Mononuclear Ruthenium Complexes that Catalyze Water to Dioxygen Oxidation

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Doctoral Thesis

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Dedicated to my daughter and wife.
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Abstract

The theme of this thesis is the development of mononuclear Ru-based complexes that are capable of catalyzing the water oxidation (or O₂-evolving) reaction, e.g. \(2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-\). Several families of mononuclear Ru water oxidation catalysts were designed and prepared. They feature with anionic ancillary ligands that contain carboxylate or phenolate donors. The properties of the catalysts were investigated in various aspects including coordination geometry, electrochemical behavior, and ligand exchange. All catalysts showed outstanding catalytic activity towards water oxidation in the presence of cerium(IV) ammonium nitrate as a sacrificial oxidant. High-valent Ru intermediates involved in the reactions were characterized both experimentally and theoretically. The kinetics of catalytic water oxidation was examined based on one catalyst and a prevailing catalytic pathway was proposed. The catalytic cycle involved a sequence of oxidation steps from Ru\(^{\text{II}}\)–OH₂ to Ru\(^{\text{V}}\)=O species and O–O bond formation via water-nucleophilic-attack to the Ru\(^{\text{V}}\)=O intermediate. By comparing properties and catalytic performance of Ru catalysts herein with that of previously reported examples, the effect of anionic ancillary ligands was clearly elucidated in the context of catalytic water oxidation. Aiming to further application in an envisaged artificial photosynthesis device, visible light-driven water oxidation was conducted and achieved primarily in a homogeneous three-component system containing catalyst, photosensitizer, and sacrificial electron acceptor. Moreover, one model Ru catalyst was successfully immobilized on ordinary glass carbon surface through a facile and widely applicable method.

Keywords: Ruthenium complex, Homogeneous catalysis, Water oxidation, \(\text{O}_2\) evolution, Anionic ligand, Molecular catalyst, Electrocatalysis, Kinetics, Artificial photosynthesis, Light-driven, Immobilization of catalyst.
## Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>ADP</td>
<td>adenosine diphosphate</td>
</tr>
<tr>
<td>APS</td>
<td>artificial photosynthesis</td>
</tr>
<tr>
<td>ATP</td>
<td>adenosine triphosphate</td>
</tr>
<tr>
<td>bcbpy</td>
<td>4,4’-bis(ethoxycarbonyl)-2,2’-bipyridine</td>
</tr>
<tr>
<td>bda</td>
<td>2,2’-bipyridine-6,6’-dicarboxylate ligand</td>
</tr>
<tr>
<td>bpm</td>
<td>2,2’-bipyrimidine</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2’-bipyridine</td>
</tr>
<tr>
<td>Btu</td>
<td>British thermal unit</td>
</tr>
<tr>
<td>CAN</td>
<td>cerium(IV) ammonium nitrate, Ce(NH₄)₂(NO₃)₆</td>
</tr>
<tr>
<td>Cp*</td>
<td>pentamethylcyclopentadiene</td>
</tr>
<tr>
<td>CuAAC</td>
<td>copper-catalyzed azide-alkyne cycloaddition</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DPV</td>
<td>differential pulse voltammetry</td>
</tr>
<tr>
<td>$E^0$</td>
<td>standard potential of an electrode, a couple or a half reaction</td>
</tr>
<tr>
<td>$E^{1/2}$</td>
<td>measured or expected half-wave potential in voltammetry</td>
</tr>
<tr>
<td>epc</td>
<td>4-ethynylpyridine-2,6-dicarboxylate ligand</td>
</tr>
<tr>
<td>ET</td>
<td>electron transfer</td>
</tr>
<tr>
<td>FNR</td>
<td>ferredoxin nicotinamide adenine dinucleotide phosphate reductase</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GtC</td>
<td>gigaton of carbon</td>
</tr>
<tr>
<td>Hbpp</td>
<td>3,5-bis(2-pyridyl)pyrazole</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>H2cppd</td>
<td>1,4-bis(6’-carboxylate-pyrid-2’-yl)-pyridazine acid</td>
</tr>
<tr>
<td>H2cpph</td>
<td>1,4-bis(6’-carboxylate-pyrid-2’-yl)-phthalazine acid</td>
</tr>
<tr>
<td>hqc</td>
<td>8-hydroxyquinoline-2-carboxylate ligand</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IS</td>
<td>ionic strength</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>MeCN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MLCT</td>
<td>metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>NADP⁺</td>
<td>ferredoxin nicotinamide adenine dinucleotide phosphate</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>NPS</td>
<td>natural photosynthesis</td>
</tr>
<tr>
<td>OEC</td>
<td>oxygen-evolving complex of photosystem II</td>
</tr>
<tr>
<td>OECD</td>
<td>Organization for Economic Cooperation and Development</td>
</tr>
<tr>
<td>P680</td>
<td>pigment (chlorophyll) that absorbs 680 nm light, the primary electron donor of PSII</td>
</tr>
<tr>
<td>P700</td>
<td>pigment (chlorophyll) that absorbs 700 nm light, the primary electron donor of PS I</td>
</tr>
<tr>
<td>PCET</td>
<td>proton-coupled electron transfer</td>
</tr>
<tr>
<td>pda</td>
<td>1,10-phenanthroline-2,9-dicarboxylate ligand</td>
</tr>
<tr>
<td>pdc</td>
<td>2,6-pyridinedicarboxylate ligand</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>PRC</td>
<td>proton reduction catalyst</td>
</tr>
<tr>
<td>PS</td>
<td>photosensitizer</td>
</tr>
<tr>
<td>PS II</td>
<td>photosystem II</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
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<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PS I</td>
<td>photosystem I</td>
</tr>
<tr>
<td>PT</td>
<td>proton transfer</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>pynp</td>
<td>2-(pyrid-2'-yl)-1,8-naphthyridine</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>TBTA</td>
<td>tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2’;6’,2”-terpyridine</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>WNA</td>
<td>water nucleophilic attack</td>
</tr>
<tr>
<td>WOC</td>
<td>water oxidation catalyst</td>
</tr>
<tr>
<td>$\eta$</td>
<td>overpotential</td>
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List of Publications

This thesis is based on the following papers, referred to in the text by their Roman numerals I-V:

I. **Structural Modifications of Mononuclear Ruthenium Complexes: A Combined Experimental and Theoretical Study on the Kinetics of Ruthenium-Catalyzed Water Oxidation**
   Lianpeng Tong, Lele Duan, Yunhua Xu, Timofei Privalov, and Licheng Sun

II. **Water Oxidation Catalysis: Influence of Anionic Ligands upon the Redox Properties and Catalytic Performance of Mononuclear Ruthenium Complexes**
    Lianpeng Tong, Ying Wang, Lele Duan, Yunhua Xu, Xiao Cheng, Andreas Fischer, Mårten S. G. Ahlquist, and Licheng Sun

III. **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
     *Submitted manuscript.*

IV. **Visible Light-driven Water Oxidation Catalyzed by a Highly Efficient Dinuclear Ruthenium Complex**
    Yunhua Xu, Lele Duan, Lianpeng Tong, Björn Åkermark, and Licheng Sun

V. **Oxygen Evolution at Functionalized Carbon Surfaces: a Strategy for Immobilization of Molecular Water Oxidation Catalysts**
   Lianpeng Tong, Mats Göthelid, and Licheng Sun
Papers not included in this thesis:

VI. Chemical and Photochemical Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes with a Negatively Charged Tridentate Ligand
Lele Duan, Yunhua Xu, Mikhail Gorlov, Lianpeng Tong, Samir Andersson, and Licheng Sun

VII. Chemical and Light-Driven Oxidation of Water Catalyzed by an Efficient Dinuclear Ruthenium Complex
Yunhua Xu, Andreas Fischer, Lele Duan, Lianpeng Tong, Erik Gabrielsson, Björn Åkermark, and Licheng Sun

VIII. CeIV- and Light-Driven Water Oxidation by [Ru(terpy)(pic)3]2+ Analogues: Catalytic and Mechanistic Studies
Lele Duan, Yunhua Xu, Lianpeng Tong, and Licheng Sun

IX. Synthesis and Catalytic Water Oxidation Activities of Ruthenium Complexes Containing Neutral Ligands
Yunhua Xu, Lele Duan, Torbjörn Åkermark, Lianpeng Tong, Bao-Lin Lee, Rong Zhang, Björn Åkermark, and Licheng Sun

X. Visible Light-driven Water Oxidation—from Molecular Catalysts to Photoelectrochemical Cells (review)
Lele Duan, Lianpeng Tong, Yunhua Xu, and Licheng Sun
Author’s Contribution

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

Paper I: I contributed to the formulation of the research problems, performed all synthesis and a majority of experimental measurements, and wrote the experimental part of the manuscript.

Paper II: I contributed to the formulation of the research problems, performed all synthesis and a majority of experimental measurements, and wrote the experimental part of the manuscript.

Paper III: I contributed to the formulation of the research problems, performed most experiments and wrote the manuscript.

Paper IV: I contributed to the synthesis of photosensitizers, performed parts of experimental measurements and involved in writing of the manuscript.

Paper V: I contributed to the formulation of the research problems, performed most experiments and wrote the manuscript.
# Table of Contents

Abstract .............................................................................................................................. I
Abbreviations .................................................................................................................... II
List of Publications ......................................................................................................... V
Author’s Contribution ...................................................................................................... VII

1. **Introduction** ........................................................................................................... 1
   1.1 World Energy Demand—an Outlook ................................................................. 1
   1.2 Global Climate Change—the Crisis ................................................................. 3
   1.3 Solar Energy—an Opportunity ......................................................................... 6
   1.4 Photosynthesis, Natural and Artificial .............................................................. 6
   1.5 Water Oxidation Catalyzed by the OEC ........................................................... 9
   1.6 Water Oxidation by Artificial Catalysts, Heterogeneous and Homogeneous .......... 11
   1.7 Molecular Water Oxidation Catalyst ............................................................... 12
      1.7.1 Multinuclear ruthenium-based WOCs ...................................................... 13
      1.7.2 Mononuclear Ruthenium-Based WOCs ............................................... 17
      1.7.3 First-Row Transition-Metal-Based WOCs ............................................ 23
      1.7.4 Iridium-Based WOCs ............................................................................ 24
   1.8 Aim of this Thesis .............................................................................................. 25

2. **Mononuclear Ru WOCs with Tetradeutate Anionic Ligands** ...................................... 27
   2.1 Introduction .......................................................................................................... 27
   2.2 Synthesis and Characterization of Ru-pda WOCs .............................................. 29
2.3 Spectral Properties of Ru-pda WOCs ........................................... 33
2.4 O$_2$ Evolution and Mechanism Discussion ................................. 34
2.5 Summary ....................................................................................... 36

3. Mononuclear Ru WOCs with Tridentate Anionic Ligands (Part One) ......................................................................................... 39
  3.1 Introduction .................................................................................. 39
  3.2 Synthesis and Structure of the Ru-hqc Complex ......................... 40
  3.3 Labile Picoline Ligand ................................................................. 41
  3.4 Electrochemical Analysis of Ru-pdc and Ru-hqc WOCs .............. 44
  3.5 O$_2$ Evolution by the Ru-hqc WOC ............................................. 47
  3.6 Summary ....................................................................................... 48

4. Mononuclear Ru WOCs with Tridentate Anionic Ligands (Part Two) ......................................................................................... 49
  4.1. Introduction .................................................................................. 49
  4.2 Synthesis and Structures of Ru-bpc WOCs ................................ 50
  4.3 Spectral and Electrochemical Properties of Ru-bpc Complexes .. 52
  4.4 Labile Picoline Ligand ................................................................. 55
  4.5 O$_2$ Evolution Catalyzed by Ru-bpc Complexes ......................... 58
  4.5 Kinetics Study of Water Oxidation by Ru-bpc WOCs ............... 59
  4.6 Analysis of Intermediates by MS .................................................. 65
  4.7. Description of Catalytic Cycle for the Ru-bpc WOC ............... 67
  4.8 Summary ....................................................................................... 69

5. Visible-Light Driven Water Oxidation ........................................... 71
  5.1 Introduction .................................................................................. 71
5.2 Synthesis and Oxidation Potential of \([\text{Ru}^{II}(\text{bpy})_3]^{2+}\) Type Photosensitizers ........................................................................................................ 72

5.3 Visible-Light Driven Water Oxidation by Ru WOCs .................. 73
5.3.1 Visible-Light Driven Water Oxidation Involving Ru-pda WOCs .... 73
5.3.2 Visible-Light Driven Water Oxidation Involving the Ru-hqc WOC 74
5.3.3 Visible-Light Driven Water Oxidation Involving the Ru2-cpph WOC . ........................................................................................................ 76

5.4 Summary............................................................................................. 77

6. Immobilization of Molecular WOC on Conductive Carbon Surface ............................................................................................................. 79
6.1 Introduction .......................................................................................... 79
6.2 Preparation of WOC Functionalized Carbon Electrode ............... 80
6.2.1 Synthesis of the Ru-epc Complex .......................................................... 80
6.2.2 Modification of Glass Carbon Surface ............................................. 80
6.2.3 Coupling of Azide-Modified Glass Carbon and the Ru-epc Complex . ........................................................................................................ 81
6.3 Properties of WOC-Functionalized Carbon Surface .................. 81
6.4 Water Oxidation at WOC-Functionalized Carbon Surface ........... 83
6.5 Summary............................................................................................. 85

7. Concluding Remarks........................................................................... 87

Acknowledgement....................................................................................... 89

Appendices................................................................................................ 91

Appendix A. Structures of Selected Ancillary Ligands ...................... 91
Appendix B. Apparatus that Used to Detect \(\text{O}_2\) Evolution ................. 92

References.................................................................................................... 93
1. Introduction

The issue of catalytic water oxidation (or O₂ evolution) reaction as the key process in photosynthesis is rising in the context of pursuing sustainable and carbon-neutral energy.

1.1 World Energy Demand—an Outlook

The society of humankind has developed on our demand and consumption of energy, from the flaring campfire in an ancient tribe to the spectacular momentum of a modern space shuttle. And this demand has been rising all the way with the expansion of population, progress of technology and growth of economy. According to the statistics of U.S. Energy Information Administration (EIA) and International Energy Agency, global marketed energy consumption per year has grown by 43 percent from 354 quadrillion British thermal units (Btu)i in 1990 to 505 quadrillion Btu (5.3 × 10²⁰ J) in 2008.[1] In the near future, it is very unlikely that the trend of accelerating energy consumption will reverse. The International Energy Outlook 2011 (IEO2011) reference case projects a world energy consumption of 770 quadrillion Btu in 2035 (Figure 1.1), which is corresponding to an average annual rate of 1.6 percent increment based on the level of energy consumption in 2008.[1] Most of the increase in energy consumption is estimated to be contributed by countries outside the Organization for Economic Cooperation and Development (non-OECD nations), ii where demand is driven by predicted strong long-term economic growth.

