

# Synthesis and Characterization of Homogeneous Water Oxidation Catalyst Containing Single Metal Site

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**Abstract**— The aim of this paper has been to design & synthesize Ru complexes for water oxidation catalyst & understood their catalytic mechanism. The main strategy has been to lower the oxidation potential of Ru complex & stabilizes their high valent state by introducing negatively charged ligand. So in this project we are going to synthesize mononuclear Ruthenium water oxidation catalyst for water oxidation, containing one tridentate ligand & one bidentate ligand & one water molecule. We used here Ruthenium based mononuclear complexes because of their favorable properties viz kinetic ligand-exchange, variable oxidation states and coordination numbers under physiological conditions. Since last two decades variety of transition metal complexes have been studied as catalysts for oxidation of water containing Mn, Fe, Co, Ir, Cu and Ru metals. Among the most effective of these catalysts are based on Ru (II).

**Keywords**— kinetic ligand exchange, artificial oxidation, oxidation catalyst, oxygen evolution

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## I. INTRODUCTION

Development of study of Ru based water oxidation catalyst which is essential component for solar energy conversion to fuel. WOCs plays a crucial role to develop system for the generation of oxygen. The oxidation of H<sub>2</sub>O to O<sub>2</sub> is a four-electron, four-proton process in which O–O bond formation is the key chemical step. In photosystem II, these proton-coupled electron transfers (PCETs) occur via a tyrosine at the Mn<sub>4</sub>Ca oxygen-evolving complex. An important thermodynamic aspect of photosynthesis is the efficient conversion of photonic energy to electrical potential, thus providing 99% of the driving force required to convert CO<sub>2</sub> to carbohydrates. Solar energy is considered a decentralized & inexhaustible natural resources. 1h of sunlight produces more energy than the energy consumed on the planet in one year. In natural photosynthesis solar energy is converted into chemical energy by utilizing water as a raw material. The water is catalytically oxidized by the CaMnOx cluster in OEC of PSII, which is embedded in the thylakoid membrane of green plants, cyanobacteria & algae. With inspiration from nature, constructing an artificial photosynthetic device has been a goal of almost important for scientists. Chemical intermediate formed during oxidation of water are so reactive that auto oxidation of the catalyst often leads to self-destruction. In contrast OEC can be resynthesized every half hour with little or no production of oxidized intermediate such as hydroxyl radicals hydrogen peroxide or superoxide, thus the functional stability of the OEC is maintained despite its structural instability. The whole water splitting process consist of two reaction one is proton reduction & another is water oxidation. To minimize the over potential & increase the reaction rate WOCs is required. For large scale

application a qualified WOCs has to be fulfill the following criteria

1) -Long term durability, 2) -Low over potential, 3) - High activity,

4) - Low cost, 5) -Low toxicity. Unfortunately the development of effective WOCs is difficult & no WOCs have reached the level of large scale application up to date. Many research works still focus on the understanding of the basic reaction mechanism which will in turn guide chemist to design more effective WOCs. One of the main bottlenecks for artificial solar fuel production is the lack of efficient, stable and inexpensive catalytic materials for the anodic reaction, the oxidation of water:



The oxidation potential of this four-electron semi-reaction is 1.23 V, measured at pH = 0 against the normal hydrogen electron (NHE). This high oxidation potential reflects the high stability of water.

## 2. EXPERIMENTAL

### Materials

#### 1. Chemicals:

All chemicals used in this work were analytical grade. The chemicals and sources were as follows RuCl<sub>3</sub>·3 H<sub>2</sub>O; 2, 6 bis' benzimidazole pyridine; O-phenyl diamine, picolinic acid, polyphosphoric acid, sodiumhydroxide, lithiumchloride, pyridine glycoluril, activated charcoal, activated alumina powder. Were obtained from S.D fine chemicals limited

(INDIA) all other chemicals were purchased from locally available sources.

## 2. Solvents:

The solvents methanol, ethanol, acetonitrile, DMSO, polyphosphoric acid, deuterated solvents  $CDCl_3$ , acetone, hexane, diethyl ether, DMF. Were obtained from Aldrich Chemicals Co. (U.S.A.) and local chemical suppliers such as Anand agencies.

