Artificial Photosynthesis: Molecular Catalysts for Water Oxidation

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Dedicated to my wife and daughter

Abstract

Artificial photosynthesis provides a promising solution to the future sustainable energy system. Water is the only suitably sufficient protons and electrons supplier by the reaction of water oxidation. However, this reaction is both kinetically and thermodynamically demanding, leading to a sluggish kinetics unless the introduction of a catalyst.

The theme of this thesis is to design, synthesize and evaluate molecular catalysts for water oxidation. This thesis consists of seven parts:

The first chapter presents a general introduction to the field of homogenous catalysis of water oxidation, including catalysts design, examination and mechanistic investigation.

The second chapter investigates the electronic and noncovalent-interaction effects of the ligands on the activities of the catalysts.

In the third chapter, halogen substitutes are introduced into the axial ligands of the ruthenium catalysts. It is proved that the hydrophobic effect of the halogen atom dramatically enhanced the reactivity of the catalysts.

Chapter four explores a novel group of ruthenium catalysts with imidazole-DMSO pair of axial ligands, in which the DMSO is proved to be crucial for the high efficiency of the catalysts.

Chapter five describes the light-driven water oxidation including the three-component system and the sensitizer-catalyst assembled system. It is found that the common Ru(bpy)_3^{2+} dye can act as an electron relay and further benefit the electron transfer as well as the photo-stability of the system.

In chapter six, aiming to the future application, selected ruthenium catalysts have been successfully immobilized on electrodes surfaces, and the electrochemical water oxidation is achieved with high efficiency.

Finally, in the last chapter, a novel molecular catalyst based on the earth abundant metal —nickel has been designed and synthesized. The activities as well as the mechanism have been explored.

**Keywords:** artificial photosynthesis, water oxidation, ruthenium complexes, nickel complexes, cerium, photo-catalysts, photosensitizer, electrochemistry, immobilization.
Abbreviations

APT      Atom-Proton Transfer
BPG      basal-plane pyrolytic graphite electrode
bpy      2,2’-bipyridine
bppH     3,5- bis(2-pyridyl)pyrazole
btpyan   1,8-bis(2,2’:6’,2”-terpyridyl)-anthracene
CeIV     cerium (IV) ammonium nitrate, Ce(NH₄)₂(NO₃)₆
Cp*      pentamethylocyclopentadiene
CV       cyclic voltammetry
DFT      density functional theory
DMSO     dimethyl sulfoxide
DPV      differential pulse voltammetry
dtQ      3,5-di-tert-butyl-1,2-benzoquinone
dpp      2,9-dipyrid-2’-yl-1, 10-phenanthroline
$E^0$    standard potential of a reaction, redox couple and electrode
$E^{1/2}$ half-wave potential in voltammetry
EDX      energy-dispersive X-ray spectroscopy
EQCN     electrochemical quartz crystal nanobalance
GC       gas chromatography
H₂bda    2,2’-bipyridine-6,6’-dicarboxylic acid
H₂pda    1,10-phenanthroline-2,9-dicarboxylic acid
H₂pdc    2,6-pyridinedicarboxylic acid
I2M      interaction of two M–O units
isoq     isoquinoline
$k$      rate constant
Mebbp    3,5-Bis[6-(2,2’-bipyridyl)]-4-methyl-1H-pyrazole
MLCT     metal-to-ligand charge transfer
MS       mass spectrometry
NHE      normal hydrogen electrode
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>OEC</td>
<td>oxygen-evolving-complex</td>
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<tr>
<td>pbn</td>
<td>2,2'-(4-tert-butyl)pyridine-2,6-diyl)bis(1,8-naphthyidine)</td>
</tr>
<tr>
<td>PCET</td>
<td>proton coupled electron transfer</td>
</tr>
<tr>
<td>pic</td>
<td>4-picoline</td>
</tr>
<tr>
<td>POM</td>
<td>polyoxometalate</td>
</tr>
<tr>
<td>ppy</td>
<td>2-phenylpyridine</td>
</tr>
<tr>
<td>ptz</td>
<td>phthalazine</td>
</tr>
<tr>
<td>PSII</td>
<td>photosystem II</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>PY5</td>
<td>2,6-(bis(bis-2-pyridyl)methoxy-methane)-pyridine</td>
</tr>
<tr>
<td>RDS</td>
<td>rate determine step</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly occupied molecular orbital</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2'; 6', 2''-terpyridine</td>
</tr>
<tr>
<td>TAML</td>
<td>tetra-amido macrocyclic ligand</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>tpym</td>
<td>tris(2-pyridyl)methane</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>WNA</td>
<td>water nucleophilic attack</td>
</tr>
<tr>
<td>WOC</td>
<td>water oxidation catalyst</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>quantum yield</td>
</tr>
<tr>
<td>$\eta$</td>
<td>overpotential of a catalytic reaction</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>molar extinction coefficient</td>
</tr>
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</table>
This thesis is based on the following papers, referred to in the text by their Roman numerals I-VIII:

I. **Insights into Ru-Based Molecular Water Oxidation Catalysts: Electronic and Noncovalent-Interaction Effects on Their Catalytic Activities**
   Lele Duan, Lei Wang, A. Ken Inge, Andreas Fischer, Xiaodong Zou and Licheng Sun

II. **Highly Efficient and Robust Molecular Water Oxidation Catalyst Based on Ruthenium Complexes**
    Lei Wang, Lele Duan, Ying Wang, Mårten S. G. Ahlquist and Licheng Sun

III. **Toward Controlling Water Oxidation Catalysis: Tunable Activity of Ruthenium Complexes with Axial Imidazole/DMSO Ligands**
    Lei Wang, Lele Duan, Beverly Stewart, Maoping Pu, Jianhui Liu, Timofei Privalov and Licheng Sun

IV. **Visible Light-driven Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes**
    Lei Wang, Lele Duan, Lianpeng Tong and Licheng Sun

V. **Sensitizer-Catalyst Assemblies for Water Oxidation**
    Lei Wang, Mohammad Mirmohades, Allison Brown, Lele Duan, Fusheng Li, Quentin Daniel, Reiner Lomoth, Licheng Sun and Leif Hammarström

VI. **Electrochemical Driven Water Oxidation by Molecular Catalysts in situ Polymerized on the Surface of Graphite Carbon Electrode**
    Lei Wang, Ke Fan, Quentin Daniel, Lele Duan, Fusheng Li, Bertrand Philippe, Håkan Rensmo, Hong Chen, Junliang Sun and Licheng Sun

VII. **Towards Water Splitting Device: Functionalizing Electrodes with Ru catalyst by in situ Polymerization**
    Lei Wang, Ke Fan, Hong Chen, and Licheng Sun
    Manuscript.
VIII. A Nickel (II) PY5 Complex as an Electrocatalyst for Water Oxidation
Lei Wang, Lele Duan, Ram B. Ambre, Quentin Daniel, Hong Chen, Junliang Sun, Biswanath Das, Anders Thapper, Jens Uhlig, Peter Dinér and Licheng Sun
Submitted Manuscript.

Papers not included in this thesis:

IX. Catalytic Water Oxidation by Mononuclear Ru Complexes with an Anionic Ancillary Ligand
Lianpeng Tong, A. Ken Inge, Lele Duan, Lei Wang, Xiaodong Zou and Licheng Sun

X. Highly Efficient Bioinspired Molecular Ru Water Oxidation Catalysts with Negatively Charged Backbone Ligands
Lele Duan, Lei Wang, Fusheng Li, Fei Li and Licheng Sun

XI. Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes with a 2,2′-Bipyridine-6,6′-dicarboxylate (bda) Ligand: How Ligand Environment Influences the Catalytic Behavior
Robert Staehle, Lianpeng Tong, Lei Wang, Lele Duan, Andreas Fischer, Mårten S. G. Ahlquist, Licheng Sun and Sven Rau

XII. Visible Light Driven Water Splitting in A Molecular Device with Unprecedentedly High Photocurrent Density
Yan Gao, Xin Ding, Jianhui Liu, Lei Wang, Zhongkai Lu, Lin Li, and Licheng Sun

XIII. Pt-free Tandem Molecular Photoelectrochemical Cells for Water Splitting Driven by Visible Light
Ke Fan, Fusheng Li, Lei Wang, Quentin Daniel, Erik Gabrielsson and Licheng Sun

XIV. Immobilizing Ru(bda) Catalyst on a Photoanode via Electrochemical Polymerization for Light-Driven Water Splitting
Fusheng Li, Ke Fan, Lei Wang, Quentin Daniel, Lele Duan and Licheng Sun
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1. Introduction

Water is an infinite proton source on the earth which can be used to produce hydrogen by the reaction of water splitting. Hydrogen is a green and high energy density energy carrier. Thus water splitting is rising in the context of pursuing new sustainable and carbon-neutral energy systems.

1.1. The Increasing World Energy Demand

Energy is the key of the development of the world by helping human to adapt and reform the natural environments. The importance of it is reflected on the energy industry, which is still dominated by petroleum, natural gas and coal. The uneven distribution of fossil fuels and its non-renewable nature cause serious energy security issues.

On the other hand, the energy consumptions rise along with the rising of the world population. The global total primary energy consumption reached to 18.2 TWyr (572 EJ) in year 2013, increased by 2.3%, acceleration over 2012 (+1.8%). As a developed country, Sweden consumes nearly three times energy (per capita) compared to the world average level. Considering the improvement of the living standard in the developing countries and the global population growth, the total energy consumption will be doubled (~ 36 TWyr) in the middle of this century. Until now, no such energy source or techniques can meet that huge demand for energy.

Accordingly, a new and sustainable energy system has to be built. So far, several techniques are already introduced to the society, such as wind power, hydropower, biomass and solar energy (solar panel). Another potential technique is the nuclear fusion; however it is still facing a lot of challenges despite the safety issues.

Sunlight is a sustainable, clean and highly abundant energy source on the Earth. The amount of sunlight that strikes on the surface of the Earth is over 5000 times than the world’s current energy consumption. Only less than 0.1% of the sunlight energy can solve the energy consumption problems as we discussed above. Thereby, the development of new techniques for solar energy conversion has attracted great attention. Photovoltaic panel is one of the most popular solar technologies, however it only converts sunlight into electricity which is not easy to store in large scale and use when sunlight is not available, and this sets a limit to its application.

1.2. Artificial Photosynthesis —A Potential Solution

Artificial photosynthesis replicates the function of natural photosynthesis and converts sunlight, water (which is the only unlimited and carbon-neutral electron source on our planet) and carbon dioxide into high energy density...
fuels with oxygen as the only byproduct. In principle, artificial photosynthesis can not only produce green and renewable energy by converting sunlight into solar fuels but also capture the major greenhouse gas CO\textsubscript{2} and further restrain the global warming. Thereby it is now one of the most attractive techniques to develop a new and sufficient solar energy system for the future mankind.

Artificial photosynthesis aims at solar fuel production from sunlight by a direct process, such as the most popular process of water splitting into hydrogen and oxygen driven by the sunlight. There are two approaches to build such a solar fuel cell based on the concept of artificial photosynthesis: (i) homogeneous system which produces hydrogen and oxygen in the same chamber and (ii) heterogeneous system which has two separated electrodes for hydrogen and oxygen generation at different locations. Regardless of which approach is taken, the key of artificial photosynthesis is searching for catalysts which are capable to mimic the key steps in the natural photosynthesis. To make it simple, two half reactions are needed for artificial photosynthesis: (i) water oxidation \(2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2\) and (ii) reduction reactions.\(^1\) No matter which reduction reaction is taken place, the oxidation of water is widely considered as the bottleneck of artificial photosynthesis, due to its multiple proton coupling and electron transfer processes which always cause a high overpotential for the catalytic reaction. Therefore, efficient and robust water oxidation catalysts (WOCs) are crucial for the efficient conversion of solar energy to fuels.

1.3. Water Oxidation in Nature Photosynthesis

In natural photosynthesis, an enzyme complex in photosystem II (PSII) named as oxygen-evolving complex (OEC) oxidizes water to molecular oxygen on its embedded active site tetramanganese-calcium (Mn\textsubscript{4}CaO\textsubscript{5}) cluster. Extensive studies have focused on resolving the crystal structure of the OEC and its mechanism of the catalytic water oxidation. Very recently, Shen and co-

\[^1\] including proton reduction and carbon dioxide reduction (\(vs.\) NHE, pH 7)

\[
\begin{align*}
2\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2 & E^0 = -0.42 \text{ V} \\
\text{CO}_2 + \text{e}^- & \rightarrow \text{CO}^- & E^0 = -1.9 \text{ V} \\
\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ & \rightarrow \text{CO} + \text{H}_2\text{O} & E^0 = -0.53 \text{ V} \\
\text{CO}_2 + 2\text{e}^- + \text{H}^+ & \rightarrow \text{HCOO}^- & E^0 = -0.49 \text{ V} \\
\text{CO}_2 + 4\text{e}^- + 4\text{H}^+ & \rightarrow \text{HCHO} + \text{H}_2\text{O} & E^0 = -0.48 \text{ V} \\
\text{CO}_2 + 6\text{e}^- + 6\text{H}^+ & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} & E^0 = -0.38 \text{ V} \\
\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} & E^0 = -0.53 \text{ V}
\end{align*}
\]

All the potential values in the thesis are versus NHE, unless stated otherwise.
workers reported a ‘radiation-damage-free’ native structure of the OEC at 1.95 Å (Figure 1) resolutions by femtosecond X-ray pulses techniques. By this ‘damage-free’ method, shorter Mn-Mn distances than their previous studies have been found, giving hints for assigning the valence states of the Mn metal centers. In addition, the O5 in Figure 1 was also determined as a hydroxide ion at S1 state instead of a normal oxygen dianion, and this hydroxide may act as one of the substrate oxygen. All of the understandings based on the x-ray crystal structure of PSII provide clues for mechanistic studies of oxygen generation and also blueprint for designing man-made water oxidation catalysts.

\[\text{Figure 1. Left: The X-ray crystal structure of OEC. Right: Structure of the Mn}_4\text{CaO}_5 \text{ cluster in OEC. Adapted with permission from reference 7. Copyright 2015 Nature Publishing Group.}\]

For the catalytic water oxidation mechanism of the Mn\(_4\)CaO\(_5\), a widely accepted pathway is the five “S” states (redox intermediates) of the reaction cycle. As it can be seen in Figure 2, each O\(_2\) evolution includes four times of light-driven electron transfer, and different “S” states represent different valence states of the four Mn ions. There was a controversy about the O-O formation (S\(_4\)) mechanism between (i) water-nucleophilic-attack to the Mn\(^{V}=O\) species at S\(_3\) (S\(_4\)) state and (ii) radical coupling between two proximal Mn\(^{V}=O\) at S\(_4\) state. Very recently, two reports from Siegbahn group and Lubitz group shed light on this crucial O-O formation, and both of them suggested that the radical coupling pathway may be the true case in PSII.\(^8,9\) These mechanistic studies on PSII provide blue print for developing synthetic water oxidation catalysts.

\(^{ii}\) The Mn-ligand and Mn-Mn bond length in OEC were found to be longer than the actual value in previous studies; this is believed to result from the X-ray radiation damage during the measurements.
**Figure 2.** The reaction cycle of OEC. The sequence of proton coupling, electron transfer (PCET) steps and the proposed valence states of the Mn ions in each metastable state are presented. Adapted with permission from reference 9. Copyright 2015 Science.

1.4. Water Oxidation by Artificial Metal Complexes

Water oxidation catalysts can be divided into homogenous catalysts (molecular catalysts) and heterogeneous catalysts (inorganic materials). In this thesis we only focus on the molecular catalysts. It is worth mentioning two review papers from Åkermark and Brudvig groups which have comprehensively illustrated the recent development of the molecular approaches for catalytic water oxidation.\(^\text{10,11}\)

1.4.1. Principles of Catalyst Design

To design molecular water oxidation catalysts, the following factors have to be taken into consideration:

1. The oxidizing power of the catalysts should be strong enough to oxidize the water. The thermodynamic energy requirement for oxidizing a water molecule is \(E = (1.23 - 0.059 \times \text{pH})\ V\), therefore the transition state of the catalysts should have enough oxidizing power to take care of this \(E\) and overcome the overpotential for the catalytic reaction as well. One of the advantages of the molecular catalysts compared to the inorganic materials is relatively easy to tune the oxidizing power of the catalysts by changing the coordination atmospheres, such as electron donating ligands can lower the oxidation potential of the catalysts and vice versa.