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i The British thermal unit (Btu) is defined as the amount of heat required to raise the temperature of 1 pound (0.454 kg) of water by 1 °F (0.556 °C) at a constant pressure of one atmosphere. 1 Btu is equal to about 1,055 joules (J).

ii Current OECD member countries (as of September 1, 2010) are the United States, Canada, Mexico, Austria, Belgium, Chile, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Poland,
Figure 1.1. World energy consumption, 1990-2035 (in quadrillion Btu). Reprinted with permission from *IEO2011*. [1]

If we look at the world energy consumption from the aspect of fuel type, it is not surprising to find that fossil fuels have always been the major energy source of the world (Figure 1.2). Fossil fuels in all, including coal, natural gas and liquids fuels (mostly petroleum based), supplied 85 percent of the energy used worldwide in 2008. [1] Their share of total energy consumption is predicted to be declining but keeping dominant throughout the period from 2008 to 2035. Despite a predicted fast-growing rate in the following decades, the renewable energy share in total energy consumption will probably reach only 14 percent in 2035. [1]

Figure 1.2. World energy consumption by fuel type (in quadrillion Btu). Reprinted with permission from *IEO2011*. [1]

Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey, the United Kingdom, Japan, South Korea, Australia, and New Zealand.
Assessing accurate reserves of fossil fuels on earth is an extremely difficult task, because there are new resources explored every year and some reported resources can’t be proved due to political or economic reasons. However, the following data may provide a benchmark for consideration: proved world crude-oil reserves were estimated to be 1471 billion barrels by 2011 and the world crude-oil production of 2009 is 30.6 billion barrels; natural gas reserves 6,675 trillion cubic feet by 2011 and the production of 2009 105.6 trillion cubic feet; coal reserves 948 billion tons by 2009 and the production of 2008 7.5 billion tons.\(^1\) If no other sources of energy replace the role of fossil fuels in the future, a straightforward conclusion can be obtained from simple division between estimated reserves of fossil fuels and their current annual production: fossil oil and natural gas will not be available after the end of this century and coal will be depleted in next century.

### 1.2 Global Climate Change—the Crisis

Increased concentration of CO\(_2\) in the global atmosphere is one of the most urgent and critical environmental issues today. Since the atmospheric CO\(_2\) began to be continuously and directly measured at 1960s, the atmospheric CO\(_2\) concentration was found to grow at an average rate of 1.4 ppm\(^{iii}\) per year and reach 379 ppm in 2005.\(^2\) The annual rate of CO\(_2\) concentration growth during the last 10 years (1995–2005) was even larger than 1.9 ppm per year. Studies based on the EPICA (European Project for Ice Coring in Antarctica) Dome Concordia ice core indicated an atmospheric CO\(_2\) concentration range from 210 to 300 ppm in the past 650,000 years.\(^3\) Intergovernmental Panel on Climate Change (IPCC) collected multiple data sources and analyzed the tendency of atmospheric CO\(_2\) concentration change over the last 10,000 years as showed in Figure 1.3.\(^4\)

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\(^{iii}\) ppm (part per million) is the ratio of the number of CO\(_2\) gas molecules to the total number of molecules of dry air.
Figure 1.3. Atmospheric concentrations of carbon dioxide over the last 10,000 years and since 1750 (inset). Reprinted with permission from IPCC.\textsuperscript{[4]}

The increase of global atmospheric CO\textsubscript{2} concentration since the industrial revolution is primly ascribed to CO\textsubscript{2} emissions from fossil fuels consumption and cement production. A pronounced evidence for this conclusion is the decreasing $^{13}$C/$^{12}$C isotopic ratio of atmospheric CO\textsubscript{2} measured since 1980s (Figure 1.4), because the fossil-derived CO\textsubscript{2} has lower $^{13}$C/$^{12}$C isotopic ratios than that originally in the atmosphere.\textsuperscript{[4, 5]} Furthermore, the change of $^{13}$C/$^{12}$C isotopic ratio is consistent with the trends of global fossil CO\textsubscript{2} emission\textsuperscript{iv} per year that has increased by 70\% over the last 30 years.\textsuperscript{[6, 7]} Without consideration of any possible political regulation proclaimed in the future, the annual fossil CO\textsubscript{2} emissions is estimated to increase from 6.9~7.5 GtC\textsuperscript{v} per year in 2000–2005 to 13.5 GtC per year at 2050.\textsuperscript{[8]}

\textsuperscript{iv} Fossil carbon dioxide emissions include those from the production, distribution and consumption of fossil fuels and as a by-product from cement production. An emission of 1 GtC corresponds to 3.67 GtCO\textsubscript{2}.

\textsuperscript{v} Gigaton of carbon.
Although there is still some controversy, the increasing CO₂ concentration along with other anthropogenic greenhouse gas is very likely\(^{vi}\) attributed to the global warming since the mid-20th century and correlated to the following direct observations of recent climate changes:\(^{[9]}\)

1. Warmer and fewer cold days and nights over most land areas (very likely).
2. Warmer and more frequent hot days and nights over most land areas (very likely).
3. Frequency of warm spells/heat waves increases over land areas (likely\(^{vii}\)).
4. Frequency of heavy precipitation events (or proportion of total rainfall from heavy falls) increases over most areas (likely).
5. Area affected by droughts increases (likely in many regions).
6. Intense tropical cyclone activity increases (likely in many regions).
7. Tropospheric warming and stratospheric cooling (very likely).

\(^{vi}\) > 90% probability.
\(^{vii}\) > 66% probability.
1.3 Solar Energy—an Opportunity

To meet the scenario of energy consumption and avoid the potential environmental disaster, development of sustainable and carbon-neutral energy is requisite as an alternative of fossil fuels. Solar energy definitely meets these two requirements. The incoming solar radiation that reaches the upper atmosphere of earth in one hour corresponds to \(6.3 \times 10^{20} \text{ J}\), more than the global energy consumption in the whole year of 2008. The supply of solar energy, of course, is ceaseless and unbidden. However, direct solar energy only contributes a very small fraction (≤ 0.1%) of global energy consumption by the year 2009.

Because sunshine is dispersive and transient, utilization of solar energy has to be considered from two aspects: conversion and storage. Solving both issues in cost-effective approaches that can compete with traditional fossil fuels is challenging but essential to reduce the large gap between our limited exploitation of solar energy nowadays and its enormous potential.

1.4 Photosynthesis, Natural and Artificial

Natural photosynthesis (NPS) provides a blueprint for solar energy utilization to human beings. Through NPS, green plants convert solar energy into chemical energy and store it in the form of chemical bonds. The light-dependent reaction of NPS that directly relates to solar energy utilization includes three key processes: light harvesting, charge separation and catalytic reactions. The whole process of light-dependent reaction, known as ‘Z-scheme’ (shown in Figure 1.5), is accomplished in two connected functional systems: photosystem II (PS II) and photosystem I (PS I). In principle, P680 of PS II creates a light-induced charge separation, the excited electron is transferred to PS I through an electron transport chain and meanwhile one electron is extracted from the water oxidation reaction catalyzed by the oxygen-evolving complex (OEC); the donated electron from PS II is excited to a higher energy level by P700 of PS I and transferred to FNR (ferredoxin nicotinamide adenine dinucleotide phosphate reductase) where the NADP\(^+\) is
reduced. Proton gradient across the membrane which derives from the electron transfer process provides energy to the conversion of ADP to ATP.

**Figure 1.5.** Schematic diagram of light reactions of NPS (a simplified Z-scheme), including PS II and PS I. The red arrows show the pathway of electron flow.

**Figure 1.6.** Schematic diagram of reactions of APS (simplified electron flows): (a) integrated assembly; (b) photochemical cell.

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VIII Tyr = tyrosine; Pheo = pheophytin, the primary electron acceptor of PSII; \( \text{Q}_a \) = primary plastoquinone electron acceptor; \( \text{Q}_b \) = plastoquinone; Cyt b6f = cytochrome b6f complex, consisting of an Fe-S Rieske center, cytochrome f (Cyt f), cytochrome b low- and high-potential forms (Cyt bLP and Cyt bHP) and plastoquinone binding sites (PC); A0 = chlorophyll, primary electron acceptor of PS I; A1 = phylloquinone; Fx, Fa, Fb = three separated iron sulphur protein; FD = ferredoxin.
The net result of light-dependent reaction of NPS is transportation of protons and electrons via a series of light-driven processes: water to dioxygen oxidation donating electrons on one side, and production of energy-carrying agents (ATP and NADPH) accepting electrons on the other side. These reducing agents can readily liberate and provide energy to the light-independent (or “dark”) reaction of NPS where CO₂ is fixed and converted to dry carbon matter, glucose especially.

Artificial photosynthesis (APS) is a system that is able to mimic the solar-to-chemical energy conversion process of NPS with man-made materials. Currently, two appealing strategies are conceived for the achievement of APS (Figure 1.6).[^13-16] One is an integrated assembly, in which light-induced charged separation is quenched by electron-donating and electron-accepting reactions simultaneously.[^17, 18] The other is a photochemical cell, in which the excitation site attaches to one or both electrodes and the electrons flow from the anode, where oxidation (electron-donating) reaction happens, to the cathode, where reduction (electron-accepting) reaction occurs, via a redox couple or conductive wire.[^19-22] Despite different schemes of APS system, they all share the same functional components of light harvesting, charge separation and catalytic reactions corresponding to those of NPS.

The significant difference between APS and NPS is that an artificial system does not have to comply with biological rules for organisms. For example, the role of light harvesting and charge separation in APS can be played by a molecular chromophore,[^23] a semiconductor[^24, 25] or a hybrid material[^26] that are unavailable to cells of green plants owing to limitations of biological properties. While water seems to be the only sustainable and carbon-neutral substrate for electron-donating reaction, human beings indeed have more options at the electron-accepting side than nature. Compared with the elegant but extremely sophisticated process of dark reaction of NPS that converts CO₂ to glucose, the following pathways are more economical and feasible with regard to energy storage: (i) reduction of protons to hydrogen (applied as an instance in Figure 1.6),[^27] and (ii) reduction of CO₂ to CO, methanol, or methane.[^28]
There is no doubt that duplicating any functional components of NPS artificially is a tremendous challenge and deserves enormous effort from multiple disciplines. The work in this thesis focuses on the catalytic water oxidation reaction that provides electrons and protons in an APS system.

### 1.5 Water Oxidation Catalyzed by the OEC

The water oxidation (Equation 1.1) is a thermodynamically demanding half-reaction with a standard potential $E^0 = 1.23$ V vs. NHE (normal hydrogen electrode)\(^{ix}\) at pH 0. As an example of proton-coupled processes, its standard potential decreases with pH increment of reaction medium according to the Nernst equation ($E = E^0 - 0.059 \times \text{pH V}$). Because the pH shift also influences the standard potential of the electron-accepting half-reaction in APS that is coupled with protons as well, like $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$ ($E = -0.059 \times \text{pH V}$), pH change usually doesn’t vary the potential gap between water oxidation and electron-accepting half-reactions (or the Gibbs energy change, $\Delta G^o$, of the total reaction).

$$2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad \text{(Equation 1.1)}$$

This water oxidation half-reaction formally involves transfer of four electrons together with four protons from two water molecules and formation of an O–O bond. The tremendous complexity of this half-reaction is reflected by a notable overpotential ($\eta$) in efficiently electrolyzed water oxidation (or significantly high energy of activation, $\Delta G^\ddagger$, of the water-splitting reaction) kinetically. In NPS, water oxidation is catalyzed by the oxygen-evolving complex (OEC) located in the enzyme complex of PS II, so as to reduce the energy barrier and enhance the rate constant.

The latest study based on the crystal structure of PS II at a resolution of 1.9 Å revealed a cube-like Mn$_4$CaO$_5$ cluster as the active site of the OEC, of which one calcium and four manganese atoms occupies four corners of the cube and the fourth manganese atom hangs out of the cube (Figure 1.7, a).\(^{[29]}\)

\(^{ix}\) All potentials in this thesis are presented versus NHE, unless noted otherwise.
atoms in the cluster serve as oxo bridges between these five metal atoms. Meanwhile, the Mn$_4$CaO$_5$ cluster was found to be associated with four water molecules which may be involved in water oxidation as reaction substrates (Figure 1.7, b). All amino-acid residues (carboxylate) in the first coordination sphere of the Mn$_4$CaO$_5$ cluster were also verified. The ligated manner of carboxylate could be monodentate or bidentate (Figure 1.7, b). These carboxylate ligands might facilitate proton transfer and stabilize high-valent states of OEC during catalytic water oxidation.

![Figure 1.7](image)

**Figure 1.7.** Structure of the Mn$_4$CaO$_5$ cluster in the OEC. (a) Determination of individual atoms associated with the Mn$_4$CaO$_5$ cluster. (b) Stereo view of the Mn$_4$CaO$_5$ cluster and its ligand environment. Reprinted with permission from npg.$^{[29]}$

Although the exact mechanism of water oxidation catalyzed by the OEC has not been fully elucidated yet, it is widely accepted that the catalytic cycle for each O$_2$ evolution includes stepwise light-driven transfer of four electrons from the OEC.$^{[12, 30]}$ Each of the consecutive transition (oxidation) states of the OEC is called an ‘S-state’, where $S_0$ is the lowest-valent state and $S_4$ the highest-valent in the catalytic cycle. There is still controversy about how the critical O–O bond formation happens in the catalytic cycle. Proposed pathways can be categorized into: (i) nucleophilic-water-attack to the Mn$^V$-oxo species at $S_4$ state of the OEC, and (ii) coupling reaction between the Mn$^{IV}$-oxyl radical at $S_3$ state and an oxygen ligand at $S_4$ state.$^{[30]}$
Advances of probing the structure of the OEC and understanding its catalytic mechanism inspire the development of artificial catalysts for water oxidation, which is imperative in the envisaged APS system

1.6 Water Oxidation by Artificial Catalysts, Heterogeneous and Homogeneous

Although researchers haven’t yet developed an artificial model for water oxidation which is comparable to the OEC in terms of efficiency and persistence, substantial progress towards this goal has been made within recent years in both heterogeneous and homogeneous catalysis communities. Heterogeneous water oxidation catalysts (WOCs) refer to bulk metal (like Ni and Pt) or metal oxide (like CoO$_x$, RuO$_2$ and perovskite) materials that can mediate the water oxidation reaction. Advantages of heterogeneous WOCs include relative durability and feasible scalability. Usually, their catalytic activity is tested in an electrocatalytic cell after they are incorporated onto the anode electrode. While some comprehensive reviews have summarized related concepts and recent advances about heterogeneous WOCs,$^{[31, 32]}$ this topic is beyond the scope of the thesis and will not be discussed here.

On the other side, homogeneous (or molecular) WOCs have shown promising performance and drawn considerable attention nowadays. Similar to the OEC, all reported molecular WOCs that are capable of oxidizing water contain metal cores and ancillary organic ligands in the form of coordination complexes. From the aspect of synthesis, they can be easily modified with both structurally- and electronically- substituents. This allows study of structure-performance correlation upon systematically structure design of catalysts. Meanwhile, their solubility in aqueous medium makes insight into the catalytic mechanism possible via various spectroscopic methods. These advantages of molecular WOCs are pushing their catalytic performance forward.