## Physical method:

The ligands and complexes synthesized during the study have been characterized by infrared spectroscopy (IR); UV-Visible; Nuclear magnetic resonance (NMR); Mass spectrometry; and the electrochemical method. These methods are briefly outlined as follows:

### 1. Infrared Spectroscopy (IR):

The spectra of the solid samples were recorded by using KBr pellets as in the so called Shimadzu FTIR-8400 spectrophotometer at Department of the chemistry, Savitribai Phule Pune University, Pune.

### 2. UV-Visible spectroscopy:

UV –Visible absorption measurements were carried on JASCO V-630 Spectrophotometer using matched pairs of 1 cm quartz cells at Central Instrumental Facility, Department of chemistry, Savitribai Phule Pune University, Pune.

### 3. NMR Spectroscopy:

$^1H$  NMR Spectra of the ligands and complexes were measured on a Varian –Mercury 400 MHz spectrometer with  $CDCl_3$ , DMSO- $d_6$  as solvents at room temperature and all the chemical shifts are given relative to tetramethylsilane (TMS) as the internal standards at Department of Chemistry Savitribai Phule Pune University, & Central Instrumental Facility SPPU.

### 4. Cyclic Voltametry :

Cyclic voltametric measurement were carried out using a set of CH-1130A instrument, a three electrode system consisting of glassy carbon as working electrode Pt-wire as counter electrode and Ag / AgCl as reference electrode. Experiments were carried out in DMF solvent containing 0.1 M tetraethyl ammonium perchlorate (TEAP) as a supporting electrolyte. The total volume utilized was 5-7 mL and the concentration of the complexes used in the range of 10<sup>-3</sup> M used for oxidation potential measurement.

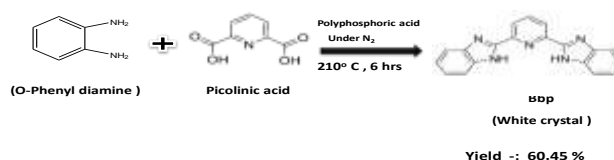
## 3. Synthesis and Characterization:

### 3.1 Synthesis of ligands and their characterization:

#### [2, 6, bis (benzimidazole-2-yl) pyridine]

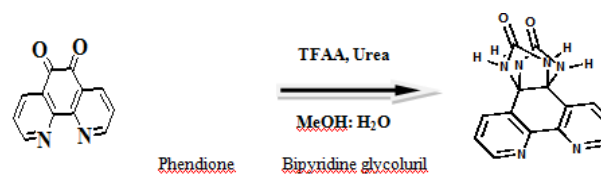
Under  $N_2$  atmosphere, 500 mg of pyridine 2, 6, carboxylic acid, 701.49 mg ortho phenylene diamine were added to 16 mL of polyphosphoric acid. The mixture was cooled to 150 °C & then

poured into 1 L of water. The mixture was then neutralized to pH 8 with ammonium hydroxide. The solid was collected by filtration & repeatedly washed with plenty of water. The solid was dissolved in hot methanol & treated with active charcoal to give compounds pure crystals. It was characterized by NMR, IR, and Mass Spectrometry.



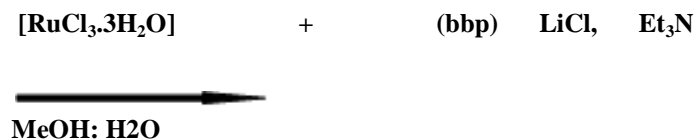
### 2. Synthesis Of Ligand Bi-Pyridine Glycoluril (Bpg):

Phendione (1 g, 4.75 mmol) & urea (855.85 mg, 14.25 mmol) & trifluoro acetic acid (1130 mg) (10.26 mmol) were added to 20 mL Methanol in round bottom flask and refluxed for 8 hrs. Then mixture was evaporated to (sticky mass) dryness. 15-20 mL of water were added to dry powder and filtered the mixture followed by recrystallization with methanol. It was characterized by NMR Spectroscopy.