2. The catalyst should have a coordination site available for accepting a water molecule. It is obvious that a water molecule has to coordinate to the catalyst to fulfill the water oxidation reaction. Usually, there are three different situations: (i) the water molecule itself is one ligand of the catalyst; (ii) the water molecule coordinates to the metal ion by ligand exchange, and further form the real catalyst; (iii) the water molecule coordinates to the metal ion as
an additional ligand, such as a seventh ligand, upon the oxidation of a catalyst to its high valence states.

3. The ligands should be easy to synthesize and strong enough to tolerate the harsh conditions for water oxidation.

4. Polymetalate ligands are usually needed to prevent the ligands from dissociation.

1.4.2. Catalysts Evaluation and Mechanistic Studies

Turnover number (TON) and turnover frequency (TOF) are two major parameters that usually taken into consideration to examine the activities of catalysts. It is important to employ the same conditions for making a comparison. To obtain these information, three different methods are commonly used:

1. Chemical driving force. One commonly used chemical oxidant is Ce(NH₄)₂(NO₃)₆ (CeIV), and CeIV driven water oxidation is shown in Equation 1. CeIV is a water soluble single-electron chemical oxidant. It has a very high oxidation potential around 1.7 V under acidic conditions. Moreover, the distinct absorption at 360 nm of CeIV allows detailed kinetics studies on the catalytic reaction by the means of spectroscopy. The drawback of CeIV is that the low pH and highly oxidizing power may harm the durability of the catalysts.

   \[
   \text{Equation 1.} \quad 4 \text{Ce}^{IV} + 2 \text{H}_2\text{O} \xrightarrow{\text{WOC}} \text{O}_2 + 4 \text{H}^+ + 4 \text{Ce}^{III}
   \]

2. Visible light as the driving force. Derivatives of [Ru(bpy)₃]²⁺ (bpy, 2,2’-bipyridine) are commonly used as photosensitizer (Figure 3). The metal-to-ligand charge transfer (MLCT) absorption of [Ru(bpy)₃]²⁺ locates at the range of ~500 nm, suggesting a sufficient driving force for oxidizing water. Besides, a sacrificial electron acceptor such as Na₂S₂O₈ is needed. The advantage of such system is that the neutral conditions (pH = 7) can be used; however, the photo-stability of the Ru-based sensitizer is usually unsatisfactory, and therefore high concentrations of the sensitzers are normally employed.

![Figure 3. Light-driven water oxidation by molecular WOCs.](image-url)
3. Potentialstat as the driving force. The applied potentials on WOCs can be easily changed. As shown in Figure 4, water is oxidized on the anode under the assistant of WOC, and meanwhile the protons can be reduced to hydrogen on the cathode. Thereby the pH of the bulk solution won’t change which is one of the advantages of this method. However, the performance of the catalysts can be influenced by the electron transfer and mass transport (diffusion) at the interfaces of the electrodes.

![Figure 4. Electrochemical water oxidation.](image)

The beauty of molecular catalysts is that comprehensive mechanistic studies can be carried out. Detailed reaction pathway can be drawn for a catalyst on the basis of its kinetics and the PCET information. The O–O bond formation is the most important step in the catalytic cycle, and there are two well accepted pathways for this bond formation (Figure 5): (i) water nucleophilic attack (WNA); (ii) interaction of two M−O units (I2M).

![Figure 5. WNA and I2M mechanism for O–O bond formation.](image)

1.4.3. Ruthenium Complexes as WOCs

The pioneering molecular WOC was reported by Meyer and co-workers in 1982.\(^\text{12}\) It is a \(\mu\)-oxo-bridged dinuclear Ru-based complex \(\text{cis,cis-}[(\text{bpy})_2(H_2O)\text{Ru}^{\text{III}}(\mu-O)\text{Ru}^{\text{III}}(H_2O)(\text{bpy})_2]^{4+}\) (1, Figure 6) named as ‘blue dimer’ due to its blue colour. By using Ce\(^{IV}\) as oxidant at pH 1 condition, ‘blue dimer’ showed certain activity (TON =13, TOF = 0.004 s\(^{-1}\)) toward Ce\(^{IV}\) driven water oxidation. For the mechanistic studies, their latest kinetics studies\(^\text{13}\) on ‘blue dimer’ suggested that the O–O bond formation goes through the WNA
pathway. The detailed mechanistic investigation based on ‘blue dimer’ inspired a great number of WOCs which achieved better performance.\textsuperscript{14,15}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{images/figure6}
\caption{Selected polynuclear Ru WOCs and the corresponding TON and TOF based on Ce\textsuperscript{IV}-driven water oxidation. \textsuperscript{a} Electricity as diving force; \textsuperscript{b} visible light-driven water oxidation.}
\end{figure}

The low TON of ‘blue dimer’ was most likely due to the reductive cleavage of the \(\mu\)-O bridge that leading to the deactivation. To obtain more robust WOCs, several groups had introduced rigid chelating ligands to replace the \(\mu\)-O as the bridges. Complex \textit{in, in-}[(H\textsubscript{2}O)(tpy)Ru\textsuperscript{II}(\(\mu\)-bpp)Ru\textsuperscript{II}(tpy)(H\textsubscript{2}O)]\textsuperscript{3+} (2 in Figure 6, tpy = 2,2\textsuperscript{′}, 6\textsuperscript{′}, 2\textsuperscript{″}-terpyridine) with a new bridging ligand 3,5- bis(2-
pyridyl)pyrazole (bppH) was prepared by Llobet and co-workers.\textsuperscript{16} Due to the in,in- configuration of the Ru-oxo, the O–O bond formation by 2 occurred solely via an intramolecular 12M pathway, this was supported by detailed kinetics studies and O\textsuperscript{18} labelling measurements.\textsuperscript{17} A subsequent work from the same group replaced the tpy with a facial tpym (tris(2-pyridyl)methane) ligand, and the resulting complex 3 had two Ru-OH\textsubscript{2} units in a trans position. This Ru-OH\textsubscript{2} group’s rearrangement lead 3 to catalyse water oxidation via an intermolecular 12M O–O bond formation pathway.\textsuperscript{18} Llobet and co-workers further demonstrated that the O–O bond formation pathway is tunable by fine ligands architecture, for instance, complex 4 ([(py-SO\textsubscript{3})(OH\textsubscript{2})Ru(\mu-Me)Mebbp]Ru(OH\textsubscript{2})(py-SO\textsubscript{3})]\textsuperscript{3\textsuperscript{-}}, Figure 6) goes through a WNA O–O formation (py = pyridine; Mebbp = 3,5-Bis[6-(2,2’-bipyridyl)-4-methyl-1H-pyrazole]).\textsuperscript{19} Tanaka and co-workers adopted another approach to exam their Ru-based WOCs by using electrochemical driving force. For example, complex 5 ([HO](dtQ)Ru(\mu-btppy)Ru(dtQ)(OH)]\textsuperscript{2\textsuperscript{+}} (btppy = 1,8-bis(2,2’;6’,2”-terpyridyl)-anthracene; dtQ = 3,5-di-tert-butyl-1,2-benzoquinone) in Figure 6, was able to catalyze water oxidation with a high TON of 33,500 under a sufficient applied potential of 1.92 V.\textsuperscript{20} The proposed O–O formation pathway was an intramolecular interaction between a Ru\textsuperscript{11}O\textsuperscript{2+} and a Ru\textsuperscript{11}OH moiety supported by density functional theory (DFT) calculation.\textsuperscript{21}

Later, Thummel and Sun groups synthesized several groups of dinuclear Ru-based WOCs. They used similar strategy to assemble the catalysts, in which two Ru centers are hold by the bridging ligand at the equatorial planet, and four pyridine derivatives as the axial ligands. Complex 6 from Thummel group afforded a TON of 538 in 20 hours with an initial TOF of 0.046 s\textsuperscript{-1}.\textsuperscript{22} Inspired by the negative charged ligands in the natural OCE, Sun and Åkermark et.al introduced carboxylate group into the equatorial ligands, the resulted complex 7 gave a considerably high TON of 1700, and also a significantly lower overpotential compared to those of catalysts bearing neutral equatorial backbones.\textsuperscript{23} A subsequent study was to synthesize a cis-dimeric Ru complex 8 by installing a phenyl group in the middle of the backbone.\textsuperscript{24} Thanks to the synergistic effect between the two ruthenium ions, complex 8 showed excellent activity and durability for water oxidation, driven by both Ce\textsuperscript{IV} (TON > 10,000, TOF > 1 s\textsuperscript{-1}) and visible light (TON ~ 60, TOF ~ 0.1 s\textsuperscript{-1}). It is worth to note that the mononuclear ruthenium complexes trans-[Ru(pbnn)(4-R-py)\textsubscript{2}(OH\textsubscript{2})]\textsuperscript{2\textsuperscript{+}} (9 in Figure 7; pbnn: 2,2’-(4-tert-butyl)pyridine-2,6-diyl)bis(1,8-naphthydine); R: -Me, -CF\textsubscript{3} and -NMe\textsubscript{2}) discovered by Thummel and co-workers in year 2005 were also capable of catalysing water oxidation.\textsuperscript{25} With R= Me, complex 9 gave a TON of 260 with an initial TOF of 0.014 s\textsuperscript{-1} by using Ce\textsuperscript{IV} as the driving force. Later, the same group also synthesized complexes 10 ([Ru(dpp)(4-picoline)\textsubscript{2}]\textsuperscript{2+}; dpp = 2,9-dipyrid-2’-yl-1, 10-phenanthroline; TON = 416, TOF = 0.028 s\textsuperscript{-1} with Ce\textsuperscript{IV} as oxidant) and 11 ([Ru(tpy)(pic)\textsubscript{2}X]\textsuperscript{2+}; pic= 4-picoline, TON = 89 when X = pic with Ce\textsuperscript{IV} as the chemical oxidant), both of which were proved to be active WOCs.\textsuperscript{26} For these
catalysts, it was usually believed that Ru\textsuperscript{V}═O works as the active species which triggers the O–O bond formation via a WNA mechanism. However, Fujita and Thummel concluded that 9 follows a thermodynamically favorable direct pathway via Ru\textsuperscript{IV}═O instead of the higher valence state of Ru\textsuperscript{V}═O in neutral and basic conditions, based on both kinetics and DFT evidence.\cite{27}

![Figure 7. Selected single-site Ru complexes reported by Thummel and co-workers. TONs and TOFs are given in parentheses (TON, TOF), all of the data are based on Ce\textsuperscript{IV} driven water oxidation.]

\begin{align*}
\text{Figure 7. Selected single-site Ru complexes reported by Thummel and co-workers. TONs and TOFs are given in parentheses (TON, TOF), all of the data are based on Ce\textsuperscript{IV} driven water oxidation.}
\end{align*}

Besides the aforementioned single-site Ru-based WOCs developed by Thummel group, Meyer and co-workers also contributed a handful single-site Ru WOCs with detailed mechanistic studies.\cite{15,28,29} The complexes shown in Figure 8 can be named as [Ru(\text{NNN})(\text{NN})L]\textsuperscript{2+} according to their coordination geometries, where \text{NNN} and \text{NN} represent tridentate and bidentate N-heterocyclic ligands respectively, and \text{L} stands for H\textsubscript{2}O in this case. All of these complexes were studied in acidic conditions with Ce\textsuperscript{IV} as the oxidant. Detailed mechanistic studies based on kinetics and DFT calculations suggested that water-nucleophilic-attack to the Ru\textsuperscript{V}═O species generated Ru\textsuperscript{III}–O–O–H which can be further oxidized to Ru\textsuperscript{IV}–OO or Ru\textsuperscript{V}–OO peroxo, and this peroxo releases the O\textsubscript{2} and returned to its Ru\textsuperscript{II} or Ru\textsuperscript{III} state.
Figure 8. Selected single-site Ru complexes studied by Meyer and co-workers. TONs and TOFs are given in parentheses (TON, TOF), all of the data are based on Ce$^{IV}$ driven water oxidation.

[Ru(tpy)(bpy)(OH$_2$)]$^{2+}$ types of mononuclear Ru WOCs were also intensively studied by the groups of Sakai,$^{30,31}$ Berlinguette,$^{32,33}$ and Yagi.$^{34}$ The substituents effect of both tpy and bpy moieties were carefully examined, as shown in Figure 9. Electron-withdrawing groups on the bpy ligand depressed the catalytic rates but promoted the TON, while the same substituents on the tpy ligand enhanced the catalytic rates but with lower TONs. Yagi and co-workers reported an electro-donating group (ethoxyl-) at the 4-substituent position of the tpy remarkably enhanced both TON and TOF. For the reaction mechanism, WNA on the Ru$_{V}$═O species to form the O−O bond was still believed to be the major pathway; however, competing reaction pathways such as incorporation of an O-atom from NO$_3$− (counter ion of Ce$^{IV}$) and WNA at the Ru$_{IV}$═O stage were also proposed by Berlinguette et.al. The preference for each of these O−O bond formation pathways was related to the applied conditions and electron density at the Ru center. Moreover, the rate determine step (RDS) was proved to be sensitive to the electron density at the Ru center as well.

Figure 9. Selected [Ru(tpy)(bpy)(OH$_2$)]$^{2+}$ type complexes that studied by the groups of Sakai, Berlinguette, and Yagi. TONs and TOFs are given in parentheses (TON, TOF), all of the data are based on Ce$^{IV}$ driven water oxidation.
Figure 10. Selected ruthenium complexes bearing negatively charged ligands that studied by Sun and co-workers. TONs and TOFs are given in parentheses (TON, TOF), all of the data are based on Ce$^{IV}$ driven water oxidation. $^a$ Visible light-driven water oxidation.

As aforementioned, negatively charged ligands enhanced the catalytic performance of complexes 7 and 8 dramatically. Sun and co-worker adopted the same strategy for developing mononuclear Ru WOCs. The catalytic activity of complex [Ru(pdc)(pic)$_3$] (17 in Figure 10, H$_2$pd = 2,6-pyidinedicarboxylic acid) was improved dramatically compared to that of complex 11.$^{35}$ This enhancement was most likely due to the factor that the negatively charged carboxylate can stabilize the high valence states of the Ru center and also lower the overpotential of water oxidation. When the pic ligand was replaced by the bpy, the resulted complex [Ru(pdc)(bpy)(pic)] (18 in Figure 10) almost lost its activity, indicating that the replacement of the labile pic ligand by the aqua ligand is the key factor for the high efficiency.$^{35}$ The reaction order of first order in complex 17 indicated a WNA pathway for the O–O bond formation.
The success of complex [Ru(bda)(pic)$_2$] (19 in Figure 10, H$_2$bda = 2,2'-bipyridine-6,6'-dicarboxylic acid) made it becoming a prototype of Sun group in this field.\(^{36,37}\) The unusual large O-Ru-O angle of 122.99° allowed the water to coordinate to the Ru center (high valence state) as a seventh ligand. In addition, the negative carboxylate ligands can stabilize the high valence states of the Ru center and lead to a very low overpotential for oxidizing water. Based on kinetics, electrochemistry and DFT calculations, a detailed pathway for oxygen generation was proposed by Sun et.al as depicted in Figure 11. By introducing axial ligands that have bigger π system which is beneficial for the rate determine radical coupling step, the activities of [Ru(bda)(isoq)$_2$] (20, isoq = isoquinoline) and [Ru(bda)(ptz)$_2$] (21, ptz = phthalazine) were promoted dramatically, as shown in Figure 10.\(^{37,38}\) Later, 1,10-phenanthroline-2,9-dicarboxylic acid (H$_2$Pda) was introduced to replace the H$_2$bda ligand by Sun and co-workers.\(^{39}\) The resulted complex 22 (Figure 10) showed very close coordination geometry with that of complex 19, however both its TON and TOF decreased dramatically. DFT simulations on 22 suggested that the O–O bond forms via the WNA pathway.