The catalytic activity of molecular WOCs is typically evaluated in aqueous medium using Ce(NH$_4$)$_2$(NO$_3$)$_6$ (CAN) as a sacrificial one-electron oxidant.
Acidic conditions (pH ≤ 1.0) are normally employed so as to avoid hydrolysis and decomposition of CAN. The corresponding electron-accepting half-reaction and total reaction are described in Equation 1.2 and Equation 1.3 respectively. The standard potential of the CAN reduction half-reaction is 1.61 V vs. NHE.\[^{33}\] However, the formal redox potential of Ce\(^{IV}/\text{Ce}^{III}\) couples are influenced by many factors including the pH value of solutions, the concentration of CAN and the type of counter ions present in the solution.\[^{34}\]

And under some circumstances, it could be higher than 1.80 V.\[^{35, 36}\] It should be pointed out that even though the CAN-driven water oxidation (Equation 1.3) is thermodynamically spontaneous at pH ≥ 0, the reaction is too sluggish kinetically to be considered in the absence of WOCs. In some cases, CAN or its hydrolyzed product was postulated to play a role of oxygen donor, rather than a simple electron acceptor, that directly involved in the O=O bond formation step.\[^{37, 38}\]

\[
4 \text{Ce}^{IV} + 4 e^- \rightarrow 4 \text{Ce}^{III} \quad \text{(Equation 1.2)}
\]

\[
2 \text{H}_2\text{O} + 4 \text{Ce}^{IV} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{Ce}^{III} \quad \text{(Equation 1.3)}
\]

Besides CAN, [Ru\(^{III}(\text{bpy})_3\)]\(^{3+}\) (bpy = 2,2’-bipyridine) and its derivatives are also employed as oxidants in homogeneous water oxidation. The standard reductive potential of [Ru\(^{III}(\text{bpy})_3\)]\(^{3+}\) (Equation 1.4) is 1.26 V and those of its derivatives shift depending on the electronic effect of their substituent groups. Unlike CAN, [Ru\(^{III}(\text{bpy})_3\)]\(^{3+}\) can be applied under neutral or slightly basic conditions in case the investigated molecular WOCs are unstable in strongly acidic solutions.\[^{39-41}\]

\[
4 \text{[Ru}^{III}(\text{bpy})_3]\] + 4 e^- \rightarrow 4 \text{[Ru}^{II}(\text{bpy})_3]\] \(^{2+}\) \quad \text{(Equation 1.5)}
\]

### 1.7 Molecular Water Oxidation Catalyst

Many research groups around the world have devoted in the challenging field of developing molecular WOCs and as a result quite a few complexes based on various transition-metals have been discovered lately with appealing properties and promising activity towards water oxidation. Instead of fully reviewing the history and current advance of the topic,\[^{42-45}\] this section of
introduction will focus only on the previous results that are related to the theme of this thesis.

An ideal molecular WOC should carry the following desirable features: (i) highly catalytic efficiency which can be assessed by the turnover frequency\(^x\) (TOF) of the WOC; (ii) durability under catalytic conditions, which can be evaluated by the turnover number (TON) of the WOC; (iii) small catalytic overpotential that conduces to electron transfer from WOC to photosensitizer (PS) in an APS system;\(^{[46, 47]}\) (iv) simplicity of the structure which usually means low cost of production and facility of scaling up. Optimizing the current generation of molecular WOCs to fulfill all these requirements needs deep understanding in the catalytic mechanism and fundamental information about how the WOC structure influences its properties and catalytic performance. Therefore, recent effort in the development of molecular WOCs is mainly directed on these issues (structure, mechanism, property and activity) which will be highlighted in this thesis too (Figure 1.8).

![Figure 1.8](image.png)

**Figure 1.8.** Highlighted aspects in the study of molecular WOCs. These aspects are closely related with each other.

### 1.7.1 Multinuclear ruthenium-based WOCs

About three decades ago, Meyer’s group found that ruthenium(II) polypyridyl complexes containing aqua ligand can be oxidized to high-valent state, Ru\(^{IV}\)

\(^x\) TOF in this thesis is defined as TON in unit time, second typically.
for instance, through a relatively narrow potential range.\textsuperscript{[48, 49]} This valuable feature is attributed to a comprehensive consequence of proton-coupled electron transfer (PCET) during oxidation and $d\pi$(Ru)$-p\pi$(oxo) interaction in the high-valent Ru–oxo species. The former effect avoids the highly charged intermediates and the latter stabilizes the high-valent ruthenium core.\textsuperscript{[50, 51]} In 1982, Meyer’s group reported a dinuclear Ru complex cis,cis-[(bpy)$_2$(H$_2$O)Ru$_{III}$(μ-O)Ru$_{III}$(OH$_2$)(bpy)$_2$]$^{4+}$ (1 in Figure 1.9), so-called ‘blue dimmer’, as a pioneering example of molecular WOCs.\textsuperscript{[52, 53]} This complex contains two aqua-Ru$_{III}$ centers linked by a dianionic oxide bridge. At pH 1.0, the blue dimmer reaches its Ru$_V$–O–Ru$_V$ state with a redox potential of 1.46 V vs. NHE. Using CAN as an oxidant, the dimmer is able to catalyze water oxidation yielding a TOF of $4.2\times10^{-3}$ s$^{-1}$ and a TON of no less than 13.\textsuperscript{[54, 55]} Despite some controversy,\textsuperscript{[56-58]} the catalytic mechanism of blue dimmer from the latest experimental results is proposed as a water-nucleophilic-attack pathway, of which the scenario is depicted in Figure 1.10 a.\textsuperscript{[59]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Figure 1.9. Structures of selected dinuclear Ru-based WOCs.}
\end{figure}
While the blue dimmer suffers from cleavage of the oxide bridge that resulting in catalytic inactivity, some research groups have designated more rigid chelating ligands as bridges. These bridging ligands are not only connecting the two ruthenium centers in a robust way, but also preorganizing their relative positions. It turns out that coordination geometry of the two metal cores can significantly influence their interaction through space and therefore their catalytic performance and mechanism. Llobet’s group employed 3,5-bis(2-pyridyl)pyrazole (Hbpp) as a bridge ligand and prepared the dinuclear Ru complex \( \text{in,in-}[\text{(H}_2\text{O})(\text{tpy})\text{Ru}^{\text{II}}(\mu\text{-bpp})\text{Ru}^{\text{II}}(\text{tpy})(\text{H}_2\text{O})]^{3+} \) (2 in Figure 1.9, tpy = 2,2′:6′,2″-terpyridine), of which the two Ru–OH\(_2\) moieties were poised in a face-to-face manner.\(^{[60]}\) Kinetics analysis and oxygen labeling experiments revealed that 2 catalyzes \( \text{O}_2 \) generation via an intramolecular pathway where the \( \text{O}–\text{O} \) bond formation is proposed to derive from the interaction of two Ru"=O units (Figure 1.10 b).\(^{[61]}\)

Tanaka’s group adopted 1,8-bis(2,2′:6′,2″-terpyridyl)-anthracene (btpyan) as a backbone and 3,5-di-tert-butyl-1,2-benzoquinone (dtQ) as another ancillary ligand in the preparation of the dinuclear Ru WOC \([(\text{HO})(\text{dtQ})\text{Ru}^{\text{II}}(\mu\text{-btpyan})\text{Ru}^{\text{II}}(\text{dtQ})(\text{OH})]^2^+ \) (3 in Figure 1.9).\(^{[62]}\) Upon application of a sufficiently high potential (1.92 V), ITO (indium tin oxide) electrode modified with 3 is able to electrocatalyze water oxidation with a TON of 33,500.\(^{[63]}\) DFT calculation purported a catalytic mechanism of intramolecular interaction between a Ru"=oxyl radical and a Ru"=OH moiety.\(^{[64, 65]}\)

Thummel’s group synthesized a family of bis-tridentate ligands as bridging ligands.\(^{[66]}\) Their approach of assembling binuclear Ru complexes is to hold two metal cores with the bridging ligand first and occupy other coordination sites with monodentate pyridine ligand later.\(^{[66, 67]}\) Complex 4 in Figure 1.9 shows a representative geometry in the series of dinuclear Ru complexes. Typically the bis-tridentate bridging ligands orientate the two Ru centers in a cis-position, and a \( \mu\text{-Cl} \) linkage lies between the two metal centers. Addition of CAN into the solution (pH 1.0 triflic acid) of 4 generates a large amount of \( \text{O}_2 \), affording an initial TOF of 0.046 s\(^{-1}\) and a TON of 538 during 20 hours.
Inspired by the oxygen-rich coordinating surroundings within the OEC, our group introduced carboxylate groups into the bridging ligand and synthesized $\text{[Ru}^\text{II}_2(\text{cppd})(\text{pic})_6]^+ \ (5$, $\text{H}_2\text{cppd} = 1,4\text{-bis}(6'\text{-carboxylate-pyrid-2'yl})\text{-pyridazine acid})$ and $\text{[Ru}^\text{II}_2(\text{cpph})(\text{pic})_4(\mu\text{-Cl})]^2+ \ (6$, $\text{H}_2\text{cpph} = 1,4\text{-bis}(6'\text{-carboxylate-pyrid-2'yl})\text{-phthalazine acid})$.\cite{68, 69} While the assembly of cppd$^{2-}$ and Ru precursors was leading to a trans-geometry of 5, cpph$^{2-}$ orients the two Ru centers of 6 in a cis-position. This difference of coordination manner results in a remarkable superior activity of 6 (TOF = 1.2 s$^{-1}$, TON = 10,400) to that of 5 (TOF = 0.28 s$^{-1}$, TON = 4,740). Obviously, the two Ru nuclei can have cooperative effect with each other during the catalysis of water oxidation, and their closer proximity benefits the interaction.

Unlike the organic bridging ligands discussed above, Bonchio’s and Hill’s groups reported, independently in 2008, a tetranuclear Ru WOC $\text{[Ru}_4(\mu\text{-O})_4(\mu\text{-OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ ([Ru$_4$POM$_2$], POM = polynoxometalate [$\gamma$-SiW$_{10}$O$_{36}$]) bearing only inorganic POM as ancillary ligands.\cite{70, 71} POM is believed to resist oxidation decomposition which may occur to organic ligands under the harsh water oxidation conditions. In the presence of excess CAN, a TON of 500 and a TOF of 0.125 s$^{-1}$ was attained for the catalytic water oxidation by the complex. While the catalytic mechanism of [Ru$_4$POM$_2$] deserves more attention and investigation, its tetranuclear metal core is reminiscence of the active site of the OEC. Meanwhile, its pronounced
catalytic efficiency manifests the diverse possibilities of constructing molecular WOCs.

1.7.2 Mononuclear Ruthenium-Based WOCs

The original motivation of building multiple nuclear Ru WOCs might stem from chemists’ knowledge about the tetra-manganese site of the OEC or their intuition of using multiple sites to extract two oxygen atoms from water simultaneously. Nevertheless, studies upon dinuclear Ru WOCs indicate that not both metal cores are necessarily involved in the O–O bond formation step.[72] During the past several years, a few mononuclear Ru complexes have been discovered to be capable of oxidizing water to dioxygen.[31] Their emergence is regarded as a recent breakthrough in the field of developing molecular WOCs. Compared with multiple nuclear WOCs, the relatively simple structures of mononuclear WOCs usually mean more feasible approach of synthesis and facile determination of their spectrometric properties. According to their coordination geometries, reported mononuclear Ru WOCs can be roughly classified into the following three categories: (i) [Ru(NNN)(NN)L] type, (ii) [Ru(NNN)(N)2L] type, and (iii) [Ru(NNNN)(N)2] type, where NNNN, NNN, NN and N represent tetra-, tri-, di-, and mono-dentate nitrogen-heterocyclic ligands, and L for monodentate non-nitrogen ligand, water or halogen typically.

[Ru(NNN)(NN)OH2] type of aqua Ru complexes constituent a major part of competent mononuclear WOCs. Structures of selected examples (7-12) are displayed in Figure 1.11. Their catalytic performance for the water oxidation is marked in terms of TON and TOF values, when available. Despite the similar coordination motif of 7-12, their different ancillary ligands, including polypyridyl, polypyrazolyl and triazonane, significantly influence their stability and catalytic efficiency. A mechanism investigation about [Ru(NNN)(NN)OH2] catalysts was initiated by Meyer’s group, based upon [RuII(tpy)(bpm)(OH2)]2+ (8, bpm = 2,2′-bipyrimidine).[72-74] In an acidic CAN medium, 8 is oxidized to the high-valent [RuV=O]3+ form through a sequence of ET and PT (proton transfer) processes. Water-nucleophilic-attack (WNA)
to the \([\text{Ru}^{\text{V}=\text{O}}]^{3+}\) species generates the hydroperoxide \([\text{Ru}^{\text{III}}-\text{OOH}]^{2+}\) complex. This is the critical \(\text{O}–\text{O}\) formation step in the catalytic cycle. Further oxidation of the hydroperoxide species generates \([\text{Ru}^{\text{IV}}(\text{OO})]^{2+}\) or \([\text{Ru}^{\text{V}}(\text{OO})]^{3+}\) peroxo intermediates (depending on the different pH values of reaction mediums), which releases the dioxygen and return to its \(\text{Ru}^{\text{II}}\) or \(\text{Ru}^{\text{III}}\) state. The schematic catalytic cycle of water-nucleophilic-attack (also called ‘acid-base’) pathway is concluded in Figure 1.12 a. In the case of 8, the rate-determining-step is regarded as \(\text{O}_2\) liberation from \([\text{Ru}^{\text{IV}}(\text{OO})]^{2+}\) or oxidation from \([\text{Ru}^{\text{IV}}(\text{OO})]^{2+}\) to \([\text{Ru}^{\text{V}}(\text{OO})]^{3+}\).

![Structures of selected \([\text{Ru}(\text{NNN})(\text{NN})\text{L}]\) type of mononuclear Ru WOCs.](image)

**Figure 1.11.** Structures of selected \([\text{Ru}(\text{NNN})(\text{NN})\text{L}]\) type of mononuclear Ru WOCs. Their catalytic performance is given in the form of \((\text{TON}, \text{TOF})\).\(^{\text{xi}}\)

Mechanistic investigations upon other \([\text{Ru}(\text{NNN})(\text{NN})\text{OH}_2]\) candidates suggest general validity of the WNA pathway for the water oxidation catalyzed by this class of molecular WOCs. However, different tridentate or bidentate ancillary ligands can influence the reaction rate of individual steps

\(^{\text{xi}}\) The TON and TOF values are obtained from various sources of literatures. They may be attained under different experimental conditions or according to different calculative methods. These factors should be taken into account, when TON or TOF numbers are compared.
of the WNA catalytic cycle.\textsuperscript{[75]} For instance, WNA step was measured as the slowest step in the case of 9.\textsuperscript{[76]}

$[\text{Ru}^{II}(\text{tpy})(\text{bpy})\text{OH}_2]^{2+}$ (7) is another extensively studied catalyst in the $[\text{Ru}(\text{NNN})(\text{NN})\text{OH}_2]$ category. Even though its $\text{Ru}^\text{IV}/\text{Ru}^\text{V}$ redox process is barely discerned in the electrochemical potential sweep,\textsuperscript{[77]} the catalytic capability of 7 towards water oxidation has been verified in the presence of large excess CAN.\textsuperscript{[36, 78, 79]} Yagi \textit{et al.} reported that a 4-substituted ethoxy group at the tpy moiety of 7 could remarkably improve its catalytic performance.\textsuperscript{[80]} Berlinguette’s group carefully examined the substituent effect at the bpy moiety of 7.\textsuperscript{[36, 79]} They proposed a predominant WNA catalytic pathway (Figure 1.12 a) for water oxidation by 7 and its derivatives. The position of rate-determining step in the WNA cycle changes according to the electron density of the bpy moiety. Concomitant reactions that diverging from the prevailing WNA pathway were also observed. These auxiliary paths were proposed to include abstraction of O atoms from NO$_3^-$ anions by $[\text{Ru}^\text{V}=\text{O}]^{3+}$ species and WNA to the $[\text{Ru}^\text{IV}=\text{O}]^{2+}$ species. Sakai’s group investigated the catalytic behavior of 10 and 11 in neutral aqueous medium instead of commonly used acidic one.\textsuperscript{[81, 37]} Based on their observations of O$_2$-evolving kinetics, they proposed that the O–O bond was formed via intermolecular radical coupling between $[\text{Ru}^\text{IV}=\text{O}]^{2+}$ and hydroxocerium (IV) species (in the case of 11) or between two $[\text{Ru}^\text{IV}=\text{O}]^{2+}$ species (in the case of 10, Figure 1.12 b).