### 3. Synthesis of Precursor Complex [Ru (bbp)Cl<sub>3</sub>]:

Take 80.4 mL absolute ethanol to that add 168 mg of [RuCl<sub>3</sub>.3H<sub>2</sub>O] and 150 mg of bbp. The whole mixture is reflux for 3 hrs with vigorous magnetic stirring. Cooled to room temperature. A fine brown powder appeared, filtered from reddish yellow solution. Washing of product with 30 ml portion of ethanol followed by 30 ml portion of diethyl ether & air dried. It was characterized by UV-Visible Spectroscopy

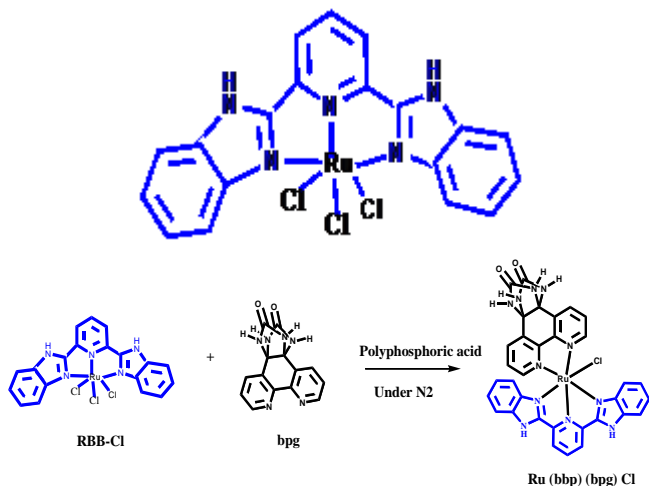


### 4. Synthesis of [Ru (bbp) (bpg) Cl ]<sup>+</sup>:

Take [Ru(bbP)Cl<sub>3</sub>] complex (50 mg, 0.12 mmol) & Bpg (2 mg, 0.12 mmol) were refluxed for 4 hrs in MeOH/ H<sub>2</sub>O (20 ml,3:1) under argon. The reaction mixture was filtered hot, & the filtrate was evaporated & then to that add activated alumina and dried clearly. The product was purified by column

chromatography on alumina eluting with acetone: methanol (8:2) ratio. The major band was collected & concentrated. Some part of collected fraction was kept for crystal growing result into dark brown shiny crystals after two-three days. The remaining fraction was solidified into dark brown powder by evaporating the solvent.

rate of oxygen evolution was calculated from the plot of oxygen evolution as function of time. The initial rate constant was calculated from the slope of the plot of initial rate of oxygen as a function of the concentration of the catalyst. The turn over number (TON) and Turn over frequency TOF was determined using a Microsoft Excel and data obtained from Pressure transducer



### Synthesis Of $[\text{Ru}(\text{bbp})(\text{bpg})(\text{H}_2\text{O})]^{2+}$ :

Complex  $[\text{Ru}(\text{bbp})(\text{bpg})\text{Cl}]\text{Cl}$  150 mg, (0.214 mmol) and  $\text{AgNO}_3$  90.45 mg, (0.532 mmol) were added to 15 ml of acetone : water mixture with the ratio 2:1 in round bottom flask and refluxed for one hour followed by stirring for 6 hours. The mixture was filtered and heated for one hour, and stirred it for two hour. After that solution was filtered and concentrated to around 5 ml and approximately 5-6mg of  $\text{NH}_4\text{PF}_6$  salt was added to it, result into fine brown color solid. The solid was filtered off and dried under vacuum. It was characterized by NMR, IR, Mass, UV-Visible spectroscopy and Cyclic voltammetry.