It is believed that the organic frameworks suffer from the degradation after long term reaction time, which is one of the deactivation pathways of WOCs. In order to avoid this issue, a purely inorganic ligands containing WOC Ru$_4$POM$_2$ (23, Figure 12, POM = γ-SiW$_{10}$O$_{36}$) was reported independently by the groups of Hill and Bonchio.\(^{40,41}\) Hill and Bonchio evaluated the catalyst under different conditions. Hill and co-workers used chemical oxidant [Ru(bpy)$_3$]$_3^{3+}$ to drive water oxidation under neutral conditions (pH 7), while Bonchio and co-workers conducted the measurements in acidic conditions using Ce$^{IV}$ as the oxidant. Their results were close.

**Figure 11.** Water oxidation pathway of 19 and the X-ray single crystal structure of its dimeric Ru$^{IV}$ intermediate. Adapted with permission from reference 33 and 35. Copyright 2009 American Chemical Society. Copyright 2012 Nature Publication.

![Diagram of water oxidation pathway and X-ray single crystal structure](image-url)
Figure 12. The structure of 23. \(^a\)TON, TOF from Hill and co-workers; \(^b\)TON, TOF from Bonchio and co-workers.

It is necessary to point out that not all the reported Ru based WOCs are enclosed in this introduction.\(^{15,42,43,44,45}\) Recent progress on this subject can shed light on the development of earth abundant metal based water oxidation catalysts in the point view of ligand design and mechanistic studies.

1.4.4. Iridium Complexes as WOCs

The initial molecular WOCs based on iridium complexes, analogues of [Ir(ppy)\(_2\)OH\(_2\)]\(^+\) (ppy = 2-phenylpyridine) were reported by Bernhard and co-workers.\(^{46}\) This family of Ir WOCs catalysed water oxidation with impressive TONs but relatively low TOFs, for instance, complex 24 in Figure 13 affords TON over 2700 but with a TOF of 0.004 s\(^{-1}\). Brudvig and Crabtree \etal\ developed a group of Ir catalysts by replacing one of the ppy ligand with Cp\(^*\) (pentamethylcyclopentadiene) ligand, the resulted non-aqua complexes (‘half-sandwich’ geometry) showed much higher efficiency for catalysing water oxidation (25, Figure 13).\(^{47}\) Later, Bernhard group further improved the performance of 25 by introducing a pyridinium-carbene ligand to replace the ppy, the resulted catalyst 26 gave a remarkably high TON over 10,000.\(^{48}\) Their mechanistic study (DFT) on this complex suggested a WNA pathway for the O–O formation.
IrO$_2$ has long been recognized as an efficient and robust heterogenous WOC with the recorded low overpotential.$^{49,50}$ Besides, there are several Ir complexes that were believed to be the precursor of the heterogeneous IrO$_2$ nanoparticles which were the real catalysts for water oxidation.$^{51-54}$ Therefore, it is rather important to distinguish molecular Ir complexes from IrO$_2$ particles for the water oxidation catalysis. Recently, Brudvig and co-workers introduced a practical method which is electrochemical quartz crystal nanobalance (EQCN) to deal with this issue.$^{52}$ Taking iridium WOC as the model, they proved that EQCN can probe the homogeneity of molecular WOCs directly by using electrochemical method.

1.4.5. Molecular WOCs Based on First-Row Transition-Metal Complexes

Nature chose Mn$_4$Ca cluster as the active site of OEC, thereby the interest of searching WOCs based on Mn complexes initiated from chemical mimicking of the Mn$_4$Ca cluster. However, only few Mn-based complexes have been reported with the function of catalysing water oxidation.$^{55-59}$ Åkermark group presented a dinuclear Mn complex (27, Figure 14) which was capable of catalysing oxygen generation from water by using single-electron sacrificial chemical oxidant.$^{60}$ Later on, cobalt WOCs emerged. Hill and co-workers prepared a homogenous and purely inorganic Co-based WOC called B-type [Co$_4$(H$_2$O)$_2$($\alpha$-PW$_9$O$_{34}$)$_2$]$^{10-}$ (28 in Figure 14).$^{61}$ Catalyst 28 provided a TON of 1000 with an intial TOF 5 s$^{-1}$, by using [Ru(bpy)$_3$]$^{3+}$ as the one-electron sacrificial chemical oxidant. Moreover, both Nocera and Berlinguette groups designed mononuclear Co complexes that can function as electro-catalysts for water oxidation.$^{62,63}$ The Co-hangman-corrole complex (29 in Figure 14) discovered by Norcera and co-workers afforded a TOF of 1 s$^{-1}$ at 1.4 V vs. Ag/AgCl. The hanging carboxylic
group can pre-organize water molecules within the hangman cleft which was beneficial for the O–O bond formation. The PY5-Co complexes (PY5 = 2,6-(bis(bis-2'-pyridyl)methoxy-methane)-pyridine; 30 in Figure 14) designed by Berlinguette et al. catalyzed water oxidation electrochemically with impressive rate constant ~ 79 s⁻¹. Again, a WNA pathway was proposed for the O–O bond formation for this catalyst.

The pioneering molecular WOCs based on iron complex Fe³⁺-TAMLs (TAML = tetraamido macrocyclic ligand, 31 in Figure 14) were reported by Collin and co-workers.⁶⁴ For instance, 31 achieved a TON of 16 with an initial TOF of 1.3 s⁻¹ by using Ce⁴⁺ as the driving force. Later on, Costas and co-workers designed another family of Fe-based WOCs bearing tetradentate nitrogen-based ligands.⁶⁵ For instance, 32 afforded a TON of 1050 with an initial TOF of 0.061 s⁻¹ by using NaIO₄ as the chemical oxidant.

Several copper complexes were also reported as molecular WOCs recently.⁶⁶-⁶⁹ It is worth to note that Meyer and co-workers developed an in situ copper complex (33 in Figure 14) which can mediate water oxidation in pH 11 phosphate buffer with a remarkable TOF of 33 s⁻¹ (520 mV overpotential).⁶⁷ Once more, the WNA pathway was assigned to the O–O bond formation for this catalyst. The last type of earth abundant WOC is based on nickel complexes,⁷⁰,⁷¹ such as complex 34 in Figure 14. Interestingly, DFT calculations based on complex 34 suggest that the O–O bond formation in the catalytic water oxidation cycle goes through an unusual HO–OH coupling mechanism based on the cis-isomer of the complex 34.
Figure 14. Selected molecular WOCs based on earth abundant metal complexes. \([\text{Ru(bpy)}_3]^{3+}\) used as chemical oxidant; \(b\) electocatalytic water oxidation; \(c\) Ce\(^{IV}\) as chemical oxidant; \(d\) NaIO\(_4\) as chemical oxidant; TONs and TOFs are given in parentheses (TON, TOF).

1.5. Photo-catalysts for Water Oxidation

To achieve artificial photosynthesis, water splitting driven by solar light is crucial. Accordingly, photo-catalysts which can efficiently catalyze water oxidation with visible light as driving force are needed. Although a great
number of active WOCs have been reported, photo-catalysts that bearing sensitizer and catalyst in one molecule are rarely documented.\textsuperscript{72-74} Sun et.al connected the commonly used $[\text{Ru(bpy)}_3]^{2+}$ photosensitizer and WOC 19 together, affording complex 35 (Figure 15) which was active for light driven water oxidation with a TON of 38. They also concluded that the coupled system showed much higher activity than that of the separated system under the same conditions. Later, two similar complexes were prepared by the groups of Meyer (complex 36) and Thummel (complex 37) independently. Complex 36 didn’t show any activity for light driven water oxidation, while complex 37 achieved a remarkably high TON (134). This significant difference of the catalytic performance between complexes 36 and 37 is most likely due to the different linking bridges. Since this type of all-in-one assemblies show promising activities, more studies are desired on not only the new catalysts design but also the corresponding mechanistic studies.

\begin{center}
\includegraphics[width=\textwidth]{complexes.png}
\end{center}

\textit{Figure 15.} Selected photo-catalysts for water oxidation. TONs and TOFs are given in parentheses (TON, TOF).

1.6. The Aim of This Thesis

The aim of this thesis has been to:

1) Study the correlations between the structure and activity of the Ru-bda WOCs systems. To design and synthesize novel WOCs with improved performances.

2) Design efficient and robust photo-catalysts for water oxidation, and study their corresponding mechanisms.

3) Immobilize efficient WOCs onto the electrodes surfaces towards the functional devices for water splitting.
2. Correlations between Structure and Activities of Ru-bda WOCs: Electronic and Noncovalent-Interaction Effects

(Paper I)

2.1. Introduction

Previously, our group has reported a series of highly efficient Ru-bda WOCs (19-21, Figure 10).\(^{36-38,75}\) The key mechanistic information is that this family of catalysts mediate the O–O bond formation via a bimolecular radical coupling pathway. As such, the introduction of isoquinoline ligands which have strong \(\pi-\pi\) interactions can lower the energy barrier for the radical coupling step, and accordingly enhance the TOF of complex 20. Moreover, phthalazine with high dissociation energy was employed as the axial ligand and a high TON was obtained further by complex 21 (TON over 50,000). It is obvious that the activities of these catalysts can be easily influenced by the axial ligands. However, there are still no systematic studies on the electronic and noncovalent-interaction effects from the axial ligands. Therefore, it is interesting to reveal the structure–activity relationship by systematically studying the axial ligands effect on the activity, for instance the electronic and hydrophobic effect. With this in consideration, we designed complexes 38-44 (Figure 16) with pyridine axial ligands that contain electron-withdrawing and electron donating groups as well as hydrophobic and hydrophilic groups.

\[\text{Complex 38} \quad \text{Complexes 39–44}\]

\[\text{Figure 16. Chemical structures of complexes 38–44.}\]
2.2. Synthesis

The target complexes 38-44 were synthesized by simply adapting the same procedures for complex 19 (Figure 17). First, complexation of cis-[Ru(DMSO)_4Cl_2] with the deprotonated bda$^{2-}$ was conducted in the solvent of methanol. Second, excess of the individual axial ligands were added into the above mixture, yielding the corresponding mononuclear Ru-bda complexes 38-44. All of the desired products were characterized by NMR, elemental analysis and high-resolution MS (mass spectrometry). Most of the Ru-bda complexes can be easily oxidized in air due to the strong σ/π donating bda$^{2-}$ ligand, the generated Ru$^{III}$ species will disturb the $^1$H NMR spectra. In order to obtain sharp NMR signals, addition of a small amount of ascorbic acid as reductant can prevent the Ru complexes from oxidation by air.

Figure 17. Synthesis of complexes 38-44, ‘L’ stands all the axial ligands.

2.3. Results and Discussions

2.3.1. Electrochemical Properties

Figure 18 (Left) depicts the differential pulse voltammogram (DPV) and the cyclic voltammogram (CV) of complex 40. In DPV curve, three redox waves corresponding to Ru$^{III}$−OH$_2$/Ru$^{II}$+$H_2$O, Ru$^{IV}$−OH/Ru$^{III}$−OH$_2$, and Ru$^{V}$$\equiv$O/Ru$^{IV}$−OH were observed at 0.67 V, 1.09 V and 1.30 V, respectively. However, the third redox wave was not shown in the CV due to the current rising, indicating that the Ru$^{V}$ species triggers oxygen evolution at this condition. A reduction peak at about −0.3 V that appeared at the cathodic scan corresponding to the electrochemically reduction of the generated oxygen from the anodic scan.
Figure 18. Left: the DPV and CV curves of complex 40. Right: DPVs (normalized) of complexes 38-44.

The first redox wave $E_{1/2}(\text{Ru}^{III}-\text{OH}_2/\text{Ru}^{II}-\text{OH}_2)$ of these complexes increases when the axial ligands varies from the electron donating one to electron withdrawing one as expected (Figure 18 Right). However the onset potentials of 38-44 for water oxidation are close, implying the less pronounced electronic effect at higher Ru valence states of these Ru-bda complexes.

2.3.2. Water Oxidation by Ru-bda Complexes

Water oxidation catalyzed by complexes 38-44 were carried out in acidic solutions using Ce$^{IV}$ as sacrificial electron acceptor. The kinetics of the oxygen evolution were monitored by a gas pressure sensor, and then the amount of oxygen gas was determined by GC. Typically, oxygen bubbles (no CO$_2$ production was observed) can be observed at once when the catalyst solution was injected into the acidic aqueous of Ce$^{IV}$. The TONs and TOFs of this group of catalysts are listed in Table 1.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>38</th>
<th>39</th>
<th>40</th>
<th>41</th>
<th>42</th>
<th>43</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF (s$^{-1}$)</td>
<td>9.8</td>
<td>119</td>
<td>115</td>
<td>25</td>
<td>25</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>TON</td>
<td>360</td>
<td>4800</td>
<td>4500</td>
<td>580</td>
<td>760</td>
<td>790</td>
<td>$-^a$</td>
</tr>
</tbody>
</table>

Conditions: For TOF measurements, 3.6 mL of solution, catalyst ($8 \times 10^{-7}$ mol, 2.16 $\times 10^{-4}$ M) and Ce$^{IV}$ (1.18 $\times 10^{-3}$ mol, 0.327 M). For TON measurements 3.22 mL of solution, catalyst ($4 \times 10^{-8}$ mol, 1.20 $\times 10^{-5}$ M) and Ce$^{IV}$ (1.18 $\times 10^{-3}$ mol, 0.365 M). *complex 44 was not examined due to its poor solubility in water. Room temperature.

Since the oxygen generation kinetics remains second order in the concentrations of Ru-bda catalysts, it is reasonable to believe that the water oxidation catalysis still follows the same radical coupling mechanism. By comparing 19 with 38, we can see that the introduction of the hydrophilic ligands inhibits the O–O bond formation step and decreases the efficiency of the catalysts. On the contrary, hydrophobic axial ligands could enhance the activity of the catalysts, taking complex 39 for instance. It has also been
reported that the longevity of Ru-bda catalysts are related to the strength of the bond between the axial ligands and the Ru center. This seems that electron donating ligands is necessary for designing robust Ru-bda catalysts. In this work, complexes 42 and 43 bearing electron donating axial ligands, however, are overplayed by complexes 39 and 40 which containing electron withdrawing ligands. Thereby, we conclude that electron rich ligands have negative effects on the activity of the catalysts, although they may contribute positively to the stabilities of the catalysts.

2.4. Summary

A group of mononuclear Ru-bda complexes (38-44) have been designed and synthesized to study the relations between the nature of the axial ligands and the catalyst activity. By the combined evidence from electrochemistry and water oxidation catalysis, we can conclude that the electron withdrawing ligands will enhance the catalytic activity of Ru-bda WOCs while electron donating ones present the opposite effect. Moreover, it is also clear that the high activity of Ru-bda catalysts also benefit from the hydrophobic effect of the axial ligands.
3. Ru-bda Complexes with Halogen Substituted Axial Ligands

(Paper II)

3.1. Introduction

Previously, we have studied the correlations between the structure of the axial ligands and the activities of Ru-bda complexes towards catalytic water oxidation. By comparing complexes 40 and 41 from the last chapter, it is interesting to see that one single -Br substitute dramatically enhanced both the TON and TOF. This bromide substitute is a hydrophobic function group with certain electronic effect. In order to further study the relations between halogen substitute axial ligands and the catalytic activities aiming at highly efficient Ru-bda WOCs, we were then motivated to design and synthesize complexes 45-47 as shown in Figure 19. It is observed that the hydrophobic effect of the halogen substitute indeed enhanced the catalytic activities dramatically. Complex 45 shows extremely high TOF of 1000 s⁻¹ with a very low catalyst concentration (6.25×10⁻⁵ M), complex 47 affords a record TON of 100,000 for molecular WOCs by using Ce⁴⁺ as chemical oxidant.