\textbf{(a) Water nucleophilic attack} \\
$[\text{Ru}^{II}-\text{OH}_2]$ $\rightarrow$ $[\text{Ru}^{IV}=\text{O}] + \text{H}_2\text{O}$ $\rightarrow$ $[\text{Ru}^{III}=\text{OOH}]$ $\rightarrow$ $[\text{Ru}^{IV}(\text{OO})]$ $\rightarrow$ $[\text{Ru}^{II}-\text{OH}_2]$ \\
e^-, H^+$ \\

\textbf{(b) Intermolecular oxygen units interaction} \\
$2\times[\text{Ru}^{II}-\text{OH}_2]$ $\rightarrow$ $[\text{Ru}^{IV}+\text{O}=\text{O}=\text{Ru}^{IV}]$ $\rightarrow$ $[\text{Ru}^{IV}+\text{O}=\text{O}=\text{Ru}^{IV}]$ $\rightarrow$ $2\times[\text{Ru}^{III}-\text{OH}_2]$ \\
e^-, H^+$ \\

\textbf{Figure 1.12. Schematic pathways of water oxidation catalyzed by mononuclear Ru complexes.}
Thummel, Fujita, and Yagi et al. found that the orientation of ancillary ligand can also influence the catalytic performance of mononuclear Ru WOCs significantly. Under the same acidic CAN conditions, trans-$[\text{Ru}^{II}(\text{tpy})(\text{pynp})\text{OH}_2]^{2+}$ (12, pynp = 2-(pyrid-2'-yl)-1,8-naphthyridine) exhibits higher O$_2$-evolving rate in nearly an order of magnitude than that of cis-$[\text{Ru}(\text{tpy})(\text{pynp})\text{OH}_2]$ (the structure is not shown), where the 8-nitrogen of pynp is proximal to the ligated water.$^{[82, 83]}$ This remarkable difference is ascribed to the interaction between aqua- and pynp ligands, yet the detailed mechanism is unknown. It is very intriguing that non-aqua complex $[\text{Ru}^{II}(\text{tpy})(\text{pynp})\text{Cl}]^+$ (13), as a chloride analogy of 12, shows even higher catalytic efficiency than 12.$^{[84]}$ In fact, 13 was reported as an active WOC by Thummel’s group about two years earlier than the disclosure of water oxidation capability of 12. In this previous study, 13 was proposed to retain its Cl ligand and form a seven-coordinate Ru$^{IV}$-aqua species during catalysis of water oxidation. In contrast to the case of 13, Sakai and Berlinguette et al. found that $[\text{Ru}^{II}(\text{tpy})(\text{bpy})\text{Cl}]^+$ (14) undergoes Cl/H$_2$O exchange in aqueous medium.$^{[78, 79]}$ Thereby, it is referred that under acidic CAN solution, 14 doesn’t play a role of catalyst mediating water oxidation but be a precursor of complex 7 which is an authentic molecular WOC.

**Figure 1.13.** Structures of selected $[\text{Ru}^{II}(\text{NNN})(\text{N})_2\text{L}]$ type of mononuclear Ru WOCs. Their catalytic performance is given in the form of (TON, TOF).$^{x1}$

In 2005, Thummel’s group reported an $[\text{Ru}(\text{NNN})(\text{N})_2\text{L}]$ type of mononuclear complex 15, which is one of the first examples of mononuclear
Ru WOCs.\cite{ruwocs} Its structure is displayed in Figure 1.13, together with other representative [Ru(\textit{NNN})(\textit{N})_2L] WOCs. A recent mechanism study on the water oxidation by 15 revealed a O–O bond formation process via WNA that may happen either at its [Ru\textsuperscript{IV}=O]\textsuperscript{2+} or [Ru\textsuperscript{V}=O]\textsuperscript{3+} state.\cite{mechanism}

Very recently, Thummel’s group observed an ‘unusual’ catalytic performance of a non-aqua complex [Ru\textsuperscript{II}(tpy)(pic)_2I]\textsuperscript{+} (17, TOF = 0.16 s\textsuperscript{-1}), whose catalytic efficiency is even higher than that of its aqua analogy [Ru\textsuperscript{II}(tpy)(pic)_2OH]\textsuperscript{2+} (16).\cite{thummel} Taking the slow iodide/water exchange into account, they proposed that 17 retains its halogen ligand during water oxidation catalysis and the catalytic path includes a seven-coordinative aqua intermediate aforementioned in the case of 13. On the other side, we observed a long induction period of several hours in the O\textsubscript{2}-evolving experiment of [Ru\textsuperscript{II}(tpy)(pic)_3]\textsuperscript{2+} (18).\cite{our_result} We suggest that 18 can’t catalyze water oxidation before one or more of its picoline ligands are replaced by water. And the aqua complex 16 is responsible for the reactive catalysis of O\textsubscript{2} evolution by 18.

In all, the whole picture of catalytic mechanism for [Ru(\textit{NNN})(\textit{N})_2L] WOCs seems quite complicated. Different ancillary ligands direct to diverse possible paths via six- or seven-coordinative intermediates.

In the category of [Ru(\textit{NNNN})(\textit{N})_2] WOCs, there is only a few examples disclosed. The first instance (19 in Figure 1.14) in this series was reported by

![Figure 1.14. Structures of selected [Ru(\textit{NNNN})(\textit{N})_2] type of mononuclear Ru WOCs. Their catalytic performance is given in the form of (TON, TOF).\textsuperscript{xi}](attachment:figure1.png)
Its tetradentate polypyridyl ligand can be regarded as a mergence of two bpy ligands in a rigid manner so that the cis/trans interconversion happening to [Ru(bpy)₂L₂] type of complexes (like 20) is prevented. From the synthetic point of view, this rigid tetradentate ligand prevents the formation of oligomers, which otherwise occurs during the metal-ligand assembly, if one flexible tetradentate ligand can chelate with two metal cations. Compared with cis-20, complex 19 owns a tremendously superior catalytic reactivity. The catalytic performance of trans-20, however, is difficult to be determined, because it inevitably converts to the favored cis-isomer during reaction. DFT calculation propose a O–O bond formation involving WNA to the seven-coordinated [(NNNN)(N)₂Ru⁴⁺=O] intermediate during the water oxidation by 19. Besides the equatorial polypyridyl, axial monodentate ligands (pic) that strongly coordinate to the Ru center are requisite for the formation of a seven-coordinated intermediate presumed. Derivatives of 19 containing various substituents at the equatorial ligand were also prepared by Thummel’s group. Their catalytic activity, however, has not been revealed yet.

Our research group have designated and prepared a family of [Ru(ONNO)(N)₂] (ONNO represents tetrarodentate ligands involving two oxygen and two nitrogen donors) WOCs featuring with anionic bda (H₂bda = 2,2’-bipyridine-6,6’-dicarboxylic acid) ancillary ligand. Complex 21 in Figure 1.14 is a prototype of them. Under typical acidic CAN conditions, this family of complexes catalyzes water oxidation with impressive high efficiency, more than 300 TON per second for the most reactive candidate. Combined experimental and theoretical study upon 21 purports a catalytic pathway via bimolecular coupling between two tentative seven-coordinated Ru⁴⁺=O species (Figure 1.12 b). Properties and catalytic mechanism about 21 will be further discussed in Chapter 2.

The list of Ru WOCs is expanding, and certainly not all reported examples are enclosed in the introduction. Nevertheless, the description in this chapter reflects current understandings about Ru WOCs generally. Recent advances in this subject not only pave the way towards application of Ru...
WOCs in practice, but also inspire the development of first-row transition-metal-based molecular WOCs.

### 1.7.3 First-Row Transition-Metal-Based WOCs

Molecular complexes based on first-row transition metals, including manganese, cobalt and iron, have been discovered to be able to oxidize water to dioxygen.\[^{45}\] The intrinsic interest of developing Mn WOCs originates from mimicking the metal core of the OEC. However, only a number of Mn complexes reported so far show catalytic water oxidation activity with limited TON.\[^{100-102}\] Moreover, requirement of oxygen-transferring oxidants (like peroxide and hypochlorite) in most cases of Mn WOCs leads to controversy about whether O\(_2\) generates from the water oxidation or simply decomposition of the oxidant. Very recently, B. Åkermark and coworkers prepared a dinuclear Mn WOC (22) which is the first example capable of catalyzing water oxidation using [Ru\(^{III}\)(bpy)_3]\(^{3+}\) as a single-electron oxidant.\[^{41}\]

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![Figure 1.15](image)

Figure 1.15. Structures of selected first-row transition-metal-based WOCs. *NaIO\(_4\) was used as oxidant. Their catalytic performance is given in the form of (TON, TOF).\(^{xi}\)

Cobalt- and iron- based WOCs emerged in the past two years. In 2010, Hill’s group reported an homogeneous cobalt-based WOC, B-type [Co\(_4\)(H\(_2\)O\(_2\))(\(\alpha\)-PW\(_9\)O\(_{34}\))\(_2\)]\(^{10-}\) (23), which contain only carbon-free POM as ancillary ligands.\[^{40}\] The coordinative geometry of 23 is very similar to that of the tetranuclear Ru complex aforementioned. Using [Ru\(^{III}\)(bpy)_3]\(^{3+}\) as a sacrificial...
oxidant, 23 attained an initial TOF of 5 s\(^{-1}\) and a TON of 1000 (limited by the sufficiency of oxidant). Later on, Berlinguette’s and Nocera’s groups reported single-site Co complexes that can mediate water oxidation electrocatalytically.\(^{103-105}\) It should be noted that cobalt oxide film and nanoparticles are known as heterogeneous catalysts for water oxidation.\(^{32,106-107}\) Richard G. Finke \textit{et al.} pointed out that, under the condition of electrocatalytic water oxidation, molecular Co complexes can be oxidized to CoO\(_x\) which is actually the dominate WOC.\(^{108}\) Concerned decomposition of Co WOCs during the reaction makes the border between homogeneous and heterogeneous catalysis blurry.\(^{109}\)

For Fe WOCs, there are only two families of complexes reported so far. One series is Fe\(^{III}\)-TAML (TAML = tetraamido macrocyclic ligand) complexes, such as 24 in Figure 1.15, reported by Collins and coworkers in 2010.\(^{110}\) They exhibit fast O\(_2\)-evolving rate (initial TOF = 1.3 S\(^{-1}\)) but short longevity (ca. 20s) in the presence of CAN as an oxidant. The other series is Fe\(^{II}\) complexes containing tetradeutate nitrogen-based ligands, of which a module (25) is displayed in Figure 1.15.\(^{111}\) They were prepared and tested by Costas’s group. Using CAN or NaIO\(_4\) as an oxidant, these iron complexes can drive O\(_2\) evolution constantly for several hours with moderate efficiency.

Although the catalytic mechanism of these first-row transition-metal-based WOCs are still not known as much as that of ruthenium-based WOCs, the abundant reservoir of Fe, Mn and Co on earth makes corresponding WOCs very attractive and promising.

\subsection{1.7.4 Iridium-Based WOCs}

The water oxidation ability of Ir complexes was initially exploited by Bernhard and coworkers.\(^{112}\) They prepared a series of analogues of [Ir\(^{III}\)(ppy)\(_2\)(OH\(_2\))\(_2\)]\(^+\) (26, ppy = 2-phenylpyridine) and evaluated their catalytic reactivity in 2008. In the presence of CAN, 26 can mediate O\(_2\) evolution in a slow rate but keep it catalytic activity over a remarkable long period, more than 7 days. Brudvig and Crabtree \textit{et al.} found that introduction of Cp\(^*\) (1,2,3,4,5-pentamethylcyclopentadiene) as a substitute of one ppy ligand,
affording Ir complexes with coordinate geometry (so-called ‘half-sandwich’) as that of 27, can dramatically enhance the catalytic rate of Ir WOCs.\textsuperscript{[113]} They postulated a WNA pathway for homologs of 27 based on DFT calculation.\textsuperscript{[114]} Bernhard and Albrecht \textit{et al.} modified the ppy ligand of 27 and prepared Ir complex 28 as a competent WOC which earned a TON of 10,000 over a reaction time of more than 5 days.\textsuperscript{[115]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/figure1.png}
\caption{Structures of selected iridium-based WOCs. Their catalytic performance is given in the form of (TON, TOF).\textsuperscript{x1}}
\end{figure}

On the other side, there is evidence showing formation of IrO\textsubscript{x}/\textsubscript{y}-like nanoparticles after exposure of a variety of Ir-based WOCs in the solution of CAN.\textsuperscript{[116]} Brudvig and Crabtree also reported the generation of amorphous iridium oxide film when the Cp*Ir-aqua complex was electro-deposited on the conductive surface.\textsuperscript{[117]} Because of the highly catalytic activity of iridium oxide, the delicacy of organometallic Ir complexes leads to the discussion and ambiguity about whether the molecular Ir complexes play the role of authentic homogeneous WOCs or only a precursor of the heterogeneous iridium oxide type of catalysts.\textsuperscript{[118, 119]}

\section*{1.8 Aim of this Thesis}

When I started my PhD project at the autumn of 2008, my colleagues Dr. Yuhua Xu and Dr. Lele Duan had been working on the water oxidation subject. At beginning, I vigorously participated in their research. And then we tried to figure out more specific questions from our experimental observations
so as to achieve deeper understanding about the WOCs. Those initial findings from our research group will be highlighted in the following chapters, because they are the foundation of my work discussed in the thesis. Findings and methods from other research groups are also referred in this thesis. Some of them have been discussed in the previous sections. Others will be described in the related chapters after.

The work in this thesis is targeting molecular (homogeneous) Ru-based WOCs. The content of Chapter 2, 3 and 4 is about design, preparation, and evaluation of novel Ru WOCs. The strategy of our study here is to correlate the properties and catalytic manner of Ru complexes with their coordination structures based on designed candidates. In Chapter 5 and 6, the topics are extended to integration of WOCs in light-driven water oxidation system and immobilization of WOCs on conductive surface. Those works can be considered as preliminary exploration towards application of WOCs in artificial photosynthesis device.
2. Mononuclear Ru WOCs with Tetradeutate Anionic Ligands

(Paper I)

2.1 Introduction

In 2009, our research group prepared mononuclear Ru complex [Ru\textsuperscript{II}(bda)(pic)\textsubscript{2}] (21, H\textsubscript{2}bda = 2,2’-bipyridine-6,6’-dicarboxylic acid) and investigated its catalytic activity towards water oxidation.\textsuperscript{[92, 93]} It is found that the kinetics of water oxidation reaction is second order in the concentration of catalyst 21. More importantly, an uncommon Ru\textsuperscript{IV} dimeric complex, μ-(HOHOH)-[Ru\textsuperscript{IV}(bda)(pic)\textsubscript{2}](PF\textsubscript{6})\textsubscript{3}•2H\textsubscript{2}O (Figure 2.1, right), was isolated and characterized as an intermediate during the catalytic water oxidation reaction. In the crystal structure of the dimmer, two Ru\textsuperscript{IV} centers were bridged by a [HOHOH]\textsuperscript{−} group and either of them was seven-coordinated.