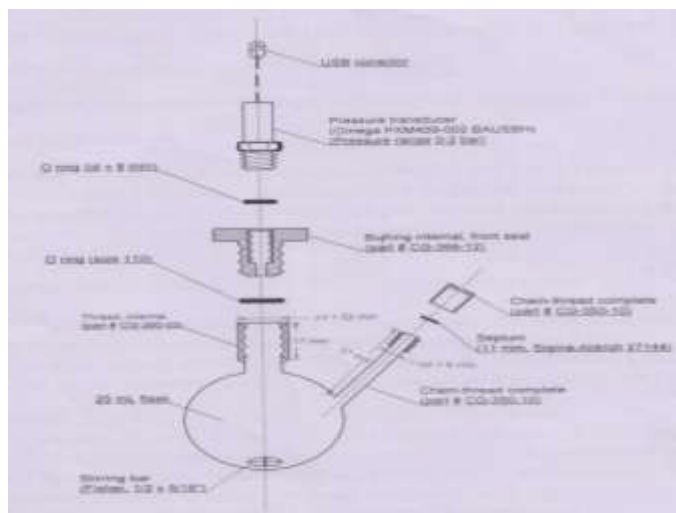
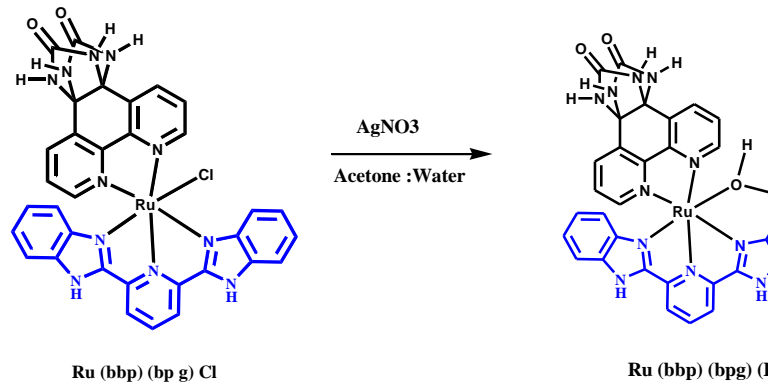


Fig.2. 25 mL flask with Pressure Transducer



### Oxygen evolution:

oxygen evolution measurement can be done by using pressure transducer method. A 2-naked flask, fitted with a septum cap and with ceric ammonium nitrate. The  $\text{CeIV}$  solution was taken into round bottom flask purged with  $\text{N}_2$  to provide an oxygen free solution and then the  $\text{RuII}$  catalyst was purged, gave an  $\text{O}_2$  reading every 10 sec for up to 6.5 hrs. The initial

## 4. Result and Discussion:

### 4.1 UV-Vis Spectroscopy:

The complex  $[\text{Ru}(\text{bbp})(\text{bpg})(\text{H}_2\text{O})]^{2+}$  exhibits the absorption bands at 270 -600 nm in the UV & Visible region due to Metal to Ligand charge transition and ligand based  $\pi-\pi^*$  transition. The Molar extinction coefficient value ( $\epsilon_{\text{max}}$ ) values for the complex were  $10^3-10^4 \text{ mol}^{-1} \text{ cm}^{-1}$  in visible region.

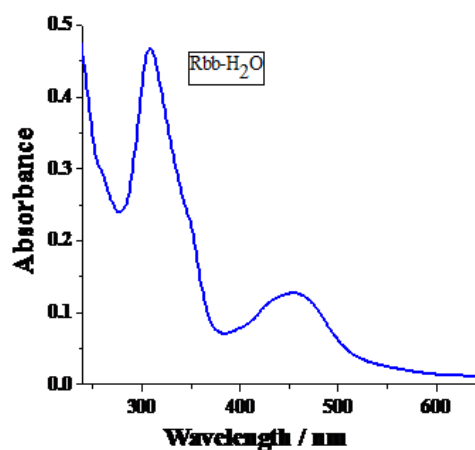


Fig.3. UV-Vis spectra of 20  $\mu\text{M}$  RBB- $\text{H}_2\text{O}$  in B.R. Buffer acid at 25 °C