Figure 19. Chemical structures of complexes 45-47.
3.2. Synthesis and Structural Characterization

Axial ligands 6-fluoroisoquinoline, 6-bromoisoquinoline and 6-bromophthalazine are commercially available. Complexes 45-47 were synthesized according to the well-studied methods (Figure 17). Complex 45 was purified from the reaction mixture by silica column chromatography while complexes 46 and 47 were precipitated out as pure products due to their low solubility in methanol. All desired products were characterized by NMR, elemental analysis and high-resolution MS.

According to the $^1$H NMR, the signals of protons 4 and 5 of complexes 45-47 (Figure 20) appear at very close chemical field compared with that of complexes 20 and 21, suggesting that there is no obvious electronic effect from the halogen group. For complex 47, it is possible to obtain a mixture of several isomers due to the unsymmetrical axial ligand, and hard to identify the exact isomer just on the basis of $^1$H NMR spectral analysis. However, according to DFT calculations, the isomer of complex 47 as shown in Figure 19 is the energetically most favored structure.

![Figure 20. $^1$H NMR spectra of complexes 20, 21 and 45-47.](image)
3.3. The Labile Carboxylate Ligation

It was proved that the carboxylate ligation in Ru-bda complexes is labile especially in aqueous solutions. In this chapter, we carried out some investigations on this labile ligation in order to study the co-solvent effects on the catalytic activities. Taking 45 as the model complex, $^1$H NMR measurements have been conducted under different conditions.

Figure 21. $^1$H NMR spectra of complex 45.

Figure 21 depicts $^1$H NMR spectra of complex 45 in various deuterated solutions and the corresponding structures: methanol–$d_4$ (lower), D$_2$O/CD$_3$CN (v/v = 9/1) (middle), and pH 1 (0.1 M CF$_3$SO$_3$D) D$_2$O/CD$_3$CN (v/v = 9/1) (upper). It is obvious that complex 45 remains in its C$_{2v}$ symmetry in pure deuterated methanol. However its C$_{2v}$ symmetry breaks off when deuterated acetonitrile was introduced (D$_2$O/CD$_3$CN as solvent), as evidenced by a group of five broad protons resonance signals which belong to bda$^{2−}$ with a ratio of 1:1:1:2:1 (middle). Based on this asymmetric $^1$H NMR spectra, it is reasonable to believe that 45 is still a six-coordinate complex with the structure of [Ru(κ$^3$O,N,N−bda)(6-fluorooisoquinoline)$_2$(CD$_3$CN)]. The feature of broaden peaks (protons from bda$^{2−}$) is most likely due to the fast exchange between the coordinated and uncoordinated carboxylates. Surprisingly, complex 45 remains C$_{2v}$ symmetry in an acidic aqueous solution with 10% CD$_3$CN; however, with a significant changed chemical shift of the bda$^{2−}$ protons. Thereby we conclude that two molecules of acetonitrile are coordinated to the metal center under low pH condition, resulting complex [Ru((κ$^2$N,N−bda)(6-fluorooisoquinoline)$_2$(CD$_3$CN)$_2$] as shown in Figure 21.
3.4. Electrochemical Properties

Figure 22 shows the CV curves of the first redox waves (Ru$^{III/II}$ couples) of complexes 20, 21 and 45-47. The electron-withdrawing abilities of these axial ligands can be reflected by the variation values of $E_{1/2}$(Ru$^{III/II}$): phthalazine < 6-bromophthalazine < isoquinoline < 6-Bromoisoquinoline < 6-fluoroisoquinoline. Nevertheless, the halogen substitutes show negligible electronic effects on the oxidation potentials of these Ru complexes. For instance, $E_{1/2}$(Ru$^{III/II}$) values of complexes 20 and 45 (or 46) differ only by just 20 mV; a similar feature is observed for $E_{1/2}$(Ru$^{IV/III}$) and $E_{1/2}$(Ru$^{V/VI}$) (less than 20 mV) as well. All the electrochemical data are summarized in Table 2.

![CV curves of complexes 45-47. Complexes 20 and 21 were introduced as references.](image)

**Figure 22.** CV curves of complexes 45-47. Complexes 20 and 21 were introduced as references.

**Table 2.** Electrochemical data of Ru-bda complexes 20, 21 and 45-47.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$(V vs NHE)$^a$</th>
<th>$E_{Ru}^{III}$$^a$</th>
<th>$E_{Ru}^{IV}$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.66</td>
<td>1.13</td>
<td>1.31</td>
</tr>
<tr>
<td>45</td>
<td>0.68</td>
<td>1.14</td>
<td>1.33</td>
</tr>
<tr>
<td>46</td>
<td>0.67</td>
<td>1.14</td>
<td>1.31</td>
</tr>
<tr>
<td>21</td>
<td>0.58$^b$</td>
<td>1.10</td>
<td>1.30</td>
</tr>
<tr>
<td>47</td>
<td>0.60</td>
<td>1.11</td>
<td>1.30</td>
</tr>
</tbody>
</table>

*Samples (1 mM) dissolved in pH 1 (0.1 M CF$_3$SO$_3$H) aqueous solution containing 20% CF$_3$CH$_2$OH were measured at 100 mV/s. *Assignment of proton-coupled oxidation waves are indicated: Ru$^{II}$ = Ru$^{II}$-OH$_2$; Ru$^{III}$ = Ru$^{III}$-OH$_2$; Ru$^{IV}$ = Ru$^{IV}$-OH$_2$; Ru$^{V}$ = Ru$^{V}=O$. *Previously reported at 0.43 V$^b$ was measured at working electrode pyrolytic graphite electrode (basal plane).
3.5. Water Oxidation Catalysis

In order to have a fair comparison with complexes 20 and 21, the catalytic water oxidation measurements for complexes 45-47 were conducted under the conditions identical to those of our previous studies.\textsuperscript{37,38} First, the Ru-bda catalyst was dissolved in the aqueous solutions by using acetonitrile as a co-solvent. Then the catalyst solution was injected into an acidic Ce\textsuperscript{IV} solution, and the oxygen evolution was monitored by pressure sensor. All of the halogen substituted Ru-bda complexes were expected to be better WOCs, however, as shown in Figure 23 (Left), complex 47 showed a surprisingly low TON of ~10000 compared to that of complex 21 (55000 reported in the previous study), even though these two catalysts exhibit quite close chemical structure as well as the electrochemical properties. Considering the NMR studies (Figure 21), we thereby assumed that the co-solvent (acetonitrile) might be the reason for the decrease in activity. In order to understand these chemical aspects as well as eliminate the negative co-solvent effect, a well-known less coordinating organic solvent CF\textsubscript{3}CH\textsubscript{2}OH was introduced to replace the coordinating CH\textsubscript{3}CN. After this minor modification, better performances were observed for each catalyst as expected (Figure 23, right), invoking a dramatic co-solvent effect (all of the data are summarized in Table 3).

![Figure 23. Oxygen evolution curves catalyzed by complexes 21 and 47. Left: CH\textsubscript{3}CN as the co-solvent; right: CF\textsubscript{3}CH\textsubscript{2}OH as the co-solvent.](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(^a)TOF (s(^{-1}))</th>
<th>(^a)TON</th>
<th>(^b)TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>787 ± 35</td>
<td>11 300 ± 640</td>
<td>8 300 ± 280</td>
</tr>
<tr>
<td>45</td>
<td>1000 ± 58</td>
<td>24 000 ± 880</td>
<td>19 600 ± 360</td>
</tr>
<tr>
<td>46</td>
<td>585 ± 32</td>
<td>35 293 ± 352</td>
<td>28 500 ± 565</td>
</tr>
<tr>
<td>21</td>
<td>530 ± 36</td>
<td>61 300 ± 990</td>
<td>55 000 ± 370</td>
</tr>
<tr>
<td>47</td>
<td>385 ± 12</td>
<td>101 000 ± 870</td>
<td>15 126 ± 413</td>
</tr>
</tbody>
</table>

\(^a\) CF\textsubscript{3}CH\textsubscript{2}OH as solvent to dissolve Ru complexes. \(^b\) CH\textsubscript{3}CN as solvent instead.
To study the mechanism of the deactivation caused by acetonitrile, electrochemical measurements of complex 45 were firstly carried out by using two different co-solvents separately, while the pH remains the same. As it can be seen in Figure 24, the redox wave of Ru$^{II}$−OH$_2$/ Ru$^{III}$−OH$_2$ was negatively shifted by more than 200 mV in the CF$_3$CH$_2$OH/H$_2$O system in comparison with that in the CH$_3$CN/H$_2$O system, while the Ru$^{III}$−OH$_2$/ Ru$^{IV}$−OH redox couples in both systems showed up at similar potentials. Besides, both of the redox couples show decent reversibility in the presence of acetonitrile, indicating no chemical reaction is happened at least in the CV time scale. Furthermore, the onset potentials of catalyst 45 are close to each other in these two solvents, suggesting that the acetonitrile is not involved in the active species. Based on this fact, DFT calculations were carried out to investigate the ability of CH$_3$CN competing with water molecule for a Ru center, by comparing the relative free energies of the corresponding complexes (Ru$^{II}$-bda binding with three different solvent molecules: CH$_3$CN, H$_2$O and CF$_3$CH$_2$OH). Taking 45 as the model complex, it is clear that CH$_3$CN is the only one which can replace a carboxylate with a favorable free energy of -5.3 kcal mol$^{-1}$, this is in agreement with the previous NMR experiments (Figure 21). On the other hand, CF$_3$CH$_2$OH coordinated complex 45 is even less stable than the corresponding H$_2$O coordinated complex by ~1.0 kcal/mole, indicating that CF$_3$CH$_2$OH can be a good candidate of co-solvent for catalytic water oxidation, which is in consistence with the experimental results (Table 3).

![Figure 24. CVs of complex 45 in pH 1 (0.1 M CF$_3$SO$_3$OH) aqueous solution containing 20% CF$_3$CH$_2$OH and CH$_3$CN.](image)

### 3.6. PCET, Kinetics and Catalytic Cycle for Water Oxidation

PCET processes were investigated by the means of Pourbaix diagram$^{iii}$. Under the catalytic conditions (pH 1), one oxidation sequence of Ru$^{II}$ + H$_2$O →

$^{iii}$ Pourbaix diagram is a diagram of redox potentials and pH values. It gives possible stable phase of a electrochemical system; however, it does not provide kinetics information.
Ru$^{III}$−OH$_2$ → Ru$^{IV}$−OH → Ru$^{V}$═O was observed, and both the second and third steps are 1e$^-$/1H$^+$ coupled processes based on the Nernst slopes of -59 mV per pH unit. According to the inflections of the Pourbaix diagram, the p$K_a$ of [Ru$^{III}$(κ$_3$O,N,N-bda)(6-F-isonicotinoyl)]$^+$ was estimated to be 6.9. Interestingly, a new redox process was observed after the step of Ru$^{IV}$−OH → Ru$^{V}$═O under relative high pH conditions (Figure 25 and Figure 26). This unusual redox wave was tentatively assigned to the oxidation of [Ru$^{IV}$−O−O−Ru$^{IV}$]$^{2+}$/[Ru$^{IV}$−O−O−Ru$^{IV}$]$^{3+}$. DFT calculations$^iv$ on this redox potential were conducted to support this assumption (Figure 27). The calculated redox potential of [Ru$^{IV}$−O−O−Ru$^{IV}$]$^{2+}$ to [Ru$^{IV}$−O−O−Ru$^{IV}$]$^{3+}$ is around 1.69 V, which is in a good agreement with the experimental value. Moreover, the spin density of the two oxygen atoms (the peroxo bridge) in the oxidized complex were calculated to be around 0.5, indicating the oxidation process is most likely localized on the peroxo bridge. Thereby we believe that it is the first pieces of practical evidence that supports our previously DFT calculations.$^{37}$

Figure 25. Pourbaix diagram of complex 45.

Figure 26. DPVs curves of complex 45 obtained at pH 1.0 and 8.8 solutions respectively.

$^iv$Performed by Mårten S. G. Ahlquist and Ying Wang at the Division of Theoretical Chemistry & Biology, KTH.
Figure 27. The calculated structure for $[\text{Ru}^{IV}O-O\text{Ru}^{IV}]^{2+}$ (left) and $[\text{Ru}^{IV}O-O\text{Ru}^{IV}]^{3+}$ (right).

The rates of catalytic water oxidation by complex 45 were recorded by following the oxygen evolution at different catalysts concentration. As shown in Figure 28, the initial rate (0~5 s) of $O_2$ generation is dependent on the $[45]^2$ linearly, indicating a second order reaction kinetics. The rate constant $k_{obs}$ was calculated to be $2.54 \times 10^5$ (LM$^{-1}$s$^{-1}$).

![Figure 28](image)

Figure 28. Water oxidation catalyzed by 45. Left: Plots of $O_2$ generation vs. time at various concentrations of 45. Right: The rate constant $k_{obs}$ that calculated by plotting the $O_2$ generation rates against the $[45]^2$.

On the basis of the above findings, we proposed a pathway of water oxidation catalyzed by complex 45 as depicted in Figure 29. As our previous study, the same I2M mechanism is involved in the rate determine O$-$O formation step, which owing to: (1) the negatively charged carboxylate ligands which can increase the electron density of the active species Ru$^{V=O}$ and further adverse to the water molecule nucleophilic attack to it; (2) the high spin density of the oxo favours the radical coupling pathway. The auxiliary pathway for the
oxygen liberation (dash line in Figure 29) might overwhelm under some specific conditions, such as excess Ce\textsuperscript{IV} or higher pH condition.

\[
2 \text{Ru}^{II} + 2 \text{H}_2\text{O} \\
-2 \text{e}^- \\
\rightarrow \\
2 \text{Ru}^{III}\cdot\text{OH}_2 \\
-2 \text{e}^-, -2 \text{H}^+ \\
\rightarrow \\
\text{O}_2 + 2 \text{H}_2\text{O} \\
\rightarrow \\
\text{Ru}^{IV}\cdot\text{O} \cdot \text{O} \cdot \text{Ru}^{IV} \cdot \text{e}^- \\
\rightarrow \\
\text{Ru}^{IV}\cdot\text{O} \cdot \text{O} \cdot \text{Ru}^{IV} \\
\rightarrow \\
2 \text{Ru}^{IV}\cdot\text{OH} \\
\rightarrow \\
-2 \text{e}^-, -2 \text{H}^+ \\
\rightarrow \\
2 \text{Ru}^{IV} \cdot \text{O} \\
\rightarrow \\
2 \text{Ru}^{IV} = \text{O}
\]

\textbf{Figure 29. Proposed pathway of catalytic water oxidation by 45.}

3.7. Summary

Three novel halogen substituted Ru-bda WOCs 45-47 have been prepared and characterized. Detailed studies on these complexes convincingly proved that the hydrophobic effect of halogen substitutes dramatically enhanced both the catalytic rate and the catalyst stability for water oxidation. By introducing halogen atoms, complex 45 achieves an impressively high initial TOF of 1000 s\(^{-1}\), and complex 47 exhibits an extremely high TON over 100 000; both values are the highest reported values to our best of knowledge. Acetonitrile as the co-solvent can negatively affect the reactivity, and thereby the less coordinating organic solvent CF\textsubscript{3}CH\textsubscript{2}OH is a better candidate. It is vital to note that the radical intermediate \([\text{Ru}^{IV} \cdot \text{O} \cdot \text{O} \cdot \text{Ru}^{IV}]^{\cdot\cdot}\) observed by electrochemical method further support the auxiliary pathway for oxygen liberation which is proposed by DFT calculations in our previous study. The high activities of this group of Ru–bda WOCs are promising; future work is to embed these Ru–bda WOCs on the surface of electrodes by using suitable immobilization methods, aiming at the functionalized water splitting devices.
4. Imidazole-DMSO type of Ru-bda WOCs

(Paper III)

4.1. Introduction

Imidazole as an important biological molecule is present in the first coordination sphere (in the form of histidine) of the natural OEC. Yet, it is seldom employed by artificial WOCs. There was only one report from Thummel and co-workers that prepared and investigated two imidazole-containing Ru-WOCs (48 and 49 in Figure 30), but unfortunately both of them were not active for water oxidation. Based on the success of the Ru-bda WOCs, and also the considerations of that (1) imidazole and its derivatives are close to pyridine type ligands accordance with the metal-coordination properties; (2) they are more electron-donating ligands as well, we are then motivated to design complexes 50-54 (Figure 30) and study the performance of the desired imidazole containing Ru-bda WOCs. The results suggest that the imidazole/DMSO pair as axial ligands for Ru-bda catalysts is more suitable than imidazole/imidazole pair (Figure 31). Besides, it is worth to mention the novelty of a synthesized WOC containing two non-nitrogen donor atoms, oxygen and sulfur in one ligand of DMSO.

