400(8) 1291.200(4) Color and habit Brown needles Brown prism Ζ 2 2 dcal (g/cm<sup>3</sup>) 1.622 1.606 Temperature (K) 296(2) 296(2)

Table S1. Crystal data and structure refinement parameters for 1 and 2

wavelength (A°)		0.71073		0.71073		
$\mu$ (mm <sup>-1</sup> )		5.087		5.291		
Bond length (Å)		1	Bond length (Å)	)	2	
Ir1-N1	2.08		Ir1-N1		2.08	
Ir1-C11	2.04		Ir1-C23		2.04	
Ir1-Cl1	2.40		Ir1-Cl1		2.40	
C28-O1	1.19		C28-N2		1.13	
C28-O2	1.32		C11-N1		1.43	
C18-N1	1.42		Ir-Cg*		2.21	
Ir-Cg	2.21		Ir-Cav**		1.84	
Ir-Cav	1.84					
GOF on F2		1.031		0.998		
final R indices[I > $2\sigma(I)$ ]		R1 = 0.0200		R1 = 0.0208		
		wR2 = 0.0502		wR2 = 0.0522		
R indices (All data)		R1 = 0.0234		R1 = 0.0255		
		wR2 = 0.0485		wR2 = 0.0500		

 Table S2. Selected bond lengths for 1 and 2.

\* Cg = metal centroid bond distance.

\*\* Cav= average metal-carbon bond distance.

Bond Angle (°)	1	Bond Angle (°)	2
N1-Ir1-Cl1	85.20	N1-Ir1-Cl1	86.38
C22-Ir1-Cl1	84.97	C23-Ir1-Cl1	85.54
N1-Ir1-C22	78.07	N1-Ir1-C23	77.89
C18-N1-Ir1	124.63	C11-N1-Ir1	123.18
01-C28-O2	121.80	N2-C28-C25	179.60

 Table S3. Selected bond angles for 1 and 2.

### References.

1. D. D. Perrin, W. L. F. Armango, D. R. Perrin, Purification of laboratory Chemicals; Pergamon: Oxford, U.K., 1986.

(a) M. A. Bennett and A. K. Smith, J. Chem. Soc., Dalton Trans., 1974, 233–241; (b) M.
 A. Bennett, T. N. Huang, T. W. Matheson and A. K. Smith, Inorg. Synth., 1982, 21, 74–78;
 (c) W. Kang, K. Moseley and P. M. Maitlis, J. Am. Chem. Soc., 1969, 91, 5970–5977; (d) R.
 G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson S19

and S. T. Michel, *Inorg. Chem.*, 1990, **29**, 2023–2025; (e) C. White, A. Yates, and P. M. Maitlis, *Inorg. Synth.* 1992, **29**, 228–234.

S. Mukhopadhyay, R. K. Gupta, R. P. Paitandi, N. Rana, G. Sharma, B. Koch, L. K. Rana,
 M. S. Hundal and D. S. Pandey, *Organometallics*, 2015, 34, 4491–4506.

4. G. M. Sheldrick, Acta cryst. 2008, A64, 112-122.

5. (a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tools* Utrecht University, Utrecht, The Netherlands, 2000; (b) A. L. Spek, *Acta Crystallogr. A* 1990, **46**, C31.