![Figure 2.1](image)

**Figure 2.1.** Left: Crystal structure of complex 21. Right: Crystal structure of complex μ-(HOHOH)-[Ru\textsuperscript{IV}(bda)(pic)\textsubscript{2}](PF\textsubscript{6})\textsubscript{3}•2H\textsubscript{2}O. In both situations, thermal ellipsoids are at 50% probability; hydrogen atoms except the H–O type are omitted for clarity. Reprinted with permission from ACS.\textsuperscript{[92]}
In view of these findings, a pathway of intermolecular interaction between two Ru$^\text{V}=\text{O}$ unites (Figure 1.12 b) was proposed as the key O–O bond formation step of water oxidation catalyzed by 21. It was further supported by experimental and theoretical studies recently.$^{[94,95]}$

The following structural features of 21 is rationalized to the unique seven-coordinate intermediate and the bimolecular catalytic mechanism: (i) the large O-Ru-O cleft (Figure 2.1, left, angle of O2-Ru1-O3 is 122.99°) allows straightforward access of solvent water molecule to the Ru center; (ii) the flexible bipyridyl backbone (Figure 2.1, right, dihedral angle of O2-N1-N2-O4 is 23.13°) further adapts distortion of coordination geometry at various valences of the Ru center. Thus, we considered that preorganization of the geometry of the complex in certain motif is critical to its catalytic behavior during the water oxidation reaction. Under the motivation of examining ligand effect in this particular case, we designed and synthesized [Ru$^\text{II}$(pda)(pic)$_2$] derivatives (29a~c) which carry a tetradeutate anionic pda ligand (H$_2$pda = 1,10-phenanthroline-2,9-dicarboxylic acid). Unlike bda ligand, pda owns a rigid backbone that can preserve planar under catalytic water oxidation conditions, no matter what valence of the coordinative ruthenium core reaches. Therefore, the big O-Ru-O cleft angle in 29a~c is expected unchangeable during reaction. A comparative study between 29 and 21, taking the disparity and similarity of their ancillary ligands into account, provides insight about structure-mechanism relationship of WOCs.

Figure 2.2. Structures of complexes 29a~c and 21.
2.2 Synthesis and Characterization of Ru-pda WOCs

1,10-Phenanthroline-2,9-dicarboxylic acid (H₂pda) was synthesized according to the literature procedure.\textsuperscript{[120]} 2,9-Dimethyl-1,10-phenanthroline as the starting material was first oxidized to the dialdehyde intermediate by selenium dioxide and then to the dicarboxylic acid product by concentrated nitric acid (Figure 2.3).

![Figure 2.3. Synthesis of 1,10-Phenanthroline-2,9-dicarboxylic acid (H₂pda).](image)

The synthesis of complexes 29a–29c was accomplished in a two-step one-pot reaction (Figure 2.4). At first, a mixture of H₂pda and DBU in MeOH was slowly added to a MeOH solution of \textit{cis}-[Ru\textsuperscript{II}(DMSO)₄Cl₂].\textsuperscript{[121, 122]} After refluxing overnight, the reaction system was added excess amount of corresponding 4-substituted pyridines and kept refluxing for another 6 hours. The crude product was purified by column chromatography over alumina using gradient elution. The yields of desired product complexes are quite low, about 10%, owing to generation of [Ru\textsuperscript{II}(Hpda)₂] as a primary byproduct. All complexes were characterized by \textsuperscript{1}H NMR, high-resolution MS, and elemental analysis. The structure of 29a was further examined by density functional theory (DFT) at the B3LYP/lacvp** level (Figure 2.6 a). The optimized coordinative geometry of 29a revealed an expanded O-Ru-O angle (130.45°) even larger than the O-Ru-O angle (124.67°) of 21. Solubility of these Ru-pda complexes, however, is not as good as that of 21 in either ordinary organic solvents or aqueous mediums, causing difficulties of some spectroscopic measurements upon 29a–29c in homogeneous solutions.

\textsuperscript{xii} DFT calculation discussed in this section was conducted by Dr. Timofei Privalov at Stockholm University.
The $^1$H NMR spectra (in $d_4$-methanol) of 29a–29c render identical resonance for their two axial 4-substituted pyridines and three peaks (two doublets and one singlet) for the pda ligand, in agreement with the $C_{2v}$ symmetry of 29a–29c in MeOH solution. Nevertheless, the proton resonance of pda splits into five groups of peaks, when the $^1$H NMR of 29a–29c were recorded in the mixed deuterated acetonitrile/methanol (1/9, v/v) or acetonitrile/water (1/9, v/v) solvents. This breakage of symmetry in the presence of acetonitrile is indicative of association of acetonitrile to the Ru$^{II}$ center and dissociation of one carboxylate group in the protic medium. When the aqueous solution (water containing 10% acetonitrile) of 29a was injected into high-resolution mass spectrometer, both [29a+H]$^+$ and [29a+MeCN+H]$^+$ species were observed in the mass spectrum (Figure 2.5 a). The signal of the former species, however, was dramatically stronger than that of the latter one. The dominant [29a+H]$^+$ signal under the MS conditions implies that (i) the coordinative interaction between 29a and acetonitrile is not robust and allows rapid dissociation of acetonitrile from the Ru$^{II}$ center; (ii) the protic atmosphere in aqueous solution might stabilize the [29a–MeCN] species. DFT model of [29a–MeCN] in explicit protic environment (Figure 2.6 b) illustrated a seven-coordination-like structure, in which the location of Ru$^{II}$ center is close to one side of the pda cavity and one Ru$^{II}$–O(carboxylate) bond is obviously longer than the other. The energy profit of 29a–MeCN coordination was calculated to be merely ca. 2 kcal/mole. In conclusion, the Ru$^{II}$ core of 29a–29c can form a weak coordinative interaction with acetonitrile, leading to the infirmness of one of their two Ru$^{II}$–O(carboxylate) bonds.
Figure 2.5. (a) HR-MS spectrum of 29a in acetonitrile/H2O (1/9, v/v); insert is enlarged signal of [Ru II(pda)(pic)2 + CH3CN + H]⁺. (b) HR-MS spectrum of 29a in acetonitrile/H2O (1/9, v/v) after treatment with 4 equivalents of CAN.

After addition of 4 equivalents of CAN in the acetonitrile/water solution of 29a, a seven-coordinate [Ru IV(pda)(pic)2-OH]⁺ complex as well as a [Ru III(pda)(pic)2]⁺ complex were trapped and distinguished in the mass spectra (Figure 2.5 b). DFT simulation suggests a [Ru III–OH2]⁺ complex (Figure 2.6 c) as the favored formation of trivalent 29a in protic solvent. It is reasonable that the Ru III rather than Ru II core prefers to bind with water, because trivalent ruthenium is ‘harder’. The calculated binding energy of the seventh coordinated water is so small, only −6.1 kcal/mol, that it can’t survive under the MS conditions. Moreover, the weak Ru III–O(aqua) bond here implies probable high dynamic equilibriums between trivalent 29a⁺.

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xiii When high-valent ruthenium complexes and the catalytic mechanism were studied by DFT calculation, [Ru II(pda)(py)2] (29b) and [Ru II(bda)(py)2] accordingly were used as the investigated substrates due to high computation efficiency. From the experimental aspect, 29b and 29a showed very similar chemical properties and catalytic activity.
[Ru$^{\text{III}}$–MeCN]$^+$ and [Ru$^{\text{III}}$–OH$_2$]$^+$ species in aqueous medium. The identified [Ru$^{\text{IV}}$–OH]$^+$ complex is a key intermediate that may involve in the catalytic water oxidation by 29a. Unlike the [Ru$^{\text{II}}$–MeCN] or [Ru$^{\text{III}}$–OH$_2$]$^+$ species, the optimized structure of [Ru$^{\text{IV}}$(pda)(pic)$_2$-OH]$^+$ (Figure 2.6 d) poses a more symmetrical seven-coordination geometry, including a very solid Ru$^{\text{IV}}$–O(hydroxyl) bond. This seven-coordinate [Ru$^{\text{IV}}$–OH]$^+$ is probably generated from [Ru$^{\text{III}}$–OH$_2$]$^+$ via a PCET process (Figure 2.6).

![Figure 2.6](image)

**Figure 2.6.** Optimized structures of [Ru$^{\text{II}}$(pda)(pic)$_2$] (a); [Ru$^{\text{II}}$(pda)(pic)$_2$–CH$_3$CN] (b), methyl groups of pic ligands are omitted; [Ru$^{\text{III}}$(pda)(py)$_2$–OH$_2$]$^+$ (c); and [Ru$^{\text{IV}}$(pda)(py)$_2$–OH]$^+$ (d). Some hydrogen atoms are omitted for clarity. All distances are in Å.
2.3 Spectral Properties of Ru-pda WOCs

All 29a~29c show two metal-to-ligand charge transfer (MLCT) absorbance bands in their UV-vis spectra, when methanol is employed as the solvent. One absorbance appears at around 350 nm, corresponding to the ruthenium-to-pyridines charge transfer; the other at about 480 nm, corresponding to the ruthenium-to-pda charge transfer. Electronic effect of the substituents at the pyridine ligand can influence the former band but hardly the latter one. In the presence of acetonitrile, blue-shift of both MLCT bands occurs due to the weak coordination between acetonitrile and the ruthenium core.

![Figure 2.7](image)

**Figure 2.7.** Left: Cyclic voltammograms of 29a (1.0 mM) in CF₃SO₃H aqueous solution (pH 1.0) containing 10% acetonitrile. Right: Cyclic voltammograms of 29a (1.0 mM) in phosphate buffer solution (pH 7.0) containing 10% acetonitrile. Scan rate is 100 mV/s. [Ru II(bpy)3Cl2] (E¹/₂ = 1.26 V vs. NHE) is employed as an external reference.

The cyclic voltammogram (CV) curve of 29a displays a quasi-reversible wave at E¹/₂ = 0.97 V and an irreversible wave at E = 1.36 V in pH 1.0 aqueous medium (Figure 2.7, left). They are assigned to the Ru II/Ru III and Ru III/Ru IV redox events respectively. Meanwhile, an onset of catalytic current that is obviously higher than the background current emerges at about 1.55 V, a clearly more positive potential than the redox potential of Ru III/Ru IV couples. Thereby further oxidation of the Ru IV species is prerequisite before the catalyst oxidizes water to dioxygen. It is inferred that (i) water oxidation current is triggered by Ru V species; (ii) the Ru IV/Ru V redox wave overlaps
with the catalytic current and thus can’t be discerned. When the CV scan of 29a was conducted in pH 7.0 buffer, the Ru$^{III}$/Ru$^{IV}$ redox process occurred at 1.13 V and the catalytic current initiated at about 1.21 V. Both potentials are notably less positive than those in acidic situation. Considering the concomitance of Ru$^{IV}$/Ru$^{V}$ redox event and catalytic potential of water oxidation by 29a, shift of redox waves and catalytic onset reflect Nernst effect of PCET in the Ru$^{III}$ to Ru$^{IV}$ and Ru$^{IV}$ to Ru$^{V}$ oxidation steps. Adding up results from MS, CV and DFT calculations above, we propose a proton coupled oxidation sequence $[\text{Ru}^{III}-\text{OH}_2]^+ \rightarrow [\text{Ru}^{IV}-\text{OH}]^+ \rightarrow$ formally $[\text{Ru}^{V}=\text{O}]^+$ for 29a. Catalysts 29b and 29c exhibit similar CV curves with that of 29a in both acidic and neutral mediums and thus undergo same sequential PCET steps tentatively. Their redox potentials are concluded in Table 2.1.

Table 2.1. Cyclic voltammetric data for 29a~29c.$^a$

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$E^{1/2}$ (pH = 1.0)$^b$</th>
<th>$E^{1/2}$ (pH 7.0)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29a</td>
<td>0.97, 1.32$^{ir}$, 1.54$^{cp}$</td>
<td>0.81$^{ir}$, 1.13$^{ir}$, 1.21$^{cp}$</td>
</tr>
<tr>
<td>29b</td>
<td>0.98, 1.36$^{ir}$, 1.56$^{cp}$</td>
<td>0.82$^{ir}$, 1.14$^{ir}$, 1.22$^{cp}$</td>
</tr>
<tr>
<td>29c</td>
<td>1.01, 1.41$^{ir}$, 1.58$^{cp}$</td>
<td>0.83$^{ir}$, 1.20$^{ir}$, 1.25$^{cp}$</td>
</tr>
</tbody>
</table>

$^a$Scan rate is 100 mV s$^{-1}$ and reported in V vs. NHE; the concentration of sample is 1 mM; $ir =$ irreversible; $cp =$catalytic onset potential. $^b$ In pH 1.0 CF$_3$SO$_3$H solution containing 10% acetonitrile. $^c$ In pH 7.0 phosphate buffer containing 10% acetonitrile.

2.4 O$_2$ Evolution and Mechanism Discussion$^{xii,xiii}$

The catalytic O$_2$ evolution by 29a~29c were carried out in acidic solutions containing large excess CAN. The amount of evolved O$_2$ was monitored by an optical probe (YSI 5331/5300) and calibrated by GC at the end point of each trial (Figure 2.8). All three complexes are capable of oxidizing water to dioxygen with TONs of 336 for 29a, 310 for 29b, and 190 for 29c over a six-hour period of measurement. 29a and 29b show very proximate initial TOF which is defined as the slope of the time-resolved O$_2$-evolving plot at time = 0. The initial TOF of 29c is considerably lower than that of 29a or 29b. It is inferred that an electron-withdrawing substituent, bromide in this case, is detrimental to the catalytic activity of Ru-pda series of complexes.
Figure 2.8. O$_2$ evolution vs. time plots for 29a (blue), 29b (red) and 29c (green). Condition: pH 1.0 CF$_3$SO$_3$H solution, [CAN] is 0.167 M, and [29a–c] is 0.33 mM.

While the concentration of CAN was kept as constant and largely excess, the initial rate of O$_2$ evolution depended linearly on the concentration of catalyst 29a, demonstrating a pseudo first-order kinetics (rate[O$_2$] = $k[29a]$, Figure 2.9). This is in severe contrast to the previously reported second-order kinetics of O$_2$ evolution for catalyst 21. Moreover the initial TOF (0.76 s$^{-1}$) of 29a is significantly lower than that (32 s$^{-1}$) of 21.$^{[94]}$ Thus we rule out an O–O bond formation pathway via coupling of two Ru-oxo unites and propose water-nucleophilic-attack to the [Ru$^{V}=O$]$^+$ species of 29a–c as the key O–O bond formation step of their catalytic cycle of water oxidation.