Figure 30. Molecular structures of Ru complexes 48-54.
4.2. Synthesis and Structural Characterization

For the synthesis, we followed the same procedure as our previous work, however, unusual products were obtained. Interestingly, instead of the desired $C_{2v}$ symmetric type- $[\text{Ru}(\kappa_4\text{bda})(\text{imidazole})_2]$ (50-54), complexes $[\text{Ru}(\kappa_3^{O,N,N-}\text{bda})(\text{DMSO})(\text{imidazole})_2]$ (50a-53a) were obtained, in which one of the coordinated carboxylate was replaced by an imidazole ligand (Figure 31). It is worth to note that the equatorial imidazole ligands in these complexes are readily dissociated from the ruthenium center in acidic solution, leading to the formation of the true catalysts (50b-53b). The dissociation process was determined by $^1$H NMR (Figure 32). The crystal structure of 53b is shown in Figure 33, and its O2–Ru1–O3 bite angle (124.69°) is slightly bigger (by 1.7°) than that of previously reported complex [Ru(bda)(picoline)$_2$] (19), suggesting that this ruthenium center is even more accessible for a seventh ligand, such as water molecules. Complexes 53 and 54 were also synthesized by using a DMSO free ruthenium source (RuCl$_3$) and the same ligands (Figure 31), so that we can conduct a fair comparison with previous catalysts as well as study the effect of the DMSO ligand.

![Diagram]

Figure 31. Synthesis and structures of complexes 50a-53a, 50b-53b, 53 and 54.
Figure 32. Upper: low-field $^1$H NMR spectra of 53a in CD$_3$OD indicating its asymmetrical structure. Below: (a) low-field $^1$H NMR spectra of 53a in acidic D$_2$O (0.1 M CF$_3$SO$_3$OD); (b) free imidazole ligand in the same deuterated solvent. The $^1$H NMR spectra changed from asymmetrical to symmetrical suggesting that the equatorial imidazole ligand indeed dissociate from the Ru center in acidic aqueous solution.

Figure 33. X-ray crystal structure of 53b with 50% of thermal ellipsoids, hydrogen atoms are omitted for clarity.
4.3. Electrochemical Properties

Before the discussion, it is interesting to mention that all of the imidazole containing Ru-bda catalysts are soluble in aqueous solution, meaning that the co-solvent effect as we discussed in last chapter can be avoided. Taking into account that complexes 50a-53a will lose one equatorial imidazole ligands and transform to 50b-53b in acidic aqueous solution, thereby all of the redox potentials reported here correspond to complexes 50b-53b. For the sake of simplicity, we take 53 and 53b as the model complexes for discussion. Figure 34 depicts the CVs of complexes 53 and 53b in pH 1 aqueous solutions. The half-wave potentials of first redox process (Ru$^{III/II}$) were found at 0.70 and 0.91 V for 53 and 53b respectively. This 200 mV difference of the potentials is most likely due to that the imidazole ligand is more electron-donating than DMSO. Their second redox waves (Ru$^{IV/III}$) were observed at 1.08 and 1.14 V respectively, and the smaller potential difference compared to the first redox waves indicates that the electronic effect of the axial ligands only slightly influences this redox process. Moreover, the obvious redox peaks at −0.25 V are corresponding to the reduction of O$_2$ which is generated during the anodic scan, indicating that both catalysts are active for electrochemically catalytic water oxidation. All of the measured redox potentials are summarized in Table 4.

![Figure 34](image_url)

**Figure 34.** CV curves of complexes 53 and 53b in pH 1 aqueous solutions (0.1M CF$_3$SO$_3$OH).
Table 4. Electrochemical, TON and TOF data of complexes 19, 50b-53b, 53 and 54.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}^{\text{ox}}$ (V vs. NHE$^a$)</th>
<th>$E_{\text{onset}}$ (V)</th>
<th>TON$^b$</th>
<th>TOF$^c$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>50b</strong></td>
<td>0.90 1.15 1.39 1.45</td>
<td>2032</td>
<td>137.6</td>
<td></td>
</tr>
<tr>
<td><strong>51b</strong></td>
<td>0.89 1.13 1.37 1.43</td>
<td>2365</td>
<td>146.2</td>
<td></td>
</tr>
<tr>
<td><strong>52b</strong></td>
<td>0.92 1.14 1.38 1.44</td>
<td>550</td>
<td>150.8</td>
<td></td>
</tr>
<tr>
<td><strong>53b</strong></td>
<td>0.91 1.14 1.40 1.46</td>
<td>4050</td>
<td>176.5</td>
<td></td>
</tr>
<tr>
<td><strong>53</strong></td>
<td>0.70 1.08 - -</td>
<td>1150</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td><strong>54</strong></td>
<td>0.68 1.05 - -</td>
<td>1094</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td><strong>19</strong></td>
<td>0.86 1.11 - -</td>
<td>2000</td>
<td>41.2</td>
<td></td>
</tr>
</tbody>
</table>

Conditions: $^a$ 0.1 M CF$_3$SO$_3$H pH = 1 solution, scan rate 100 mV/s; Ru(bpy)$_3^{2+}$ as a reference with $E_{1/2}^{\text{ox}} = 1.26$ V vs. NHE. Conditions: $^b$ Catalyst concentrations (50b-53b: 1.20 $\times$ 10$^{-5}$ M; 53-54: 2.99 $\times$ 10$^{-5}$ M, Ce$^{IV}$ (0.4 M) in 3.3 mL pH 1 aqueous solutions. $^c$ Catalyst (2.16 $\times$ 10$^{-4}$ M for all) and Ce$^{IV}$ (0.4 M) in 3.7 mL pH1 aqueous solutions. Room temperature.

4.4. Catalytic Water Oxidation

The activities of this group of Ru-bda WOCs were evaluated by using chemical oxidant Ce$^{IV}$ as the driving force in acidic conditions. All of the catalytic water oxidation data were summarized in Table 4. By comparing the entries 1-4 with 5-6 (complexes with and without DMSO ligand), we can find that the DMSO containing catalysts show much higher activities (over 30 folds in term of the initial TOF) than that of the DMSO free complexes. For instance, complex 53 affords a TOF of 4.5 s$^{-1}$ while complex 53b achieves TOF over 170 s$^{-1}$ under the same conditions. At a relative low concentration (1.20 $\times$ 10$^{-5}$ M), a high TON of 4050 was achieved for complex 53b. More discussions about the influence on efficiency by the DMSO ligand are in the DFT calculations part.

4.5. Pourbaix Diagram and Kinetics of Complex 53b

The following discussion is based on complex 53b. Its DPVs at the pH range of 1 to 8 were recorded and the corresponding Pourbaix diagram was prepared as shown in Figure 35. First, a pH independent 1 e$^-$ process Ru$^{II}$ + H$_2$O / Ru$^{III}$−OH$_2$ was observed at 0.92 V over pH 1 to 5.7, followed by a pH dependent 1 e$^-$ / 1 H$^+$ ($-59$ mV/pH) process Ru$^{II}$ + H$_2$O / Ru$^{III}$−OH. The inflection at pH 5.7 suggests that the p$K_a$ of Ru$^{III}$−OH$_2$ is 5.7. Then, a 1 e$^-$ / 1H$^+$ process was found for the Ru$^{IV/III}$ process at the pH range of 1 to 8. Further oxidation of either Ru$^{IV}$−OH or Ru$^{IV}$−O species afforded the same Ru$^{V}$=O species. As a result, the redox processes of 53b under the catalytic conditions...
(pH 1.0 aqueous) can be summarized as following: Ru$^{II}$ + H$_2$O → Ru$^{III}$–OH$_2$ → Ru$^{IV}$–OH → Ru$^{V}$═O.

![Pourbaix diagram of complex 53b.](image)

**Figure 35.** Pourbaix diagram of complex 53b.

To study the kinetics of this family of Ru-bda catalysts, several measurements were carried out by monitoring the absorption decay of Ce$^{IV}$ at 360 nm. First, the absorption decays were recorded at various Ce$^{IV}$ concentrations while the catalyst concentration remains unchanged. The catalytic water oxidation is first order in Ce$^{IV}$ under low Ce$^{IV}$ concentrations ([Ce$^{IV}$] < 2.0 mM; $k = 0.124$ s$^{-1}$), indicating that Ce$^{IV}$ is involved in the rate limiting step of the catalytic cycle. However, the rate limiting step becomes independent to Ce$^{IV}$ at its high concentrations ([Ce$^{IV}$] > 2.0 mM), suggesting the oxidation of the catalyst caused by Ce$^{IV}$ is no longer the rate determine step. Similar to complex 19, a second order nature regarding to the catalyst concentration ($k = 1.86 \times 10^8$ M$^{-1}$s$^{-1}$) was obtained for complex 53b, indicating that the O−O formation pathway is still I2M.

### 4.6. The Seven-Coordinated Intermediate

It is worth to note that a seven-coordinated species of complex 53 was captured in situ by high resolution mass spectroscopy with the addition of Ce$^{IV}$. Figure 36 depicts the intermediates [Ru$^{IV}$–OH]$^+$ with m/z$^+$ = 682.8622, in agreement with the theoretical value of m/z$^+$ = 682.8650. This intermediate is in a good agreement with the previous Pourbaix diagram, the [Ru$^{IV}$–OH]$^+$ is indeed involved in the catalytic cycle. However, the same intermediate cannot be found for complex 53b under the same conditions, this may be due to the much faster reaction rate of 53b which is beyond the sensitivity of the MS.
4.7. Proposed Water Oxidation Pathway

On the basis of the above discussions, the catalytic water oxidation pathway can be summarized as below in Figure 37. This is identical to our previous results. The crucial peroxide intermediate $[\text{Ru}^{IV}-\text{O}^2=\text{O}^2=\text{Ru}^{IV}]^{2+}$ which can readily liberate dioxygen is formed via a radical coupling of two molecules of $[\text{Ru}^{IV}=\text{O}]^{2+}$. Moreover, we also do not rule out the possibility of the second pathway (Path b in Figure 37) of oxygen evolution by further oxidizing the $[\text{Ru}^{IV}-\text{O}^2=\text{O}^2=\text{Ru}^{IV}]^{2+}$ species.

\[ \text{Ru}^{II} + \text{H}_2\text{O} + \text{Ce}^{IV} \xrightarrow{\text{fast}} [\text{Ru}^{III} = \text{OH}^2]^+ + \text{Ce}^{III} \]  
(1)

\[ [\text{Ru}^{III} = \text{OH}^2]^+ + \text{Ce}^{IV} \xrightarrow{\text{fast}} [\text{Ru}^{IV} = \text{OH}]^+ + \text{Ce}^{III} + \text{H}^+ \]  
(2)

\[ [\text{Ru}^{IV} = \text{OH}]^+ + \text{Ce}^{IV} \xrightarrow{} [\text{Ru}^{IV} = \text{O}]^+ + \text{Ce}^{III} + \text{H}^+ \]  
(3)

\[ [\text{Ru}^{IV} = \text{O}]^+ + [\text{Ru}^{IV} = \text{O}]^+ \xrightarrow{} [\text{Ru}^{IV} = \text{O} = \text{O} = \text{Ru}^{IV}]^{2+} \]  
(4)

**Path a:**
\[ [\text{Ru}^{IV} = \text{O} = \text{O} = \text{Ru}^{IV}]^{2+} + 2 \text{H}_2\text{O} \xrightarrow{k_{\text{ox}}} 2[\text{Ru}^{III} = \text{OH}^2]^+ + \text{O}_2 \]  
(5)

**Path b:**
\[ [\text{Ru}^{IV} = \text{O} = \text{O} = \text{Ru}^{IV}]^{2+} + \text{Ce}^{IV} \xrightarrow{} [\text{Ru}^{IV} = \text{O} = \text{O} = \text{Ru}^{IV}]^{3+} + \text{Ce}^{III} \]  
(6)

\[ [\text{Ru}^{IV} = \text{O} = \text{O} = \text{Ru}^{IV}]^{3+} + \text{H}_2\text{O} \xrightarrow{} [\text{Ru}^{IV} = \text{O} = \text{O}]^{2+} + [\text{Ru}^{III} = \text{OH}_2]^+ \]  
(7)

\[ [\text{Ru}^{IV} = \text{O} = \text{O}]^{2+} + \text{H}_2\text{O} \xrightarrow{k_{\text{ox}}} [\text{Ru}^{IV} = \text{OH}]^+ + \text{O}_2 + \text{H}^+ \]  
(8)

**Figure 37.** Proposed Ce$^{IV}$-driven Water Oxidation Pathways of imidazole containing Ru-bda complexes.
4.8. Theoretical Calculations

In order to shed light on the great difference of the catalytic performance between complexes 53 and 53b, DFT calculations have been conducted by modelling the I2M O–O pathway for both complexes. The only difference in chemical structure between 53 and 53b is from the axial ligands, imidazole/imidazole for 53 and imidazole/DMSO for 53b. Thereby we believe that the different axial ligands pairs lead to the difference of the catalyst performance. In principle, both S and O in DMSO can coordinate to the Ru center as donor heteroatoms, to form Ru–S and Ru–O bonds. As expect, Ru\textsuperscript{II} state of 53b is favor to take the “softer” S as the donor axial ligand (Figure 38a). However, after the oxidation of Ru\textsuperscript{II} to Ru\textsuperscript{V} state, the DMSO ligand flipped its orientation to coordinate to the Ru center via the Ru–O bond. As shown in Figure 38, two theoretical low-energy conformers \textit{a} and \textit{b} (1.4 kcal/mol higher that of \textit{a}) were obtained for Ru\textsuperscript{V}=O of 53b. Similar calculated Ru\textsuperscript{II} and Ru\textsuperscript{V}=O species of complex 53 were obtained as well (Figure 39, \textit{γ}). The bond lengths of Ru\textsuperscript{V}=O of \textit{a}, \textit{b} and \textit{γ} are very close to each other, around 1.73 Å in all three cases.

**Figure 38.** (a) The optimized structures of Ru\textsuperscript{II}-complex of 53b by calculation, Ru-DMSO coordination with a Ru–S bond; (b) and (c): two optimized conformers (\textit{a} and \textit{b}) of the Ru\textsuperscript{V}=O of complex 53b, both of them coordinate with DMSO via Ru–O bond. All of the calculated bonds lengths are in Å.

\^ Performed by Timofei Privalov, Beverly Stewart and Maoping Pu in Stockholm University.
The calculated potentials for the sequence of the multiple oxidation process are in a good agreement with the experimental one. For instance, 0.8, 1.2 and 1.5 V are calculated for steps of Ru$_{\text{III/II}}$, Ru$_{\text{IV/III}}$ and Ru$_{\text{V/IV}}$ respectively. In addition, the p orbital-like SOMO (singly occupied molecular orbital) of this Ru$^V=O$ complex promotes the O–O bond formation via the I2M pathway. Therefore, the potential energy of I2M O–O bond formation pathway was calculated for both complexes based on the Ru$^V=O$ models a, b and γ. The results turn out, for complex 53b, ββ configuration shows the minimized energy at the transition state of the O–O bond formation step (TS$^{OO}$) compared to that of the aa and aβ configurations. Finally, Figure 40 depicts the energy diagram of the I2M O–O bond formation as well as the oxygen liberation for both complexes 53 and 53b. To summarize it briefly, TS$^{OO}(\beta\beta)$ of 53b oriented in a way which minimized the steric congestion and further resulted in a much lower energy barrier. This is the main reason why there is a huge difference of the catalytic activities between complexes 53 and 53b.
Figure 40. Calculated 12M O–O bond formation and the O$_2$ liberation step of catalysts 53 and 53b.