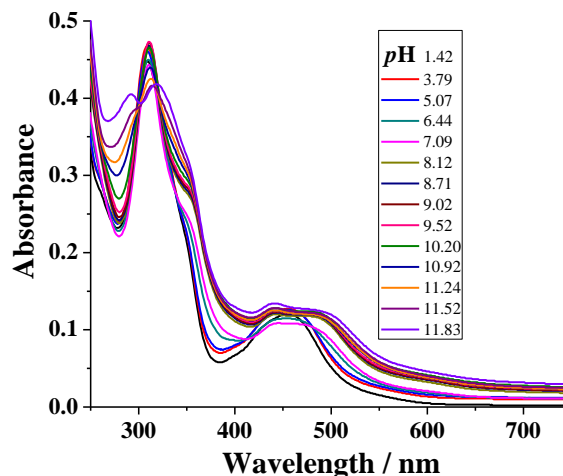
Complex	$\lambda_{\text{max}} / \epsilon (\text{M}^{-1} \text{ cm}^{-1})$

RBB-H2O	308 (9258)
	454 (2576)

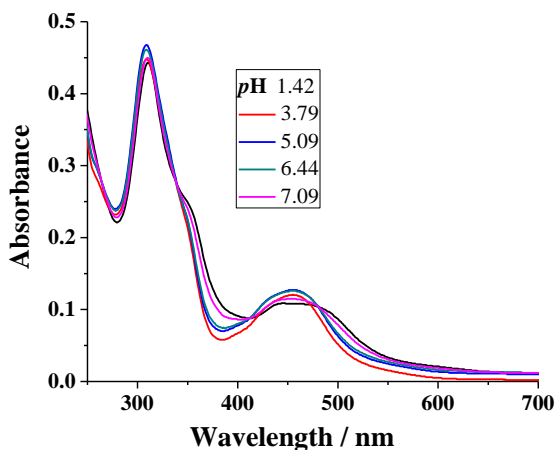
**Table:** 1.  $\lambda_{max}$  and extinction coefficient  $\epsilon$  ( $M^{-1} cm^{-1}$ ) of complex RBB-H<sub>2</sub>O

**4.2 Photometric Titration:**

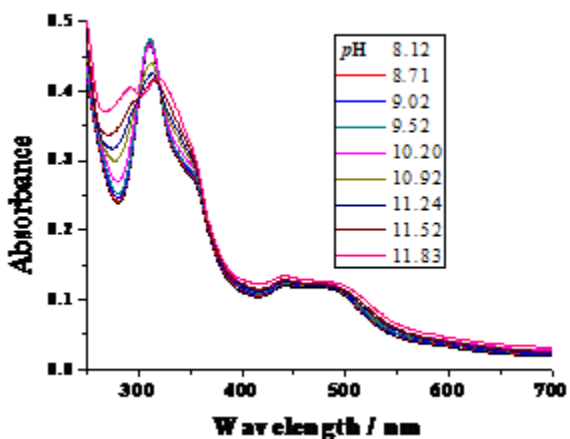
Absorbance of 20  $\mu M$  RBB-H<sub>2</sub>O in different pH obtained by using Britton Robinson Buffer (pH range 2.0 to 12) with the help of Uv-Visible spectrophotometer. Two different absorbance pattern were observed, one was below pH 7 and second was above pH 7 along with three isobastic points in each graph as shown in a, b, and c. Three pKa values were obtained by taking absorbance at fixed wavelength around corresponding isobastic point as shown in d, e and f. Where each pKa value was deprotonation at particular pH. Especially, pKa<sub>1</sub>, pKa<sub>2</sub> and pKa<sub>3</sub> were deprotonation of H<sub>2</sub>O, NH of bpg and NH of bbp respectively.



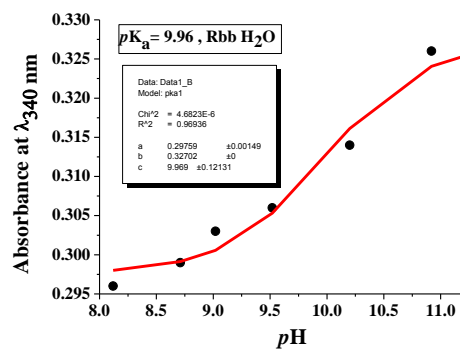
(c)