Figure 2.9. Left: Plots of O$_2$ evolution vs. time at various concentrations of 29a: 0.04 mM (black), 0.033 mM (blue), 0.025 mM (red), 0.017 mM (green), 0.008 mM (purple). Right: Initial rate of O$_2$ evolution at various concentrations of catalyst 29a, $k$ = 0.76 s$^{-1}$.
The DFT model has successfully predicted and simulated the catalytic water oxidation pathway of 21 via coupling of two [RuV(bda)(py)2=O]+ units (Figure 2.10, a).[94] It was further corroborated by the kinetics experiments recently.[95] In order to compare the potential energy profiles during water oxidation catalyzed by Ru-bda and Ru-pda complexes, the theoretical modeling was applied to [RuV(bda)(py)2=O]+ and [RuV(pda)(py)2=O]+ following both ‘two units coupling’ and ‘water nucleophilic attack (WNA)’ approaches (Figure 2.10). In each situation, the transition state of O–O bond formation step was examined and analyzed. The calculated energy barriers for O–O bond formation steps are summarized in Table 2.2. Basically, [RuV(bda)(py)2=O]+ prefers the ‘coupling’ pathway, while [RuV(pda)(py)2=O]+ favors the other, the WNA pathway.

(a) two units coupling

(b) water nucleophilic attack

![Figure 2.10](image)

**Figure 2.10.** Schemes of two proposed pathways for catalytic water oxidatoin by Ru-bda (21) and Ru-pda (29a~c) complexes: intermolecular coupling (a) and water nucleophilic attack (b). The O–O bond formation steps are highlighted.

**Table 2.2.** Computational barriers of O–O bond formation highlighted in Figure 2.10.

<table>
<thead>
<tr>
<th>Pathways</th>
<th>[RuV(pda)(py)2=O]+</th>
<th>[RuV(bda)(py)2=O]+</th>
</tr>
</thead>
<tbody>
<tr>
<td>WNA</td>
<td>13.3 kcal/mol</td>
<td>18.0 kcal/mol</td>
</tr>
<tr>
<td>RuV=O coupling</td>
<td>16.4 kcal/mol</td>
<td>11.9 kcal/mol</td>
</tr>
</tbody>
</table>

A careful comparison upon the corresponding transition states, in these two plausible schemes, uncovered two major reasons for the different reaction behaviours of [RuV(pda)(py)2=O]+ and [RuV(bda)(py)2=O]+ complexes. On one hand, the rigid pda ligand increases collision of axial ligands, when two
formally $[\text{Ru}^V(\text{pda})(\text{py})_2=\text{O}]^+$ are getting close with each other. This steric effect hinders an intermolecular coupling between two $[\text{Ru}^V(\text{pda})(\text{py})_2=\text{O}]^+$ units. On the other hand, when $[\text{Ru}^V(\text{bda})(\text{py})_2=\text{O}]^+$ is proceeding with the water nucleophilic attack reaction (highlighted step in Figure 2.10 b), the bda ligand have to abandon its adjustability to the Ru$^V$ core and the whole complex reorganizes (distort and bend) itself considerably to overcome the transition state (TS). In comparison, the reorganization of geometry occurs in much less extent, from $[\text{Ru}^V(\text{pda})(\text{py})_2=\text{O}]^+$ to the TS during the WNA process. The higher overall reorganization energy of passing the TS inhabit the WNA to $[\text{Ru}^V(\text{bda})(\text{py})_2=\text{O}]^+$.

(The optimized structures of Ru$^V$ complexes and the optimized TS discussed in this chapter are available in the supporting information of Paper I.)

### 2.5 Summary

A series of mononuclear Ru WOCs (29a~c) with pda ligands were designed and synthesized. Combined results from electrochemical and MS experiments revealed a $[\text{Ru}^{\text{III}}-\text{OH}_2]^+ \rightarrow [\text{Ru}^{\text{IV}}-\text{OH}]^+ \rightarrow$ formally $[\text{Ru}^V=\text{O}]^+$ consecutive electron transfer steps for 29a in the presence of CAN. Similar sequence of oxidation was also observed for WOC 21. However, 29a and 21 exhibit dramatically different catalytic behaviors. DFT simulation elucidated diverging O–O bond formation pathways, ‘two units coupling’ and ‘WNA’, for the formally $[\text{Ru}^V(\text{pda})=\text{O}]^+$ and $[\text{Ru}^V(\text{bda})=\text{O}]^+$ intermediates. A close examination at the TS, in each of plausible pathways, provided insight into the structure-mechanism relationship. The disparity between pda and bda ancillary ligands, no matter how subtle it looks like, can significantly influence the catalytic cycle of the water oxidation by mononuclear Ru complexes.
3. Mononuclear Ru WOCs with Tridentate Anionic Ligands (Part One)

(Paper II)

3.1 Introduction

[Ru\textsuperscript{II}(tpy)(pic)\textsubscript{3}\textsuperscript{2+} (18)] can be regarded as a prototype of [Ru(\textit{NNN})(\textit{N})\textsubscript{2}L] style WOCs that are discussed in Chapter 1. Its catalytic performance of oxidizing water was first studied by Thummel’s group\textsuperscript{[84]} and recently revisited by our group.\textsuperscript{[88]} A long induction period of about two hours was observed before 18 begins to mediate water oxidation in an acidic CAN solution. In contrary, O\textsubscript{2} evolution was detected instantly, when [Ru\textsuperscript{II}(tpy)(pic)\textsubscript{2}OH\textsubscript{2}\textsuperscript{2+} (16)] as an aqua analogue of 18 was injected into an acidic CAN solution. Based on these observations, we concluded that 18 is not able to catalyze water oxidation until at least one of its pic ligands is replaced by water molecule.

Figure 3.1. Molecular structures of [Ru\textsuperscript{II}(tpy)(pic)\textsubscript{3}\textsuperscript{2+} (18), [Ru\textsuperscript{II}(pdc)(pic)\textsubscript{3}] (30) and [Ru\textsuperscript{II}(hqc)(pic)\textsubscript{3}] (31).

In 2010, we reported the preparation and catalytic performance of [Ru\textsuperscript{II}(pdc)(pic)\textsubscript{3}] (30, H\textsubscript{2}pdc = 2,6-pyridinedicarboxylic acid) as a Ru WOC.\textsuperscript{[123]} Despite the similar coordination motif of 18 and 30, we found that
30 can be oxidized to trivalent state at a lower potential than that of oxidation of 18. Meanwhile, 30 doesn’t undergo any induction time before mediating water oxidation, when CAN is used as an oxidant. Aiming to understand the effect of anionic ligands in terms of WOCs, we designed and prepared [RuII(hqc)(pic)₃] (31) that bears tridentate dianionic 8-hydroxyquinoline-2-carboxylate (hqc) as an ancillary ligand. In principle, hydroxyl group is a stronger π- and δ- electron-donating ligand than carboxylate group. Comparative investigation upon complexes 18, 30 and 31 can help us to understand how the coordination spheres of mononuclear Ru WOCs influence their catalytic activity.

3.2 Synthesis and Structure of the Ru-hqc Complex

Complex 31 was prepared in a two-step one-pot reaction using cis-[RuII(DMSO)₄Cl₂] as starting material. The synthetic method is same as that applied in the preparation of 29a~c. In the scheme of this one-pot reaction, DMSO and chloride ligands of cis-[RuII(DMSO)₄Cl₂] are replaced by hqc and pic ligands stepwise under different reaction conditions. The yield of 31 is 47%. Its structure was characterized by ¹H NMR, MS and elemental analysis. The UV−vis spectrum of 31 in CH₂Cl₂ displays MLCT absorbance bands at 406 nm and 525 nm wavelength.

Crystal structures of 18 and 31 were displayed in Figure 3.2. Although 18 has been reported before, its steric structure has not been revealed in detail yet. Either tpy or hqc ligand chelates with the RuII center via its all three donors. Compared with the Ru1−N(tpy) bonds (1.95~2.08 Å) of 18, the Ru1−O1(hqc) (2.176 Å) or Ru1−O1(hqc) (2.170Å) bond of 31 is distinctively longer. Moreover, the three Ru−N(picoline) bonds (2.114~2.137 Å) in 31 are generally longer than the corresponding Ru−N(picoline) bonds in 18 (2.093−2.125 Å). It should be noted that the phenolate group in 31 forms a

xiv X-ray-quality single crystals of 18 and 31 were cultivated by Lianpeng Tong and resolved by Dr. Andreas Fischer at KTH.
hydrogen bond (H3O−O4) with a solvated water molecule. The same situation is expected in the aqueous solutions of 31.

Figure 3.2. X-ray crystal structures of 18 (left, ellipsoids at 30% probability) and 31 (right, ellipsoids at 50% probability); color code: Ru (purple), N (blue), O (red), C (grey) and H (green). H atoms (except water) and PF_6^- are omitted for clarity.xiv

3.3 Labile Picoline Ligandxv

Figure 3.3 shows the mass spectra of 31 before and after it was treated with 4 equivalents of CAN. For a sample of 31 in an acetone/water solution, signals corresponding to the mass of [31 + H]^+ and [31 + Na]^+ are the only observed Ru-containing species in the mass spectrum. After addition of 4 equivalents of CAN into the solution of 31, the resulting sample was directly injected into the mass spectrometry immediately. Signals of [Ru^{III}(hqc)(pic)_2 + H_2O]^+ and [Ru^{III}(hqc)(pic)_2 + CH_3COCH_3]^+ emerged in the mass spectrum immediately, besides the cluster signal of [Ru^{III}(hqc)(pic)_3]^+. Addition more CAN (8~16 equivalents) in the 31 sample didn’t lead to appearance of any other Ru species in the mass spectrum. It is inferred that one pic ligand of 31 is facilely replaced by water or coordinative organic molecular, when 31 is oxidized to its Ru^{III} state. In contrary, similar pic/water or pic/acetone ligand exchange

xv DFT calculation discussed in this section was conducted by Mr. Ying Wang, Dr. Xiao Cheng and Dr. Mårten S. G. Ahlquist at KTH.
doesn’t proceed in the case of 18. Even after 16 equivalents of CAN was added to the solution of 18, neither $[\text{Ru}^{\text{III}}-\text{OH}_2]^+$ nor $[\text{Ru}^{\text{III}}-\text{acetone}]^+$ signals could be recorded by MS, indicating relatively robust $\text{Ru}^{\text{III}}-\text{N(pic)}$ bonds of $[\text{Ru}^{\text{III}}(\text{tpy})(\text{pic})_3]^+$.

Figure 3.3. ESI-MS spectra of 31 in acetone/water (1:9) before (top) and after (bottom) the treatment of 4 equivalents of CAN.

The structure of $[\text{Ru}^{\text{III}}(\text{hq}(\text{pic})_2\text{OH}_2)]^+$ was optimized by DFT simulation with additional explicit water molecules so as to reproduce the protic circumstance of aqueous solutions. It was found that a network of hydrogen bonds, which consists of the phenolate group, the aqua ligand and water molecules around the Ru core, stabilizes the structure of the $[\text{Ru}^{\text{III}}-\text{OH}_2]^+$ species. These hydrogen bonds may also contribute to the proton shuffle and
assist to the PCET when the [Ru\textsuperscript{III}−OH\textsubscript{2}]\textsuperscript{+} species is oxidized to the Ru\textsuperscript{IV} or Ru\textsuperscript{V} state.

In order to understand the pic/water ligand exchange that is a premise for any interaction between water and non-aqua complex 18, 30 or 31, we considered two ligand exchange scenarios and examined the relative energy of activation for all three Ru\textsuperscript{III} complexes by DFT calculation. One ligand exchange route is the concerted associative pathway (Figure 3.4, path a) where coordination of a water molecule to the Ru\textsuperscript{III} core and departure of a picoline ligand happen simultaneously. The related transition state was marked as I\textsubscript{a}. The other route is dissociative pathway (Figure 3.4, path b) where one picoline ligand dissociates from the Ru\textsuperscript{III} core first, giving a 5-coordinated Ru\textsuperscript{III} intermediate (D) and then a water molecule comes into the coordinative sphere of the Ru\textsuperscript{III} center.

The energy profiles of these two ligand exchange pathways were delineated in Figure 3.5. For all three complexes, the dissociative pathways are favored. In this scenario, the calculated energy barriers of ligand exchange for 30 and 31 are nearly identical, 12.2 and 12.7 kcal/mol respectively. Nevertheless, the corresponding energy of activation for 18 (22.8 kcal/mol) is evidently higher.
These results demonstrate that at trivalent state, \(30\) and \(31\) undergo pic/water exchange through dissociative pathway in remarkably faster rate than \(18\). Apparently anionic pdc and hqc ligands are capable of facilitating the dissociation of picoline, compared with neutral tpy ligand. This labile effect of anionic ligand, carboxylate and phenolate groups particularly, can be explained from their \(d\pi\) electron–donating perspective primarily. After the dissociation of one picoline from the complex, the anionic oxygen group can donate an extra pair of electrons at its \(p\)-orbital to the electron-deficient \(\text{Ru}^{III}\) center of the intermediate (\(D\) state in Figure 4.5 b). This can stabilize the coordinatively unsaturated intermediate.

![Figure 3.5](image_url)  
**Figure 3.5.** The energy profile of associative ligand exchange pathway (a) and dissociative ligand exchange pathway (b).

### 3.4 Electrochemical Analysis of Ru-pdc and Ru-hqc WOCs

Figure 3.6 displays CV curves of \(18\), \(30\) and \(31\) in organic solvents. \(E^{1/2}\) (\(\text{Ru}^{II}/\text{Ru}^{III}\)) of \(30\) or \(31\) is dramatically less positive than that of \(18\). This is attributed to the \(\pi\)-donating ability of carboxylate or phenolate group, which enhances the electron density of ruthenium center accordingly. The more positive \(\text{Ru}^{III}/\text{Ru}^{II}\) redox potential of \(30\) in comparison with that of \(31\) reflects stronger \(\delta\)-donating ability of the phenolate ligand (of hqc) rather than that of the carboxylate ligand (of pdc).
Ligand exchange is believed to occur *in situ* while 31 is being oxidized to its trivalent state. Because the organic cosolvent (acetonitrile in this case) competes with water to coordinate with the RuIII center (as shown in the mass spectra in section 3.3), a variety of redox couples could respond during the potential sweep upon 31 under aqueous experimental conditions. The involvement of Ru-solvent species strongly intervenes in assignment of redox waves that appear in the CV curve of 31. It is, however, assumed that the [RuIII–MeCN]⁺ and [RuIII–OH₂]⁺ species exist in high dynamic equilibrium, because neither the RuIII–N(MeCN) nor the RuIII–O(aqua) bond here is robust, just like the labile RuIII–N(pic) bond aforementioned. In principle, [RuIII–MeCN]⁺ will convert to [RuIII–OH₂]⁺ instantly in aqueous medium, when [RuIII–OH₂]⁺ is oxidized to its RuIV state via PCET. (Oxidation of [RuIII–MeCN]⁺ is more difficult due to infeasible PCET of non-aqua complex.) So the presence of organic cosolvent doesn’t suppress the formation of high-valent state in the case of 30 or 31 or the catalysis of water oxidation subsequently.