4.9. Summary

A new family Ru-bda WOCs bearing imidazole and DMSO as axial ligands have been prepared and evaluated. For precatalysts 50a-53a, the equatorial imidazole ligand is readily dissociated from the Ru center in acidic conditions, leading to the formation of the corresponding real catalysts, complexes 50b-53b. By using Ce$^{IV}$ as the chemical oxidant, a high TOF over 170 s$^{-1}$ was obtained for catalyst 53b, while the reference complex 53 only affords a low TOF of 4.5 s$^{-1}$ under the same conditions. The detailed kinetics measurements, electrochemical data, MS spectrum of a seven-coordinated intermediate as well as the theoretical studies point to a well-studied bimolecular mechanism for the catalytic water oxidation. By comparing the energy barriers of the transition states of the O–O bond formation step for both complexes 53 and 53b, we found out that the imidazole/DMSO pair of axial ligands is much less hindered than that of the imidazole/imidazole one, as such it facilitates the radical coupling of two Ru$^{V}$=O species which is the rate limiting step, thus enhancing the catalytic activities.
5. Light Induced Water Oxidation

(Paper IV and V)

5.1. Introduction

Visible light-driven water oxidation is crucial for artificial photosynthesis. In this chapter, we focus on light induced water oxidation catalyzed by Ru-bda catalysts. As we discussed in the previous chapters, Ru-bda complexes hold advantages such as high activities and low overpotential for water oxidation. These two advantages are, coincidentally, necessary for light-driven water oxidation in terms of suppressing charge recombination and matching the oxidation power of the photosensitizer (or valence band of a semiconductor) respectively. Taking these advantages into account, we thereby first employed several Ru-bda complexes into the three-component systems to evaluate their performance for light-driven water oxidation (Figure 41, Left). The photo stability of the photosensitizer [Ru(bpy)$_3$]$^{2+}$ has been investigated as well. As we discussed in the first Chapter (Figure 15), three photocatalysts were reported previously, however, only complexes 35 and 37 show activities for visible light-driven water oxidation. By comparing complexes 36 and 37, we conclude that the catalytic reaction might be promoted by the short bridging ligand. However, such a short linker seems unfavourable for the activity in term of the intramolecular electron transfer. In order to further study this matter, we were then motivated to synthesize complexes 55 and 56 with shorter bridging ligands compared to complex 35. Then by adapting the knowledge that we learned from the above three-component systems, performance as well as the kinetics of 55 and 56 for light-driven water oxidation under the optimized conditions were investigated (Figure 41 right).

![Figure 41](image)

**Figure 41.** Left: Three-component molecular systems for visible light-driven water oxidation. Right: Assembled photo-catalysts for light-driven water oxidation.
5.2. Design and Synthesis

WOCs 20, 21, 40 and 53a have been employed into the three-component systems for light-driven water oxidation, and their synthesis have been presented previously. As depicted in Figure 42, commonly used photosensitizer [Ru(bpy)₃]²⁺ (P1) and two of its derivatives P2 and P3 were synthesized according to the literature method. Chloride was chose as the counter ion to achieve a decent solubility of P1-P3 in aqueous solution. Besides, carboxylate substituents were introduced into P2 and P3 in order to increase the oxidation potential of the sensitizers.

![Figure 42. Catalysts (20, 21, 40 and 53a) and photosensitizers (P1-P3) that were used in the three-component systems.](image)

Figure 43 displays the synthetic route of the complexes 55 and 56. According to the literature, ligand 2,2'-4',4''-terpyridine (e in Figure 43) was synthesized by starting with the asymmetric oxidation of 2,2'-bipyridine with 3-chlorobenzoperoxoic acid followed by nitrification with H₂SO₄/HNO₃ mixture, to afford 4-nitro-2,2'-bipyridine-N-oxide (b). The nitro group in b is readily replaced by a more electron donating bromide group to give 4-bromo-2,2'-bipyridine-N-oxide (c). Compound c was then reduced by PBr₃ to remove the oxide and generate 4-bromo-2,2'-bipyridine (d). Finally ligand e was synthesized through a Suzuki coupling reaction between d and pyridine-4-boronic acid with a yield of ~ 30%. The sensitizer P was synthesized by a similar method to P2 and P3 with the ligand e. The intermediates of g and h were also obtained by complexation of cis-Ru(DMSO)₄Cl₂ with bda²⁻ firstly and then picoline respectively. The final complexes 55 and 56 were then
prepared by simply mixing the sensitizer moiety (P) with the catalysts moieties h and g respectively in methanol. The final complexes were thoroughly characterized by $^1$H NMR, high resolution mass spectrometry as well as elemental analysis.

*Figure 43. Synthetic route of complexes 55 and 56.*
5.3. Three-component Light-driven Water Oxidation System

As shown in Figure 41, the so called three component system consists of (i) a photosensitizer as light harvesting antenna, (ii) a WOC and (iii) a sacrificial electron acceptor. P1–P3 with oxidation potentials of 1.26, 1.55 and 1.69 V respectively, were employed as photosensitizers. Complexes 20, 21, 40 and 53a were chosen as the WOCs. Sodium persulfate (Na₂S₂O₈) was employed as the sacrificial electron acceptor. The working principle for the three-component system is displayed as equation 2 and 3.

It was found that the borate buffer leads to a better performance than the phosphate buffer. Besides, a better performance of light-driven water oxidation was achieved when P2 instead of P1 (or P3) was employed as the sensitizer. Thereafter, the optimized catalytic conditions were applied to all of the four WOCs, and the TONs and TOFs are presented in Figure 44 and Table 5. Catalysts 20, 21 and 40 afford similar activities in terms of both TONs and TOFs while complex 53a gives a relatively lower activity most likely due to its unsatisfactory stability. With this series of WOCs, the best case of catalytic light-driven water oxidation performance with a TON = 251 and a TOF = 20.0 min⁻¹ was observed for the system of 40/P2/S₂O₈²⁻.

**Equation 2.** \( 4 \text{Ru(bpy)}_3^{2+} + 2 \text{S}_2\text{O}_8^{2-} + 2 \text{hv} \rightarrow 4 \text{Ru(bpy)}_3^{3+} + 4 \text{SO}_4^{2-} \)

**Equation 3.** \( 4 \text{Ru(bpy)}_3^{3+} + 2 \text{H}_2\text{O} \rightarrow 4 \text{Ru(bpy)}_3^{2+} + \text{O}_2 + 4 \text{H}^+ \)

![Figure 44. Light-driven water oxidation. The kinetic curves of O₂ generation vs. illumination time.](image-url)
Table 5. Light induced water oxidation by catalysts 20, 21, 40 and 53a.

<table>
<thead>
<tr>
<th></th>
<th>20</th>
<th>21</th>
<th>40</th>
<th>53a</th>
</tr>
</thead>
<tbody>
<tr>
<td>TON</td>
<td>218</td>
<td>232</td>
<td>251</td>
<td>74</td>
</tr>
<tr>
<td>TOF (min⁻¹)</td>
<td>18.8</td>
<td>19.1</td>
<td>20.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*The generated O₂ was measured by Micro GC. aThe first run. bTotal TON for 3 runs of illumination (after the addition of fresh sensitizer).*

As it can be seen in Figure 45, the pH of the buffered solution dropped (from 7.0 to 1.9) dramatically after a short time of illumination, and this may be due to the relative low buffer capability of the borate buffer. This increase of acidity would positively shift the onset potential for oxidizing water, leading to the evanescent of the oxygen evolution. However, the reactivity of the catalyst can be recovered by neutralizing the working buffer solution (Figure 45). After three runs, an impressive combined TON of 518 was obtained by complex 40. It is interesting to note that, the CO₂ evolution was also observed during the catalysis (Figure 45b), and this CO₂ formation is proved to be attributed to the photodecomposition of the photosensitizer.

![Figure 45. (a) Repetitive light-driven water oxidation by neutralizing the buffer solution. (b) Kinetics curves of the generation of CO₂ and O₂ vs. of illumination time. Conditions: light intensity; 300 mW/cm², λ > 400 nm, 10.0 mM Na₂S₂O₈, 0.5 mM P2, 10 μM complex 40 in 10 mL pH 7.0 borate buffer solution.](image)

Quantum yield (Φ) of photon-to-oxygen generation is the key parameters of the light-driven water oxidation systems. It is defined as the number of generated O₂ molecules divided by the number of the absorbed incident photons (equation 4). The amount of absorbed photons (nₚ) can be determined by equation 5. Take 40/P2/S₂O₈²⁻ as an example, an initial Φ of 17.1% was obtained by using a 473 nm blue light source. Considering almost all of the input light has been absorbed, a much higher Φ is expected, however, the obtained relative low quantum yield is most likely due to the serious decomposition of the photosensitizer.
Equation 4. $\Phi = \text{moles of } O_2 \text{ evolved} / \text{moles of photon absorbed}$

Equation 5. $n_p = (1-\rho)I\lambda/(N_Ahc)$

In Equation 5, $I = \text{radiant power}$, $\lambda = \text{light wavelength}$, $t = \text{irradiation time}$, $h = \text{Planck constant}$, $N_A = \text{Avogadro constant}$, $c = \text{light speed}$, and the $\rho = \text{reflectance of the air/flask interface (~10%).}$

5.4. Photosensitizer-WOC Assemblies for Light-driven Water Oxidation

To achieve a higher quantum yield for light-driven water oxidation, one way is to replace the three-component systems by a sensitizer-WOC assembly. In such a system, the inefficient diffusion controlled electron transfer can be avoided; instead, the intramolecular electron transfer ensures that the highly oxidizing photosensitizer can be regenerated rapidly, leading to slow degradation. Based on the above consideration, two assemblies 55 and 56 by linking the Ru-bda catalyst moiety to the [Ru(bpy)$_3$]$_2^{2+}$ via a single C–C bond have been prepared as shown in Figure 43.

5.4.1. Electrochemical Properties

Figure 46 depicts the CVs and DPVs of 55, 56 and sensitizer P. The CVs obviously show that the potential for the Ru$^{III/II}$ process of P (1.28 V) is higher than the water oxidation onset potentials of both complexes 55 and 56, thermodynamically suggesting a possibility for both 55 and 56 to catalyze the light-driven water oxidation. By comparing the water oxidation catalytic current of the two complexes, complex 56 expectably exhibits a higher activity. Detailed redox data of the three complexes are presented in Table 6.

![Figure 46. CVs and DPVs of complexes 55, 56 and P. 0.4 mM complexes in borate buffer solution (pH 7.0, 10% acetonitrile).]
Table 6. Redox data of Ru photosensitizer P, photo-catalyst 55 and 56.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}^{ox}$ (V vs. NHE)</th>
<th>$E_{1/2}^{red}$ (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td>55</td>
<td>0.76</td>
<td>1.03</td>
</tr>
<tr>
<td>56</td>
<td>0.82</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Conditions: 0.5 mM sample, pH 7 borate buffer, scan rate 100 mV/s; $^{[a]}$[Ru(bpy)$_3$]$_2^{2+}$ as a reference with $E_{1/2} = 1.26$ V vs. NHE. $^{[b]}$The redox potentials that attribute to photosensitizer moieties in the assemblies.

5.4.2. Photochemical Catalytic Water Oxidation

Figure 47 presents the UV–vis absorption spectra of complexes 55, 56, P and 19. The visible absorption bands (metal-to-ligand charge transfer, MLCT) of assemblies 55 and 56 exhibits almost identical shape but bigger molar extinction coefficient ($\varepsilon$) compared to that of P, indicating that there is no obvious electronic interaction between the catalyst moiety and the sensitizer moiety in the ground state of the assembly. Moreover the weak absorption of 19 implies the photochemistry from the excited state of the assembly should be exclusively contributed by the sensitizer moiety.

![UV-Vis spectra of P, 55, 56 and Ru{(bda)pic$_2$} at the working conditions.](image)

Light-driven water oxidation catalyzed by photo-catalysts 55 and 56 were conducted by using a so called two-component system consisting of a photo-catalyst and an electron acceptor (Na$_2$S$_2$O$_8$ in our case). As shown in Figure 48, impressive TONs were obtained for both complexes 55 (78) and 56 (209), which are much higher than that of the previous reported work.$^{[72]}$ At first glance, the short linker (C−C) seems better than the peptide type of bridge. A necessary control experiment was conducted as well (Figure 48). It is clear that the corresponding three component system (mononuclear catalyst 19, sensitizer [Ru(bpy)$_3$]$_2^{2+}$ and Na$_2$S$_2$O$_8$) exhibits a much lower activity
(TON ∼17) for light-driven water oxidation. Moreover, no oxygen was detected without light irradiation for both systems indicating that the oxygen evolution is driven by light.

Figure 48. Photo-catalytic water oxidation catalysed by complexes 55 (black squares) and 56 (red triangle). Conditions: catalysts (20 μM), Na₂S₂O₈ (20 mM) in pH 7 borate buffer. Control experiment (blue dots): three component system, catalyst 19 (20 μM), [Ru(bpy)₃(PF₆)₂] (40 μM) and Na₂S₂O₈ (20 mM) under the same conditions.

Previous study suggested that the dissociation of the sensitizer motifs is the major degradation pathway for this type of photo-catalysts.⁷¹ Thereby, additional free sensitizer P was introduced into the system in order to prevent this decomposition pathway. Surprisingly, the initial TOFs for both complexes 55 and 56 were enhanced dramatically with over two folds (Figure 49). Besides, the TON of complex 55 also doubled. This result supports the previous argument at first glance, however, another control experiment excludes this dissociation issues. It is the addition of [Ru(bpy)₃]²⁺, which is not bearing a coordinating pyridine unit, instead of free P, the activities was enhanced with the same extent as well (Figure 50).

Figure 49. Photo-catalytic water oxidation by 55 and 56 with the addition of free sensitizer P under the same condition as above.
Figure 50. Control experiment indicates that both free P and \([\text{Ru(bpy)}_3]^{2+}\) which has no coordinating pyridine can accelerate the light-driven water oxidation.

5.4.3. Kinetics Studies by Spectroscopic Measurements\(^vi\)

In order to further understand this enhancement of activities, kinetics studies of these complexes were conducted by means of photoemission and transient absorption spectroscopy. Photoemission spectra (Figure 51) suggested that the phosphorescence of complexes 55 and 56 are largely quenched, with relative quantum yields of 6% and 4% respectively, compared to the reference of P. At this point, the electron transfer from the catalyst moiety to the sensitizer part seems promising. As it can be seen in Figure 52, complexes 55 and 19 exhibited very close transient spectra after their excitation at 435 nm, which can be attributed to typical MLCT (the charge most likely localized on the bda\(^2-\) ligand in the case of catalyst motif). However, both case decayed to the ground state within 20 ps. A different species rose up in the case of complex 55 after 150 ps which is clearly different with that of complex 19. Additionally, a significant ultrafast band \((\tau < 0.5 \text{ ps})\) was observed in the bleach recovery of both complexes 55 and 56 at 470 nm, which is not showing in 19 neither \([\text{Ru(bpy)}_3]^{2+}\)\(^{85}\). All of the combined evidence from the spectra point to a successful electron transfer in the assemblies from the catalyst moiety to the appended sensitizer \((-\Delta G^\circ \approx 0.1 \text{ eV})\), however, the calculated yield is only less than 10% based on the weak absorption at 510 nm after 150 ps. This absorption signals at 510 nm decays in the time scale of microsecond, however it is quenched much faster in the presence of \(\text{Na}_2\text{S}_2\text{O}_8\), indicating a rapid electron transfer between the sensitizer and the \(\text{S}_2\text{O}_8^{2-}\).

Considering the ultrafast excited-state quenching of complex 55 (or 56) (within 20 ps) as shown in Figure 52, as such 55 (or 56) is expected to exhibited negligible contribution (less than 0.1%) to the intensity of the emission spectrum (excitation at \(\lambda = 470 \text{ nm})\), fwhm = 10 ns, 10 mJ/pulse).

\(^vi\) Performed by Leif Hammarström and Mohammad Mirmohades, Uppsala University.
This is in conflict with the above obtained 6% and 4% quantum yields. Thereby we conclude that this emission is due to the unbound photosensitizer that exit in the system, ca.6% and 4% respectively.