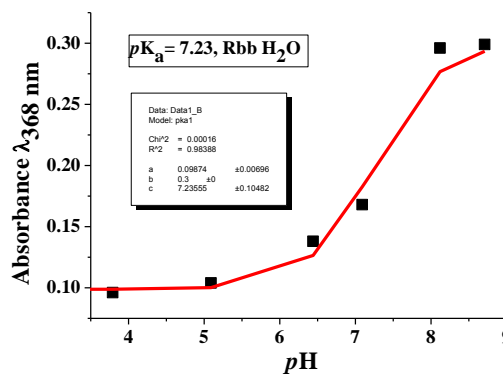
(a)



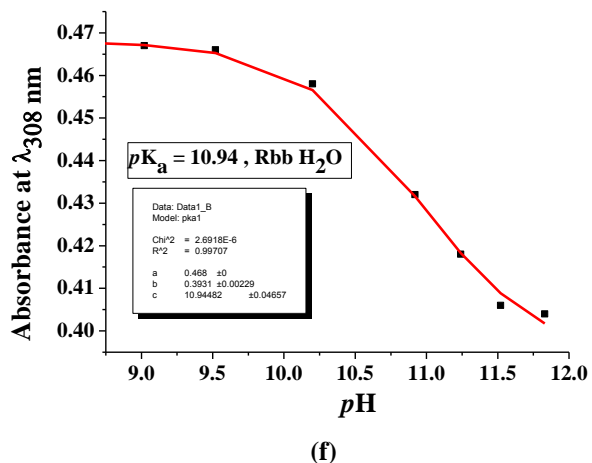
(b)



(d)



(e)



**Fig.4.** UV-Visible spectra a, b and c of 20 μM RBB-H<sub>2</sub>O at various pH in B.R.Buffer (pH range from 2 to 12) and d, e and f are the pK<sub>a1</sub>, pK<sub>a2</sub> and pK<sub>a3</sub> from corresponding isobastic points.

**Table.3.** pKa values at around various isobastic points in (a) and (b)

Complex	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>
RBB-H <sub>2</sub> O	10.94	9.96	7.23

**IR Spectroscopy:**

The solid IR spectrum of the ligand and their complex shows the respective complex has been formed. The corresponding stretching frequency are given below.

**Table: 4.** IR Spectral Data

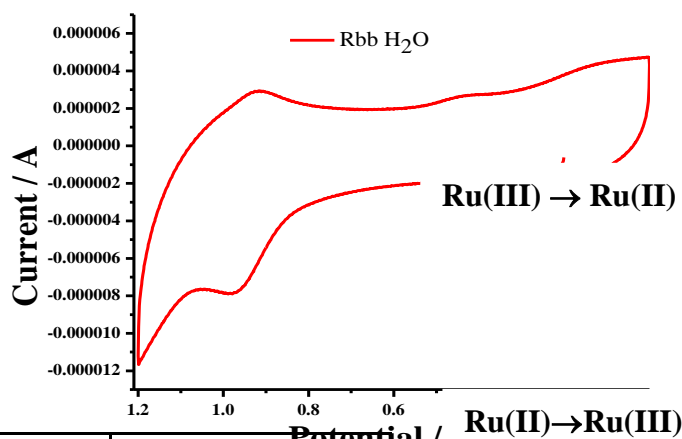
Complex/lig and	C=C	C=N	C=O	C-C	C-H	O-H	N-H	=C-H
Phendione	1573	1653	1683	-	2915	-	-	3061
Bbp	1581	1444	-	1307	2875	-	3221	3055
[Ru(bbp)(bpg)H <sub>2</sub> O]	1645	1450	1701	1325	2893	3408	3213	3095

**Electrochemistry:**

**Cyclic Voltammetry :**

Cyclic voltammetry of complex were investigated in DMF, containing TEAP as supporting electrolyte using platinum as working electrode vs. Ag / AgCl as reference electrode. The cyclic voltammogram of complex are shown in fig. at different voltages. Although the Ru (II) complex exhibit a series of ligand based reduction processes under voltammetry condition.