DFT modeling illustrates the consecutive oxidation sequence for 30 and 31 initiating from their aqua-RuIII formations in both acidic and neutral aqueous solutions (Figure 3.7). The pKₐ values of [RuIII(hqc)–O/H₂]⁺ and
[Ru\textsuperscript{III}(pdc)--OH\textsubscript{2}]\textsuperscript{+} were calculated to be 7.0 and 5.2 respectively, and those of
[Ru\textsuperscript{IV}(hqc)--OH\textsuperscript{+}] and [Ru\textsuperscript{IV}(pdc)--OH\textsuperscript{+}] to be 4.4 and -0.1. Larger $pK_a$ values of Ru-hqc species indicate that they are more reluctant to give protons away
than corresponding Ru-pdc species. It is intriguing that the electron effect of anionic ancillary ligands influences the oxidation sequence of Ru complexes in two counteracting ways. On one hand, hqc as a better electron-donating ligand than pdc facilitates the ET process, so the redox potential of [Ru\textsuperscript{IV}(hqc)=O]/[Ru\textsuperscript{V}(hqc)=O]\textsuperscript{+} (1.23 V) is less positive than that of
[Ru\textsuperscript{IV}(pdc)=O]/[Ru\textsuperscript{V}(pdc)=O]\textsuperscript{+} (1.38 V) under pH 7.0 conditions. On the other hand, high electron density of Ru center restrains the release of protons from the complex, so PCET process of [Ru\textsuperscript{IV}(hqc)=O]/[Ru\textsuperscript{III}(hqc)--OH\textsuperscript{+}] and that of
[Ru\textsuperscript{IV}(pdc)=O]/[Ru\textsuperscript{III}(pdc)--OH\textsuperscript{+}] happen at identical (0.78 V) potential in pH 7.0 solution, as a compromise of ET and PT processes.

$$\text{pH} = 7.0$$

complex 31: [Ru\textsuperscript{III}(hqc)--OH\textsuperscript{+}] \xrightarrow{0.78 \text{V}} [Ru\textsuperscript{IV}(hqc)=O]\xrightarrow{1.23 \text{V}} [Ru\textsuperscript{V}(hqc)=O]\textsuperscript{+}

complex 30: [Ru\textsuperscript{III}(pdc)--OH\textsuperscript{+}] \xrightarrow{0.78 \text{V}} [Ru\textsuperscript{IV}(pdc)=O]\xrightarrow{1.38 \text{V}} [Ru\textsuperscript{V}(pdc)=O]\textsuperscript{+}

$$\text{pH} = 0$$

complex 31: [Ru\textsuperscript{III}(hqc)--OH\textsubscript{2}]\textsuperscript{+} \xrightarrow{1.35 \text{V}} [Ru\textsuperscript{IV}(hqc)--OH\textsuperscript{+}]\xrightarrow{1.49 \text{V}} [Ru\textsuperscript{V}(hqc)=O]\textsuperscript{+}

complex 30: [Ru\textsuperscript{III}(pdc)--OH\textsubscript{2}]\textsuperscript{+} \xrightarrow{1.50 \text{V}} [Ru\textsuperscript{IV}(pdc)=O]\xrightarrow{1.38 \text{V}} [Ru\textsuperscript{V}(pdc)=O]\textsuperscript{+}

**Figure 3.7.** Calculated redox potentials for complexes 30 and 31 at pH 0 and pH 7.0; pic ligands are not marked; the potentials are versus NHE.

In neutral aqueous medium (pH 7.0 phosphate buffer containing 10% acetonitrile), 31 begins to mediate water oxidation at about 1.1 V, while an onset of catalytic current was observed at around 1.5 V in the CV curve of 31 under acidic conditions (pH 1.0 triflic acid containing 10% acetonitrile). The observed catalytic potentials for 31 in both situations are very close to its calculated Ru\textsuperscript{V}/Ru\textsuperscript{IV} redox potentials as shown in Figure 3.7. It implies that the [Ru\textsuperscript{V}(hqc)=O]\textsuperscript{+} species triggers the water to dioxygen reaction.
3.5 $\text{O}_2$ Evolution by the Ru-hqc WOC

The $\text{O}_2$-evolving reaction catalyzed by complex 31 was carried out in a typical acidic CAN solution. A pressure transducer (Omega PX138-030A5V) was applied in this work to monitor the generated $\text{O}_2$ amount. Unlike complex 18, 31 doesn’t proceed with any induction period before mediating water oxidation. As long as the complex was injected into the pH 1.0 aqueous solution containing excess CAN, instant $\text{O}_2$ evolution was detected by the pressure transducer. A TON of 680 was attained over a 12-hour period of reaction. While the concentration of CAN was kept constant and largely excess with regard to the concentration of 31, initiate rate of $\text{O}_2$ evolution is found linearly dependent on the concentration of 31 (Figure 3.8), pointing to a catalytic pathway involving only single sight Ru intermediates. The measured rate constant or initial TOF of initial $\text{O}_2$ evolution is 0.32 s$^{-1}$ that renders 31 as one of the most efficient [Ru(NNN)(N)$_2$L] type WOCs (initial TOF of 30 is 0.23 s$^{-1}$).[123]

![Figure 3.8](image-url)

**Figure 3.8.** Left: Plots of $\text{O}_2$ evolution vs. time at various concentrations of 31 in pH 1.0 CF$_3$SO$_3$H aqueous solution (3mL) containing CAN (0.083 M). The initial rates were calculated by fitting the $\text{O}_2$ vs. time curves from 0 to 150 s as a straight line. Right: Determination of $k_{\text{O}_2}$ by plotting initial rate of $\text{O}_2$ generation against the concentration of 31.
3.6 Summary

An efficient mononuclear WOC [Ru\textsuperscript{II}(hqc)(pic)\textsubscript{3}] (31) was prepared and evaluated. It has similar coordinative geometry with [Ru\textsuperscript{II}(pdc)(pic)\textsubscript{3}] (30) and [Ru\textsuperscript{II}(tpy)(pic)\textsubscript{3}]\textsuperscript{2+} (18) reported previously. MS experiments and DFT simulation revealed that 30 and 31 undergo rapid pic/water ligand exchange via a dissociative pathway, when they were oxidized to trivalent state. In contrary, 18 undergoes the ligand exchange process in severely slow rate which impedes its interaction with water and effective catalysis of water oxidation. Anionic ligands, e.g. carboxylate and phenolate, play an important role in the facility of pic dissociation. A comparative study about the electrochemical performance of 30 and 31 illustrated that better δ- and π-donating ability of hqc ligand, rather than pdc, benefits the ET process but compromise the PT process during corresponding aqua complexes accessing to their Ru\textsuperscript{V} states. However, the insolubility of 30 and 31 in water doesn’t allow detailed mechanism investigations upon these two candidates.
4. Mononuclear Ru WOCs with Tridentate Anionic Ligands (Part Two)

(Paper III)

4.1. Introduction

From our work discussed in Chapter 2 and 3, we found that anionic ancillary ligands, such as pdc and hqc, influence the catalytic performance of mononuclear Ru WOCs in a way that different from commonly applied neutral polypyridyl ligand, like tpy. The Ru complexes [RuII(pda)(pic)2] (29a), [RuII(pdc)(pic)3] (30) and [RuII(hqc)(pic)3] (31) carrying carboxylate or phenolate donors exhibit impressive efficiency for catalytic water oxidation. These RuII candidates, however, are insoluble in water. Thus, organic co-solvents are required to assist their dissolution in homogeneous aqueous medium. This disadvantage obstructs insight of mechanism study upon these Ru complexes, because organic co-solvents undergo coordinative interaction with the Ru complexes and interfere severely with the spectral results. In order to overcome this drawback of insolubility and continue to exploit the effect of anionic ligand in terms of mononuclear Ru WOCs, we designed and prepared Ru complexes [RuII(bpc)(bpy)OH2]⁺ (32, Hbpc = 2,2’-bipyridine-6-carboxylic acid) and [RuII(bpc)(pic)3]⁺ (33). Their structures are displayed in Figure 4.1. Since tridentate bpc ligand contains only one carboxylate donor, both 32 and 33 are positively charged and considerably soluble in water. The coordination motif of complex 32 is very similar to that of [Ru(NNN)(NN)L] type WOCs discussed in Chapter 1. It can be regarded as an analogy of two representative examples in this [Ru(NNN)(NN)L] category, [RuII(tpy)(bpy)OH2]2⁺ (7) and [RuII(tpy)(bpm)OH2]2⁺ (8), which contain a neutral tridentate tpy ligand (Figure 4.1). Because 7 and 8 have been extensively studied from the mechanism aspect (see Chapter 1), they are exemplified in this chapter to compare with 32 so as to elucidate the role of
anionic bpc ligand within the catalytic water oxidation reaction. On the other side, the coordinative geometry of 33 is quite similar to that of non-aqua complexes 30 and 31 discussed in last chapter. The examination of properties and catalytic performance for 33 is about to provide more information about our previous work.

Figure 4.1. Structures of complexes [RuII(bpc)(bpy)OH2]+ (32), [RuII(bpc)(pic)3]+ (33), [RuII(tpy)(bpy)OH2]2+ (7) and [RuII(tpy)(bpm)OH2]2+ (8).

4.2 Synthesis and Structures of Ru-bpc WOCs

The synthetic rout of Hbpc ligand is expressed in Figure 4.2. The synthesis of complex 33 is accomplished in a two-step one-pot reaction using cis-[RuII(DMSO)4Cl2] as a starting substrate. This approach is same as that we used in the preparation of complexes 30 and 31. The overall yield (32%) for the preparation of 33, however, is relatively low, because each RuII core is able to bind with two bpc ligands at the same time, resulting in the formation of [RuII(bpc)2] as a primarily byproduct. For the synthesis of complex 32, a different strategy was used (Figure 4.3), by which two DMSO of cis-[RuII(DMSO)4Cl2] were replaced by a bpy firstly; another two DMSO and one Cl were subsequently replaced by a bpc ligand; and finally the only Cl left was replaced by water in the presence of Ag+, affording the desired product. Both [RuII(bpy)(DMSO)2Cl2] and [RuII(bpc)(bpy)Cl] were isolated and characterized as intermediates. The structure of 32 and 33 can be characterized by 1D and 2D 1H NMR experiments unambiguously. In
addition, the $^1$H NMR spectrum of 32 recorded in deuterated DMSO revealed replacement of aqua ligand of 32 by DMSO molecule under the NMR conditions. Considering the potential interference from ligand exchange, we tried to avoid involvement of any organic solvent in the spectroscopic measurements and catalytic evaluations for 32 and 33.

![Figure 4.2. Synthesis of 2,2'-bipyridine-6-carboxylic acid (Hbpc).](image)

Figure 4.2. Synthesis of 2,2'-bipyridine-6-carboxylic acid (Hbpc).

![Figure 4.3. Synthesis of [Ru$^{II}$(bpc)(bpy)OH$_2$]$^+$ (32).](image)

Figure 4.3. Synthesis of [Ru$^{II}$(bpc)(bpy)OH$_2$]$^+$ (32).

X-ray crystal structures of 32 and 33 are presented in Figure 4.4.xvi In either situation, the Ru$^{II}$ center adopts a distorted octahedral geometry of coordination as predicted. Compared with the crystal structure of 7,[124] the corresponding Ru1–O3(aqua), Ru–N1(bpy) and Ru–N2(bpy) bonds of 32 are considerably longer accordingly. This phenomenon can’t only be explained by steric interaction among ligands, but also due to different electron effect of bpc and tpy ligands probably. A hydrogen bond between solvated water and ligated water was observed in the structure of 32. The same situation is also expected in the protic solution of 32. The average distance of Ru1–N(pic) bonds (2.092–2.120 Å) in 33 is slightly shorter than corresponding Ru–N(pic) (2.114–2.137 Å) in [Ru$^{II}$(hq)c)(pic)$_3$] (31). This is probably

---

xvi X-ray-quality single crystals of 18 and 31 were cultivated by Lianpeng Tong and resolved by Dr. A. Ken Inge at Stockholm University.
because there are two negative oxygen donors coordinated with ruthenium in 31, whereas only one in 33.

![Figure 4.4. X-ray crystal structures of 32 (left, ellipsoids at 40% probability) and 33 (right, ellipsoids at 40% probability); hydrogen atoms (except water) and PF$_6^-$ are omitted for clarity; color code: Ru (purple), N (blue), O (red), C (grey) and H (green).][xvi]

### 4.3 Spectral and Electrochemical Properties of Ru-bpc Complexes

Both UV-vis spectra of 32 and 33 in pH 1.0 HNO$_3$ exhibit Ru(d$_\pi$)→bpc(p$\pi^*$) MLCT absorbance band at about 490 nm and bpc(p$\pi$)→bpc(p$\pi^*$) local charge transition band at around 290 nm (Figure 4.5). Neither absorption profiles of 32 and 33 showed discernible decay over a 120 minutes period of observation, indicating their outstanding stability in acidic solution. When the pH of solution of 32 was titrated from 7.5 to 12.5, the color of the solution changed from light brown to dark purple owing to deprotonation of 32. Accordingly, a shift of MLCT band from 488 nm to 522 nm was observed from the UV-vis spectrum. The pK$_a$ of 32 was estimated to be 10.6 by following the decrement of absorbance at 488 nm versus pH change.
The Pourbaix diagram of 32 (Figure 4.6) supports a formally \([\text{Ru}^\text{II}−\text{OH}_2]^+ \rightarrow [\text{Ru}^\text{III}−\text{OH}_2]^{2+} \rightarrow [\text{Ru}^\text{IV}=\text{O}]^+ \rightarrow [\text{Ru}^\text{V}=\text{O}]^{2+}\) oxidation sequence in pH 1.0 medium and a consecutive \([\text{Ru}^\text{II}−\text{OH}_2]^+ \rightarrow [\text{Ru}^\text{III}−\text{OH}]^+ \rightarrow [\text{Ru}^\text{IV}=\text{O}]^+ \rightarrow [\text{Ru}^\text{V}=\text{O}]^{2+}\) oxidation process in pH 7.0 medium. Based on the Nernst effect indicated in the Pourbaix diagram, the pK\(_a\) of \([\text{Ru}^\text{II}(\text{bpc})(\text{bpy})\text{OH}_2]^+\) and \([\text{Ru}^\text{III}(\text{bpc})(\text{bpy})\text{OH}_2]^+\) were estimated to be 10.6 and 2.6 respectively. This is consistent to the result from titration experiment aforementioned. It should be noted that 32 undergoes \([\text{Ru}^\text{IV}=\text{O}]^+/[\text{Ru}^\text{V}=\text{O}]^{2+}\) redox reaction at around 1.59 V, less positive than the corresponding potential (~1.7 V) for 8 or that (> 1.8 V) for 7. This disparity originates from better \(\pi\)-donating effect of (carboxylate) bpc ligand rather than tpy ligand. Potential sweep scan upon either acidic (pH 1.0) or neutral (pH 7.0) aqueous solution of 32 evokes catalytic current of water oxidation commencing at about 1.6 V. This catalytic potential is more positive than its Ru\text{IV}/Ru\text{V} redox event, implying pentavalent or higher-valent Ru species as the trigger for water oxidation reaction catalyzed by 32.
In a pH 1.0 solution of 33, potential sweep from 0 to 1.6 V revealed \([\text{Ru}^{II}(bpc)(pic)_3]^+/[\text{Ru}^{III}(bpc)(pic)_3]^{2+}\) oxidation at 0.89 V as the only redox wave and none salient catalytic current. Under pH 7.0 aqueous conditions, however, CV sweep upon 33 triggered several redox waves besides that of \([\text{Ru}^{II}(bpc)(pic)_3]^+/[\text{Ru}^{III}(bpc)(pic)_3]^{2+}\) and catalytic current clearly higher than the background (Figure 4.7, a). One redox event among them at about 0.5 V was carefully examined by multiple CV scans over the 0.2~0.9 potential window at slow scan rate (50 mV/s, Figure 4.7, b). If the scan rate was increased to 1000 mV/s, strength of the signal at 0.5 V was remarkably suppressed (Figure 4.7, c). Moreover, this redox emerged during DPV sweep from the anode to cathode (0.9 V → 0.2 V) direction but not in the reversal process (0.2 V → 0.9 V, Figure 4.7, d). Based on the observation above, we propose that pic/water ligand exchange happen to \([\text{Ru}^{III}(bpc)(pic)_3]^{2+}\) species during the potential sweep in its neutral aqueous solution and \([\text{Ru}^{III}(bpc)(pic)_2OH_2]^{2+}\) complex is afforded \textit{in situ}. The redox wave at 0.5 V is assigned to the \([\text{Ru}^{III}(bpc)(pic)_2OH_2]^{2+}/[\text{Ru}^{II}(bpc)(pic)_2OH_2]^{2+}\) redox couples. According to the discussion in last chapter, the ligand exchange undergoes a dissociative pathway and facilitated by the carboxylate group. It is significantly restrained under acidic conditions, because protonation of the
carbonyl group weaken the pπ-donating ability of the carboxylate group in the bpc ligand.