**Figure 51.** Steady state emission spectra of P, 55 and 56, excited at 555 nm. Conditions: pH 7 borate buffer (10% acetonitrile), N₂ protection.

The Φ₂ were measured by using the same method as the three component system, resulting 6.6% for 55 and 8.5% for 56. The much smaller quantum yields of the assemblies compared to that of the three component systems are
most likely caused by the rapid unproductive quenching between the catalyst moiety and sensitizer moiety through intramolecular energy transfer. It is worth to note that the unbound sensitizer exists in the assembly systems is much less than the three component systems (thousands of times), so that the assemblies of 55 and 56 are very active and robust for photochemical catalytic water oxidation.

Based on all of the above observations, we thereby conclude that: (1) the nonproductive energy transfer quenching of the excited sensitizer moiety by the catalyst moiety is dominated; however, (2) the linked systems can dramatically improve the photo-stability of both the free sensitizer and themselves. The nonproductive mechanism is quite common for the catalyst-sensitizer coupled systems; however it can be solved by several strategies:66,87 (1) modify the bridging ligand; (2) localize the MLCT state of the photosensitizer moiety on its ligands where is situate remotely from the catalyst moiety by introducing certain electron withdrawing groups; (3) fast oxidative quenching of the photosensitizer by certain acceptor, such as, TiO2 surface, to which the ultrafast electron injection from the sensitizer can happen. The second important effect of this study is the impressive photo-stability of the linked system. Serious sensitizer degradation was observed in the three-component system. This miserable photo-stability of the sensitizer is due to its short-lived oxidized state in neutral aqueous. In the three-component system, the first electron transfer from the catalyst to the sensitizer is already controlled by the diffusion rates, moreover, further oxidation of the catalyst is expected to be much harder (lower driving force and is coupled with proton transfer as well) and therefore much slower. In the linked systems, however, the few amount of the (< 10% mol) sensitizer can drive the oxygen evolution for hours until the catalytic reaction ceases due to the pH dropping. We therefore believe that the sensitizer moiety of assemblies 55 and 56 may function as relays of electron transfer between the catalyst moiety and the free P+, similar to the reported result from Meyer and co-workers in which the linked Ru(bpy)32+ enhanced the activity of CeIV-driven water oxidation dramatically.88 The stabilization of the sensitizer moiety in 55 and 56 can be attributed to the second step of the relay, intramolecular oxidation, which is rather rapid in the higher oxidation states compared to the three-component systems.

All in all, such assemblies, in which a catalyst is linked to the sensitizer, allow a much faster electron transfer to both the appended sensitizer and the unbound sensitizer, compared to the case of a three-component system; as such the fast sensitizer regeneration may compete better with its decomposition pathway resulting in a much better photo-stability of the system.
5.5. Summary

Three-component systems based on various Ru-bda WOCs and Ru(bpy)$_3^{2+}$ derivatives as photosensitizer for visible light-driven water oxidation were investigated. A high TON was obtained by using system of 21-P2-S$_2$O$_8^{2-}$. Besides, serious decomposition of the sensitizer was observed limiting the stability of the corresponding three-component system. In order to achieve a more robust system for photochemical water oxidation, two assemblies 55 and 56, in which a catalyst was linked to the sensitizer by a simple C–C bond have been demonstrated as well. Complex 56 (TON of 209) affords a better activity for water oxidation than 55 (TON of 78). The combined evidence from both the photochemical catalytic measurements and the time-resolved spectroscopy indicate that the low quantum yield of the linked system (less than 10%) is due to the nonproductive intramolecular energy transfer. However, the sensitizer moieties in the linked system can function as electron relays between the catalyst unit and the unbound sensitizer, which can kinetically stabilize the sensitizers. The nonproductive mechanism can be avoided by a suitable design of the bridging ligands as well as the appended sensitizer to decrease rates of the competing reactions. Moreover, the electron recombination can be overcome by ultrafast electron injection into TiO$_2$ surface (subpicosecond scale). This may motivates further studies to build an efficient photo-anode.
Towards Water Splitting Devices—
Immobilization of WOCs on Electrodes

(Paper VI and VII)

6.1. Introduction
We have explicitly investigated the catalytic performance and mechanism of the molecular WOCs in the previous chapters by employing either strong oxidizing agent CeIV under acidic conditions or photosensitizer under light irradiation. In order to fairly assess the performance of the WOCs under practical conditions, molecular WOCs have to be embedded on conductive or semiconductor electrodes surfaces which are favorable for fabricating robust and effective water splitting devices for future application.

There are several documented approaches on functionalizing the electrodes by WOCs to achieve water oxidation anodes. However, none of them befits the bimolecular behavior of the highly efficient Ru-bda types of WOCs. Thereby, our strategy here is to introduce an immobilization method which is beneficial to the radical coupling pathway of O–O bond formation of Ru-bda types of WOCs. Figure 53 depicts the method employed in the present work. The Ru-bda catalysts were functionalized with a pyrrole which can act as an anchoring group through a flexible carbon chain, as such the catalyst can be immobilized onto the conductive surface by in situ electrochemical polymerization. Advantages of this strategy are (1) the flexible carbon chain with tunable length allows the catalysts close to each other in space which is beneficial to the radical coupling O–O bond formation; (2) the anchoring group is changeable by other alternatives; (3) the catalyst is tunable; (4) this method can be applied to various carbon or metal based alternative electrodes, such as semiconductor α-Fe2O3 which was also employed in the present study.

The results turn out that the efficiency of the modified electrodes is enhanced; however, the durability was unsatisfactory. To improve the stability, thiophene was employed as the anchoring group to replace the pyrrole. The functionalized electrodes with thiophene-appended anchoring group show much better stability towards electrochemical water oxidation.
6.2. Preparation of the Functionalized Electrodes

6.2.1. Synthesis of the Monomer Catalysts

Two pyrrole-appended pyridine ligands and the thiophene-appended pyridine were synthesized according to literature methods (Figure 54).\textsuperscript{95,96} Synthesis of similar unsymmetric structure with complexes 57-60 has been reported elsewhere, however, with a very low yield (<10%).\textsuperscript{97} In the present work, a modified synthetic method has been used with much higher yields over 60% (regarding to [Ru(bda)(DMSO)\textsubscript{2}], Figure 54): (1) [Ru(bda)(DMSO)\textsubscript{2}] was separated as an intermediate product from the reaction mixture of H\textsubscript{2}bda and cis-Ru(DMSO)\textsubscript{4}Cl\textsubscript{2}; (2) one equivalent of pyridine ligand bearing the pyrrole group was then added into the suspension solution of [Ru(bda)(DMSO)\textsubscript{2}] containing free DMSO; (3) finally, one equivalent of another axial ligand was added to the reaction mixture after the suspension turned to clear solution.
6.2.2. Immobilization of the Ru-bda WOCs

Basal-plane pyrolytic graphite electrodes with $\phi = 3\text{mm}$ (BPG) was employed as the electrode substrate in the present study. The Ru-bda WOCs 57-60 were embedded on to the carbon surface through a well-studied electrochemical polymerization method. By scanning successive CVs in the WOCs solution using the graphite electrode as the working electrode, the catalysts were
successfully immobilized on the carbon surface. After this procedure, the graphite electrode was thoroughly rinsed with absolute ethanol and distilled water in order to eliminate the physically adsorbed compounds.

6.3. The Functionalized Carbon Electrodes with Pyrrole-Appended Anchoring Group

It is important to note that both 57 and 58 are active for water oxidation using CeIV as the oxidant, affording TONs of 5360 and 4420, respectively. The kinetics results suggest that the radical coupling pathway is involved in the O–O formation by 57 and 58.

6.3.1. Electrochemical Properties

The CV curves of 57 and 58 after immobilization on the BPG electrode are presented in Figure 55. As expected, obvious redox waves that belong to the Ru complexes are clearly shown in the curves, for instance $E_{1/2}(\text{Ru}^{III/II})$ of 0.69 V (57) and 0.67 V (58), and the onset potentials at ~ 1.1 V. In contrast, the pristine BPG is almost silent in the same potential window. All of the redox potentials are summarized in Table 7. There is no remarkable difference in the electrochemical potentials of both complexes before and after immobilization, indicating the chemical structures of the immobilized Ru complexes remain very close to the corresponding monomer. Moreover, no RuO2 formation was observed during the CV scans evidenced by X-ray Photoelectron Spectroscopy (XPS).

![Figure 55. CVs of the functionalized carbon electrodes: 57@BPG, 58@BPG and pristine BPG as the reference. Conditions: 0.1 M phosphate buffer (pH 7.2, IS = 0.1), 100 mV/s of scan rate.](image)

---

58
Table 7. Redox potentials of monomer complexes 57 and 58 before and after the immobilization. RuO₂ is listed here as a reference compound.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{1/2}^{\text{ox}} (V vs. NHE)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru^{III/II}</td>
<td>Ru^{IV/III}</td>
<td>Ru^{V/IV}</td>
</tr>
<tr>
<td>57⁺</td>
<td>0.665</td>
<td>0.849</td>
<td>1.021</td>
</tr>
<tr>
<td>58⁺</td>
<td>0.636</td>
<td>0.864</td>
<td>1.032</td>
</tr>
<tr>
<td>57@BPG²⁻</td>
<td>0.688</td>
<td>0.850</td>
<td>1.066</td>
</tr>
<tr>
<td>58@BPG²⁻</td>
<td>0.672</td>
<td>0.864</td>
<td>1.058</td>
</tr>
<tr>
<td>RuO₂⁻</td>
<td>0.474</td>
<td>0.690</td>
<td>0.937</td>
</tr>
</tbody>
</table>

Conditions:  
²⁻ 0.1 M phosphate buffer solution (pH 7.2), containing 20% CF₃CH₂OH.  
²⁻ 0.1 M phosphate buffer (pH 7.2, IS = 0.1).

Since the success of catalyst immobilization was confirmed electrochemically, it is also possible to determine the surface coverage (Γ) according to the reported method (equation 6, where the number of electrons transfer n = 1, F = Faraday constant, A = surface area of the electrode, R = ideal gas constant, T = 298 K and obtained slope from the linear relationship between the peak current and the corresponding scan rates). As such, average concentrations of 4.2 × 10⁻¹⁰ and 6.8 × 10⁻¹⁰ mol/cm² were estimated for 57@BPG and 58@BPG, respectively.

Equation 6. \[ \Gamma = \frac{4RT}{n^2F^2A_{slope}} \]

6.3.2. Heterogeneous Catalytic Water Oxidation

A potential-step chronoamperometric measurement was conducted using 57@BPG as the working electrode in a standard three-electrode system. As depicted in Figure 56, a Tafel behaviour was observed by plotting the steady state current vs. tethered overpotential (η), however, with an unusual big slope of 245 mV. Moreover, the TOF values of 57@BPG at different overpotentials can be estimated by equation 7 (where Q is the integrated charge pass through the working electrode, assuming a 90% of Faradaic efficiency based on the result from bulk electrolysis). An impressive initial TOF of 0.64 s⁻¹ was obtained at η = 370 mV, which rose up to 10.47 s⁻¹ at η = 770 mV. It is a remarkable improvement compared to the previous result, 0.3 s⁻¹ at η = 600 mV based on the Ru-bda catalyst.

Equation 7. \[ \text{TOF} = \frac{1}{4 \times \frac{Q}{F \Gamma}} \]
Figure 56. Water oxidation catalysis at the surface of the functionalized BPG electrode. Left: Chronoamperometric current density measurements of 57@BPG (red line) and the pristine BPG (black line) as a reference. Right: Tafel plots of 57@BPG.

Bulk electrolysis of water was carried out for both 57@BPG and 58@BPG to confirm that the catalytic current is due to O₂ evolution. As shown in Figure 57 (Left), both functionalized electrodes affords quite high initial current density for generating O₂ with Faradaic efficiency around 90%, however, the catalytic current dropped dramatically within one hour. Although high TONs of 31600 and 20500 were respectively obtained for 57@BPG and 58@BPG, the catalytic current density decreases in the whole process, which might be due to serious dissociation of the embedded catalysts from the electrode surface. In order to improve this unsatisfactory durability, a protecting layer of polypyrrole was introduced to prevent the dissociation by simply electro-polymerization of pyrrole on 57@BPG. Figure 57 (Right) depicts the electrode stability after this modification. As expected, the stability was enhanced significantly, however, with a smaller initial catalytic current density which might be due to the increasing of the resistance at the interface and partial coverage of the catalyst on the surface.

Figure 57. Bulk electrolysis of water at applied potential 1.54 V. Left: 57@BPG (red) and 58@BPG (blue) as working electrodes. Right: 57@BPG (bule) and 57 + polypyrrole@BPG (red) as working electrodes.
6.4. The Functionalized Electrodes with Thiophene-Appended Anchoring Group

6.4.1. Electrochemical Properties

Complexes 59 and 60 were immobilized on the graphite surface by electropolymerization as well. As shown in Figure 58, CVs of both 59@BPG and 60@BPG show high catalytic current for water oxidation. Taking 60@BPG as an example, a reversible redox wave appeared at $E_{1/2} = 0.73$ V followed by the catalytic onset potential of water oxidation at around 1.2 V. By recording the CVs for this redox waves (Ru III/II) at differential scan rates, the surface coverage of 60@BPG of $9.6 \times 10^{-10}$ was estimated by using the same method as for 57@BPG.

![Figure 58. CVs of the functionalized carbon electrodes: 59@BPG, 60@BPG and pristine BPG as the reference.](image)

6.4.2. Heterogeneous Catalytic Water Oxidation by 60@BPG

The Tafel plot of 60@BPG has been made by using the same method as for 57@BPG. As shown in Figure 59 (Left), a higher TOF of 15.6 s$^{-1}$ was obtained compared to that of 57@BPG at $\eta = 770$ mV. More importantly, the durability of the working electrode is enhanced dramatically. Figure 59 (right) depicts the controlled potential water electrolysis by using working electrodes 57@BPG and 60@BPG, respectively. During one hour period of electrolysis at 1.54 V in a neutral phosphate buffer solution, polythiophene based 60@BPG remains almost 80% of the initial catalytic current density while polypyrrole based electrode remains only 20% of its initial current. This result strongly suggests that the polythiophene is a better candidate to obtain a more robust functionalized anode for water oxidation.
6.5. Photo Anode for Water Oxidation Based on Functionalized \( \alpha\text{-Fe}_2\text{O}_3 \)

As we discussed in the last chapter, light-driven water oxidation is the ultimate goal of the artificial photosynthesis. Thus, in the present work, we also conducted the photoelectron-catalytic water oxidation by using the same surface loading strategy to functionalize a commonly used semiconductor \( \alpha\text{-Fe}_2\text{O}_3 \) by complex 60. The reasons of choosing \( \alpha\text{-Fe}_2\text{O}_3 \) as the substrate photoanode are as following: (1) the band gap of \( \alpha\text{-Fe}_2\text{O}_3 \) is around 2.1 eV which is possible to be activated by visible light; (2) the valence band of \( \alpha\text{-Fe}_2\text{O}_3 \) is about 2.5 eV which is suitable for conducting the polymerization.

After functionalization of the \( \alpha\text{-Fe}_2\text{O}_3 \) electrode with complex 60, the resulting photoanode 60@\( \alpha\text{-Fe}_2\text{O}_3 \) was characterized by both SEM image and EDX spectroscopy \( \alpha\text{-Fe}_2\text{O}_3 \) surface. All the results confirm the successful immobilization of 60 on the surface of \( \alpha\text{-Fe}_2\text{O}_3 \). In order to confirm that the observed Ru-bda WOC on the \( \alpha\text{-Fe}_2\text{O}_3 \) surface can really promote the photoelectrochemical water oxidation, the chopping light linear sweep voltammetry measurement of 60@\( \alpha\text{-Fe}_2\text{O}_3 \) was carried out. As shown in Figure 60 (left), the one with Ru-bda WOC shows much higher photo-current than that of the pristine control photoanode, indicating that the catalyst increased the activity of the photoanode. At the last, a fairly stable catalytic current was obtained for 60@\( \alpha\text{-Fe}_2\text{O}_3 \) under neutral condition with 0.8 V bias, suggesting the catalyst is rather stable on the surface of the \( \alpha\text{-Fe}_2\text{O}_3 \) (Figure 60 right).
Figure 60. Left: Chopped light linear sweep voltammetry of a pristine α-Fe₂O₃ film (black curve) and after loading with catalyst 60 (red curve) in pH 7 phosphate buffer, light intensity: 100 mW cm⁻², scan rate: 10 mV/s. Right: Current density response of the photo-anode 60@α-Fe₂O₃ (red curve) and pristine α-Fe₂O₃ film (black curve) at pH 7 under a bias of 0.8 V.