The present study reports only details of oxidation of Ru (II) to Ru (III). The complex shows only one type of peak in the range of 0.0 to 1.2 V. The reversible peak at the higher potential corresponding to Ru(II) to Ru(III) oxidation. Reversible potential (E<sub>0</sub>) values assumed to be equal to the midpoint potential (E<sub>m</sub>) and were determined from the average of the oxidation (E<sub>ox</sub>) and reduction peak potential (E<sub>red</sub>), (E<sub>ox</sub>+E<sub>red</sub>)/2 and reported values are given below.



**Fig. 5.** Cyclic voltammogram of [Ru(bbp)(bpg)H<sub>2</sub>O] recorded as 1.0 mM in DMF with 0.1 M TBAPF<sub>6</sub> supporting electrolyte using 100 mV s<sup>-1</sup> scan rate at in an inert atmosphere, WE= glassy carbon, RE=Ag/AgCl, CE= Pt wire

**Table: 5.** Cyclic Voltammetry Data

Compound	E <sub>1/2</sub> <sup>oxid</sup> / (ΔE) mV
[Ru(bbp)(bpg)H <sub>2</sub> O] <sup>2+</sup>	0.94 V (63 mV)

**Catalytic activity:**

Thoroughly characterized complex [Ru(bbp)(bpg)H<sub>2</sub>O]<sub>2</sub><sup>+</sup> was experimentally tested for chemical water oxidation, in the presence of CAN, Ceric Ammonium Nitrate at pH 1 and at 25 °C, where [Ru(bbp)(bpg)H<sub>2</sub>O]<sub>2</sub><sup>+</sup> act as water oxidation catalyst and CAN act as sacrificial oxidant. Evolved oxygen were measured by Pressure Transducer sensor. Data Obtained from Pressure transducer was in kPa, which was further converted to number of moles by using PV= nRT equation. Finally, Thermodynamic stability and Kinetic stability were obtained in form of Turn Over Number (TON) and Turn Over Frequency (TOF) respectively.

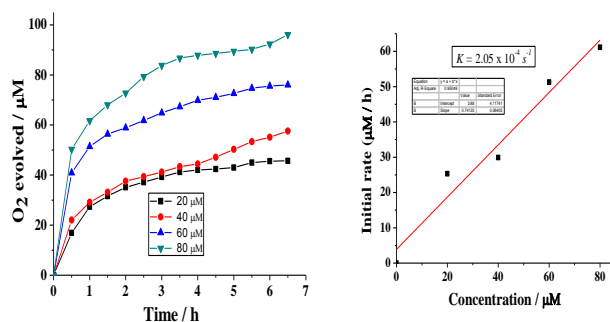
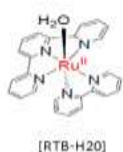


Figure 6. Chemical oxygen evolution and rate constant data of various concentration of RBB-H<sub>2</sub>O, respectively in 0.2 M Ce (IV) by using pressure transducer at 27°C.

### Catalytic Activity

Complex	TON	TOF S <sup>-1</sup>	Rate constant S <sup>-1</sup>
[RTB-H <sub>2</sub> O] <sup>2+</sup>	270	0.006	190 X 10 <sup>-4</sup>
[RBB-H <sub>2</sub> O] <sup>2+</sup>	309	0.013	2.05 X 10 <sup>-4</sup>



Finally, obtained TON, TOF and rate constant were compared with same parameters of highly studied water oxidation catalyst [Ru(bpy)(tpy)H<sub>2</sub>O] as shown in table 7.

### CONCLUSION:

This study takes significant step forward in the accomplishment of artificial photosynthesis. We have synthesized mononuclear ruthenium polypyridyl complex [Ru(bbp)(bpg)(H<sub>2</sub>O)]<sup>2+</sup>, was thoroughly characterized by various spectroscopic techniques. Its catalytic activity for chemical water oxidation has been studied by using ceric ammonium nitrate (CAN). It shows the TON and TOF up to 309 and 0.013 S<sup>-1</sup> respectively. It was found that, the TON and TOF of [Ru(bbp)(bpg)(H<sub>2</sub>O)]<sup>2+</sup> was more as compare to [RTB-H<sub>2</sub>O] and presently, it is being tested

for light driven water oxidation by using appropriate photosensitizer.

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