6.6. Summary

The strategy of electropolymerization was successfully employed for immobilizing Ru-bda WOCs onto the conductive carbon surface and also the semiconducting α-Fe₂O₃ surface. The resulted functionalized electrodes clearly show high efficiency for catalytic water oxidation. The TON of the Ru-bda WOCs is increased dramatically after the immobilization. Unsatisfactory durability of the working electrodes was obtained when using the pyrrole-appended anchoring group; however, it can be solved by either introducing a protecting layer or replacing the pyrrole unit by the thiophene unit. Moreover, the efficiency of this type of functionalized carbon electrode is expected to be enhanced in the orders of magnitudes just by simply increasing the surface area of the substrate. Visible light-driven water oxidation was also achieved by using functionalized α-Fe₂O₃ as the photoanode. This work suggests that the method of in situ polymerization can be a promising way to immobilize water splitting catalysts onto the surface of the electrode to build efficient water splitting devices.
7.

Ni(II)-PY5 as an Electrochemical WOC

(Paper VIII)

7.1. Introduction

Although many highly efficient Ru-bda WOCs have been developed in our group, yet, ruthenium still stands as a noble metal which will restrict the large-scale application of this type of catalysts. As such, searching of WOCs on the basis of earth abundant metals is of great importance. To do that, the knowledge that we have learned from ruthenium complexes can be easily adapted and then promote the process. In this chapter, we will describe our initial efforts of developing molecular WOC based on nickel complex. Our strategy is to introduce a pentadentate ligand PY5 to ligate with the Ni$^{2+}$ ion, so that the counter ion in the resulting complex (complex 61 in Figure 61) can be replaced by a water molecule. The advantages of this Ni-PY5-Cl complex are as follows: (1) the pentadentate ligand can tightly hold the Ni center in various conditions and avoid the NiOx formation; (2) nickel has several valance states which is necessary for the catalytic water oxidation. The results turn out that the Ni-PY5-Cl loses its Cl$^{-}$ in the catalytic conditions and forms the –OH$_2$ coordinated complex Ni-PY5-OH$_2$ which acts as a robust and efficient electrochemical WOC under basic conditions. The WNA pathway was proposed for the O–O bond formation.

![Figure 61. Chemical structure of complex 61.](image-url)
7.2. Synthesis of the Complex 61

The synthetic route of the PY5 ligand and the coordination of Ni$^{2+}$ in PY5 were reported elsewhere, as shown in Figure 62. As it can be seen in Figure 63, the X-ray single-crystal structure of complex 61 reveals that the divalent nickel ion is ligated by the five pyridine subunit of PY5 and a counter ion chloride which results in nearly identical octahedron geometry. The corresponding N–Ni–N bond angles and the Ni-N bond lengths are almost identical with that of the previous reported complex.

\[
\begin{align*}
\text{Figure 62. The synthetic route of complex 61.}
\end{align*}
\]
7.3. Electrochemical Properties

The CV of complex 61 in neutral phosphate buffer is depicted in Figure 64a which shows a single reversible metal based redox process (Ni^{III}/II) at +1.41 V. This is almost 0.2 V higher than the corresponding redox waves of the documented Ni oxide under the same pH conditions. There is a sharp current rise following these reversible redox waves which is most likely due to the oxidation of water. Indeed, the catalytic current increased dramatically at pH 10.8 in comparison with that at pH 7.0. The CV of 61 recorded in CH$_3$CN shows three different redox processes assigned as Ni^{III}/II at 0.6 V, Ni^{IV}/III at 1.16 V, and Ni$^{V/IV}$ at 1.43 V respectively (Figure 64b). The big peak separation of the quasi reversible Ni^{III}/II at 0.3 V is most likely due to the ligand exchange process from Cl ion to CH$_3$CN. When 5% of phosphate buffer (v:v) was introduced into the CH$_3$CN solution, a catalytic current was observed at the position of Ni$^{V/IV}$ indicating that the Ni$^V$ species triggers the oxygen evolution. The $E_{1/2}$ value of Ni^{III}/II was anodically shifted by 0.25 V; however the $E_{1/2}$ value of Ni$^{IV/III}$ remains the same.

![Figure 64](image)

**Figure 64.** (a) The CV curves of 61 (0.5 mM) in aqueous of phosphate buffer (0.2 M) at pH 7 and pH 10.8. (b) 61 in CH$_3$CN.

Additional CVs at variable pH were obtained (Figure 65a). The catalytic current increased dramatically along with increasing pH, and meanwhile the potential of the redox couple Ni^{III}/II dropped by ~59 mV per pH unit (Figure 65a) revealing a 1H$^+$/1e$^-$ PCET process. The shape of the redox waves remains the same indicating that complex 61 is stable over the pH range of 7-11. To further study the PCET process, a Pourbaix diagram shown in Figure 65b was also constructed for complex 61 over the pH range of 6.2 – 12.0. The first metal-based oxidation process appears at 1.49 V at pH 6.2 and it exhibits a pH dependency of ca. – 61 mV/pH up to pH 12.0. As such, this pH dependent redox couple is assigned as the PCET process of [Ni^{III–OH}]$^{2+}$/[Ni^{II–OH}$_2$]$^{2+}$ couple. The second metal-based oxidation process appears in the DPV curve at + 1.72 V at pH 6. For this pH dependent redox couple, a slope of –27 mV/pH is consistent with a 2 e$^-$/H$^+$ PCET process of [Ni$^V$–O]$^3+$/[Ni^{III–OH}]$^{2+}$.
7.4. Kinetics and Mechanistic Study of Catalytic Water Oxidation by Complex 61

The kinetics studies of water oxidation by 61 were conducted electrochemically. First, scan rate dependent CVs were conducted in a pH 10.8 (0.2 M phosphate buffer, I = 0.5 M) aqueous solution. As expected, the peak current \(i_p\) Ni\(^{III/II}\) couple at \(E_{1/2} = 1.41\) V increase linearly with \(v^{1/2}\) (Figure 66a). This linear relationship is so-called the Randles-Sevcik relation (equation 8),\(^{98}\) on the basis of this diffusion-controlled electron transfer, the diffusion coefficient of complex 61 can be determined as \(D \approx 1.04 \times 10^{-6}\) cm\(^2\) s\(^{-1}\).\(^{98}\) Based on Equation 9, by recording the ratio of \(i_{\text{cat}}/i_p\) (at 1.6 V), the catalytic reaction rate \(k_{\text{cat}}\) for water oxidation was calculated to be 145 s\(^{-1}\) (water as the substrate, meaning the TOF = 145 s\(^{-1}\)), as shown in Figure 66b.

\[
i_p = 0.446nFANi^{II}\left(nFD/RT\right)^{1/2}
\]

\[
i_{\text{cat}} = n'FA[Ni^{II}](Dk_{\text{cat}})^{1/2}
\]

Figure 65. (a) Normalized CVs of the reversible redox waves of Ni\(^{III/II}\) at different pH conditions. (b) Pourbaix diagram of complex 61. The potential values were obtained from its DPVs at different pH.

Figure 66. Scan rate dependence measurement. (a)Plot of \(i_p\) as function of \(v^{1/2}\). (b)Plot of \(i_{\text{cat}}/i_p\) vs \(1/v^{1/2}\). \(i_{\text{cat}}\) was measured at 1.60 V. Conditions: 0.5 mM complex 61, pH 10.8 phosphate buffer.
Figure 67. (a) Plot of peak current at $E_{1/2}$ ($\text{Ni}^{III/II}$) vs. the concentration of the complex 61. (b) Plot of catalytic current at 1.6 V vs. concentration of the catalyst 61.

Figure 67 depicts the electrode kinetics in complex 61. CV curves of complex 61 were recorded at various concentrations, and the peak current of $E_{1/2}$ ($\text{Ni}^{III/II}$) affords a linear relation against the concentration of 61, implying a diffusion controlled electrode reaction for this redox process. As shown in Figure 67b, the catalytic current is increase linearly upon increasing the concentration of complex 61 at its low concentrations range (<1.0 mM), suggesting that the O–O formation goes through WNA pathway. However, the slope levels off at relative higher concentrations (>1.0 mM), which is most likely due to that the rate limiting step of the catalytic reaction changed from the mass diffusion to the electron transfer on the electrode surface.

It has been studied that the phosphate buffer can assist water oxidation catalysis by the fact of Atom-Proton Transfer (APT) effect. In order to study this APT effect in our case, we assume that $k_{\text{cat}}$ is composed of two components $k_{\text{H}2\text{O}}$ (rate constant for the unassisted water oxidation) and $k_{\text{B}}$ (rate constant for the base assist water oxidation). Then equation 10 can be derived from equation 8 and 9.

**Equation 10.**

$$\left( \frac{i_{\text{cat}}}{i_p} \right)^2 = \frac{0.024}{V} \left( k_{\text{H}2\text{O}} + k_{\text{B}} \right)$$

By plotting the dependence of the parameter $(i_{\text{cat}}/i_p)^2$ against [B], a nice linear relationship was obtained which is in good agreement with Equation 9. As such, $k_{\text{B}}$ and $k_{\text{H}2\text{O}}$ were calculated as 1820 M$^{-1}$s$^{-1}$ and 21 s$^{-1}$ respectively, based on the slope and the intercept of the curve. In another word, the TOF for water oxidation can reach to ~2000 s$^{-1}$ when 1.0 M phosphate buffer is employed. Based on the combined evidence, we can summarize some key features of the water oxidation catalysis by 61: (1) the pourbaix diagram indicates a formally
oxidation sequence of $[\text{Ni}^{II}-\text{OH}_2]^{2+} \rightarrow [\text{Ni}^{III}-\text{OH}]^{2+} \rightarrow [\text{Ni}^{V}=\text{O}]^{3+}$ under catalytic conditions; (2) WNA is the dominant pathway for the $\text{O}−\text{O}$ formation, and it is reasonable to believe that the rate determining step of the $\text{O}−\text{O}$ bond formation is assisted by APT from phosphate buffer. As such, we proposed a catalytic cycle of water oxidation by 61 as shown in Figure 68.

![Figure 68. Proposed pathway for water oxidation by 61.](image)

7.5. Water Oxidation Performance of 61 and Description of Its Molecular Properties

To evaluate the performance of complex 61, long term bulk electrolysis of water was carried out with applied potential 1.5 V on a carbon working electrode (~1 cm$^2$). The generated $\text{O}_2$ was confirmed and quantified by GC, which affords a TON of 19 over a period of 10 h (Faradaic efficiency of 92% for $\text{O}_2$ evolution). A common concern for molecular Ni WOCs as well as other cheap metal based molecular WOCs is the stability of the catalysts under the oxidizing environment; the formation of metal oxides should be excluded to ensure the catalysts work as a molecular form. Several techniques and control experiments have been carried out in the present work to exclude the NiO formation. For instance, dynamic light scattering (DLS) and X-ray photoelectron spectroscopy measurements rule out the NiO formation in the bulk solution or on the electrode surface. Most importantly, we have also obtained a single crystal from the bulk solution after electrolysis. The X-ray crystal structure reveals that the PY5 ligand is still coordinating to the Ni ion as expected, however, the $−\text{Cl}$ is replaced by a $−\text{OH}_2$, suggesting that Ni-PY5-Cl is a pre-catalyst and the true catalyst in the catalytic cycle is Ni-PY5-OH$_2$. 
7.6. Summary

A novel Ni WOC (61) was prepared and characterized. Electrochemical properties and kinetics studies conducted for 61 point to a WNA pathway for the O–O bond formation. Water oxidation catalyzed by 61 was carried out at pH 10.8 in phosphates buffer with high catalytic rate constant and impressive catalyst stability. Homogeneous electrocatalysis of water oxidation by 61 was proved by various techniques including DLS, XPS and electrochemistry. Ligand exchange from Cl− to H2O− has been evidenced by the X-ray single crystal structure of [Ni-PY5-OH2] which was obtained from the bulk solution after electrolysis.
8. Concluding Remarks and Future prospects

This thesis focused on the catalytic water oxidation half reaction by molecular catalysts. The first half of the thesis (chapter 2-4) investigated the correlations between structure and activities of Ru-bda types of WOCs. It has been studied before, that the success of equatorial ligand bda$^{2-}$ is the fine balance between the inter- and intra-molecular electron transfer.\textsuperscript{vii} Thereby, my thesis work was mainly focusing on the axial ligands modification. The results suggest that electron withdrawing and hydrophobic effects facilitate both the activity and the durability of the catalysts. The electron withdrawing axial ligands can promote the intramolecular transfer, while hydrophobic axial ligands can benefit the coupling of two units of Ru$^{V=O}$ (RDS) in aqueous solution. The imidazole/DMSO pair of axial ligands (chapter 4) provides a very interesting perspective for designing water soluble WOCs, by which the co-solvent is not necessary. It is the sterically unhindered axial ligands which can afford the similar effect as the hydrophobic one, thus enhancing the activity of the catalysts.

In the view of artificial photosynthesis, the following part of the thesis presents the attempts of applying our Ru-bda WOCs into photosystem and on functional devices. The key information we gained from the light-driven water oxidation studies is that the electron transfer from the catalysts to the sensitizer has to be efficient. So far, this sluggish electron transfer is the main reason that results in the unsatisfactory photo-stability and relatively low activity. However, it is possible to improve this electron transfer rate by fine molecular engineering.

\textit{In situ} polymerization was introduced to immobilize the Ru-bda catalysts in order to keep their coupling nature during the catalysis. Indeed, higher efficiency of the functionalized electrode was obtained.

Finally, with the view of low cost WOCs for the future application, WOC Ni-PY5 based on the first row transition metal complex was developed. Detailed mechanistic studies provide insight into the O–O bond formation.

Actually, there are much more researchers focusing on heterogeneous WOCs, for instance, metal oxides, hydrotalcite as well as perovskite. In fact, many heterogeneous based WOCs exhibit extremely high activities as well as excellent durability, and this is the major advantage of them compared to molecular WOCs.\textsuperscript{101,102} However, I am still confident that molecular catalysts

\textsuperscript{vii} Intramolecular electron transfer: from the oxygen atom (the one in the reaction intermediates of metal oxo or peroxo) to the metal center.

Intermolecular electron transfer: from the catalysts to the electron acceptor.
are still promising. Dye-sensitized solar cells are one of the perfect examples which achieve high efficiency based on molecular components. Now days, it can reach over 13 % of efficiency with excellent durability. One of the promising approach is the so called dye-sensitized photoelectrochemical (PEC) cell, despite it is still evolving.\textsuperscript{103} Although, the efficiency of the solar energy conversion of PEC cell is miserable thus far, I am positive that it can be improved dramatically as long as the fine balance of the kinetics between the different moieties in the cell is established.

The development of novel and efficient catalysts is still the key for artificial photosynthesis regardless which approach is taken. In terms of a qualified catalyst, several crucial parameters have to be considered: low overpotential, high reactivity, great stability and of course low cost. That is exactly the goal I have pursued in this thesis. Certainly, the recent progresses are not even close to the real application of artificial photosynthesis; however, I am confident that they will establish a way to the sustainable energy system.
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Appendix A

The following is a description of my contribution to Publications I to VIII, as requested by KTH.

Paper I: I performed some of the oxygen evolution and electrochemical measurements, and was involved in the discussion as well as the writing of the paper.

Paper II-VIII: My contribution is the initiation of these projects, most of the synthetic, catalytic measurements, mechanistic studies and writing of the major part of the papers.
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