Figure 4.7. Electrochemical analysis of 33 under neutral conditions. (a): CV of 33 (0.5 mM in pH 7.1 phosphate buffer, IS = 0.1 M, scan rate = 100 mV s⁻¹). (b): CV of 33 (0.5 mM in pH 7.1 phosphate buffer, IS = 0.1 M, scan rate = 50 mV s⁻¹). (c): CV of 33 (0.5 mM in pH 7.1 phosphate buffer, IS = 0.1 M, scan rate = 1000 mV s⁻¹). (d): DPV of 33 (0.5 mM in pH 7.1 phosphate buffer, IS = 0.1 M).

4.4 Labile Picoline Ligand

From the theoretical results discussed in Chapter 3, we concluded that [Ru³⁺(pdc)(pic)₃]⁺ (30⁺) and [Ru³⁺(hqc)(pic)₃]⁺ (31⁺) undergo pic/H₂O ligand exchange in fast rate which, however, can’t be directly evaluated due to their inadequate solubility in water. Electrochemical experiments above showed that same exchange process occurred at [Ru³⁺(bpc)(pic)₃]²⁺ too. So we carried
out evaluation of the rate constant of ligand exchange by tracking the absorption change of \([\text{Ru}^{III}(\text{bpc})(\text{pic})_3]^{2+}\) in aqueous medium. Oxidizing complex 33 to its trivalent state severely bleached its MLCT absorbance band at 488 nm. The absorption profile of the resulting \([\text{Ru}^{III}(\text{bpc})(\text{pic})_3]^{2+}\) solution demonstrated decrement of absorbance at 294 nm and increment of absorbance at 279 and 365 nm over a 180 mins period of observation (Figure 4.8). Two isobestic points at 270 and 290 nm were clearly observed in the time-resolved spectra. This phenomenon is ascribed to the pic/H$_2$O ligand exchange described in Equation 4.1, where $k_{ex}$ represents the rate constant. Since the concentration of water is enormous under the experimental conditions, the ligand exchange process conforms to the first-order rate law expressed in Equation 4.2, in which \([\text{Ru}^{III}−\text{pic}]\) is the concentration of \([\text{Ru}^{III}(\text{bpc})(\text{pic})_3]^{2+}\) at time = $t$. Equation 4.3 is the integrated form of the rate law, where \([\text{Ru}^{III}−\text{pic}]_0\) is the concentration of \([\text{Ru}^{III}(\text{bpc})(\text{pic})_3]^{2+}\) at time = 0.

\[
[\text{Ru}^{III}(\text{bpc})(\text{pic})_3]^{2+} + \text{H}_2\text{O} \xrightarrow{k_{ex}} [\text{Ru}^{III}(\text{bpc})(\text{pic})_2\text{OH}_2]^{2+} + \text{pic} \quad \text{(Equation 4.1)}
\]

\[
\frac{d[\text{Ru}^{III}−\text{pic}]}{dt} = -k_{ex}[\text{Ru}^{III}−\text{pic}] \quad \text{(Equation 4.2)}
\]

\[
\ln[\text{Ru}^{III}−\text{pic}]_0 - \ln[\text{Ru}^{III}−\text{pic}] = k_{ex}t \quad \text{(Equation 4.3)}
\]

**Figure 4.8.** Kinetics study of the H$_2$O/pic exchange happening to 33. Left: Absorbance change of 33 (0.05mM) in HNO$_3$ (pH 1.0) over 180 mins, after it was oxidized to Ru$^{III}$ state; trivalent 33 was attained by mixing 33 with 1 equivalent of CAN; insert shows the enlarged part from 265 to 310 nm. Right: Fitting of the time-resolved profile of absorbance at 358 nm by first-order reaction law (Equation 4.9).
In order to correlate the rate law of ligand exchange with the observed spectral data, following parameters are defined: \( A \), \( A_0 \) and \( A_\infty \) represent absorbance of the sample at time \( t \), 0 and infinity respectively; \( \varepsilon_p \) and \( \varepsilon_a \) stand for the extinction coefficients of \([\text{Ru}^{III}\text{(bpc)(pic)}_3]^{2+}\) and \([\text{Ru}^{III}\text{(bpc)(pic)}_2\text{OH}_2]^{2+}\); \([\text{Ru}^{III}\text{−OH}_2]\) and \([\text{Ru}^{III}\text{−OH}_2]_\infty \) are the concentration of \([\text{Ru}^{III}\text{(bpc)(pic)}_2\text{OH}_2]^{2+}\) at time \( t \) and infinity respectively. xvii Thus, absorbance values observed in the UV-vis spectra can be related to the concentrations of Ru species involved in the ligand exchange reaction by Equations 4.4~4.6, assuming that all corresponding Ru species in the solution follow the Beer-Lambert law.

\[
A_0 = \varepsilon_p [\text{Ru}^{III}\text{−pic}]_0 \quad \text{(Equation 4.4)}
\]

\[
A_\infty = \varepsilon_a [\text{Ru}^{III}\text{−OH}_2]_\infty \quad \text{(Equation 4.5)}
\]

\[
A = \varepsilon_p [\text{Ru}^{III}\text{−pic}] + \varepsilon_a [\text{Ru}^{III}\text{−OH}_2] \quad \text{(Equation 4.6)}
\]

Application of Equations 4.4~4.6 into Equation 4.7 affords Equation 4.8.

\[
[\text{Ru}^{III}\text{−pic}]_0 = [\text{Ru}^{III}\text{−pic}] + [\text{Ru}^{III}\text{−OH}_2] = [\text{Ru}^{III}\text{−OH}_2]_\infty \quad \text{(Equation 4.7)}
\]

\[
[\text{Ru}^{III}\text{−pic}] = \frac{A - A_\infty}{\varepsilon_p - \varepsilon_a} \quad \text{(Equation 4.8)}
\]

\[
\ln\left(\frac{A_0 - A_\infty}{A - A_\infty}\right) = k_{ex} t \quad \text{(Equation 4.9)}
\]

By application of Equation 4.4, 4.5 and 4.8, the integral expression of rate law (Equation 4.3) can be written in the form of Equation 4.9 which directly correlates the rate constant to the variables of time-resolved absorbance (\( A \) and \( t \)). The rate constant of pic/H\(_2\)O exchange \( k_{ex} = 1.2 \times 10^{-4} \text{ s}^{-1} \) was obtained by fitting the time-resolved absorbance plot of \([\text{Ru}^{III}\text{(bpc)(pic)}_3]^{2+}\) at 365 nm (Figure 4.8 right) according to Equation 4.9. This value of \( k_{ex} \) was measured in pH 1.0 aqueous medium. In principle, the rate constant should be...
larger in neutral aqueous solution as concluded from the electrochemical experiments in section 4.3. Meanwhile, we propose that \([\text{Ru}^\text{III}(\text{pdc})(\text{pic})_3]^+\) and \([\text{Ru}^\text{III}(\text{hqc})(\text{pic})_3]^+\) discussed in Chapter 3 undergo the pic/H\(_2\)O ligand exchange in a faster rate than \(k_{\text{ex}}\) owing to their dianionic pdc or hqc ligands.

### 4.5 O\(_2\) Evolution Catalyzed by Ru-bpc Complexes

O\(_2\)-evolving experiments catalyzed by complex 32 were carried out under a typical pH 1.0 HNO\(_3\)-CAN condition. The amount of O\(_2\) generated was monitored using a pressure transducer and calibrated by GC at the end of each trial. When the concentration of CAN was kept constant and largely excessive (1500~5500 equivalents) regarding to the concentration of the catalyst, the initial rate of O\(_2\) evolution (over 0~300 s) depended linearly on the initial concentration of 32, following a pseudo-first-order expression

\[
\text{initial rate} = k_{\text{O}_2}[32]
\]

(Figure 4.9). The rat constant \(k_{\text{O}_2}\), or initial TOF, was calculated to be 0.165 s\(^{-1}\). It is a little smaller than the initial TOF of 30 (0.23 s\(^{-1}\)) or 31 (0.32 s\(^{-1}\)) discussed in last chapter, but remarkably larger than that of 7 (0.029 s\(^{-1}\)) or 8 (0.016 s\(^{-1}\)) introduced in section 4.1 and Chapter 1.

![Figure 4.9](image-url)

**Figure 4.9.** O\(_2\) evolution catalyzed by 32. Left: Plots of O\(_2\) evolution vs. time at various concentrations of catalyst 32 in pH 1.0 HNO\(_3\) (3 mL) containing CAN (0.083 M). The initial rates were calculated by fitting the O\(_2\) vs. time curves from 0 to 300 s as a straight line. Right: Determination of \(k_{\text{O}_2}\) by plotting the initial rate of O\(_2\) generation against the concentration of 32.

The catalytic performance of 33 was also accessed under the same experimental conditions. Apparent inductions periods were observed before
began to drive O\textsubscript{2} evolution, due to the premise of pic/H\textsubscript{2}O ligand exchange in this case. The length of induction time depends on the concentrations of both CAN and 33. In principle the rate constant of ligand exchange should be higher in the presence of excess CAN than that measured in section 4.4 under the stoichiometric CAN conditions, because in the former situation complex 33 might be oxidized to its tetravalent state, at which the ligand exchange proceeds much easier.

4.5 Kinetics Study of Water Oxidation by Ru-bpc WOCs

The overall CAN-driven water oxidation reaction was described in Equation 1.3. Its rate in the presence of 32 as catalyst was measured by following the consumption of CAN during the reaction period. In contrast to the dramatically excessive amount of CAN applied in the O\textsubscript{2}-evolving experiments above (section 4.5), only tens of equivalents of CAN regarding to 32 was used in this kinetics study because of two reasons. One is to keep the rate of CAN consumption sensitive to changes of either the concentration of catalyst or that of CAN. The other is to maintain the absorbance change of CAN consumption within certain range that conforms to the Beer–Lambert law, so that the CAN consumption can be monitored by the UV-vis spectroscopy. Under the conditions, the initial rate of CAN consumption is found to be first order in the concentration of catalyst (Figure 4.10) and about 0.2 orders in the concentration of CAN (Figure 4.11). These evidences rationalized a dominant pathway of water oxidation by 32 following the rate expression $\text{initial rate} = k_{\text{cat}}[32]$ and a concomitant auxiliary pathway that is related to the concentration of CAN.\textsuperscript{xviii} The rate constant $k_{\text{cat}}$ of the prevailing pathway approximates to one quarter of the slope of initial rate versus [32] plot, that is 0.02 s\textsuperscript{-1}, by neglecting the auxiliary path.\textsuperscript{xix}

\textsuperscript{xviii} The rate law expression is better described as a mixture of first- and second-order kinetic as $\text{initial rate} = k[32] + k'[32][\text{CAN}]$, where $k$ and $k'$ are the rate constant of proposed dominant and auxiliary pathways.

\textsuperscript{xix} Apparently the $k_{\text{cat}}$ is overestimated here, if the auxiliary path is taken into account: $\text{initial rate} = k[32] + k'[32][\text{CAN}] = (k + k'[\text{CAN}])[32]$, e.g. $k_{\text{cat}} = k + k'[\text{CAN}] > k$.  

59
Figure 4.10. Left: Absorption changes at 330 nm at various concentration of 32; conditions: initial [CAN] = 1 mM, pH 1.0 HNO₃. Right: Initial rate of CAN decay versus concentration of 32; the change of absorption was transferred to that of molarity according to the Lambert–Beer law, \( \Delta C = \Delta A / \varepsilon b \) (where \( \Delta C \) is the molarity change, \( \Delta A \) is absorption change, \( \varepsilon \) is molar extinction coefficient, and \( b \) is the path length of the cell).

Figure 4.11. Left: Changes of absorption at 330 nm various concentration of CAN; conditions: initial [32] = 0.025 mM, pH 1.0 HNO₃. Right: Natural logarithm of initial rate of CAN decay versus natural logarithm of concentration of CAN; the slop is about 0.2.

The kinetics of water oxidation by 32 was further investigated under stoichiometric CAN conditions using the ‘stopped-flow’ technique. Mixing 32 with equimolar quantities of CAN led to a rapid oxidation of 32 to [Ru³⁺(bpc)(bpy)OH₂]²⁺ as depicted in Equation 4.10, where \( k_1 \) was defined as the rate constant, [Ru²⁺–OH₂]⁺ represented 32 and so on. The consequence of this ET process is an immediate bleaching of MLCT bands of 32 at both 475
and 350 nm (Figure 4.12), similar to the situation of oxidation of 33 described in section 4.4. The rate of this oxidation reaction is first order with regard to the concentration of [32] (expressed as [Ru$^{II}$]) as well as that of CAN (expressed as [Ce(IV)]). It follows the second-order rate law of Equation 4.11, where [Ru$^{II}$] is always equal to the concentration of tetravalent CAN ([Ce(IV)]) at any time during the reaction. The rate constant, $k_1$, can be related to the time-resolved UV-vis spectrum by Equation 4.13 which is deduced from the integrated formation of the second-order rate law (Equation 4.12). The approach of deducing Equation 4.13 is similar to that for Equation 4.9. $k_1$ was estimated to be $2.0 \times 10^5$ M$^{-1}$s$^{-1}$ by fitting the decay of absorbance at 475 nm according to Equation 4.13 (Figure 4.12).

\[
[\text{Ru}^{II}\cdot\text{OH}_2]^+ + \text{Ce(IV)} \rightarrow \text{Ru}^{III}\cdot\text{OH}_2^{2+} + \text{Ce(III)} \quad \text{(Equation 4.10)}
\]

\[
\frac{d[\text{Ru}^{II}]}{dt} = -k_1[\text{Ru}^{II}][\text{Ce(IV)}} = -k_1[\text{Ru}^{II}]^2 \quad \text{(Equation 4.11)}
\]

\[
\frac{1}{[\text{Ru}^{II}]} = k_1t + \frac{1}{[\text{Ru}^{II}]_0} \quad \text{(Equation 4.12)}
\]

\[
\frac{(A_0 - A_\infty)}{[\text{Ru}^{II}]_0 (A - A_\infty)} = k_1t + \frac{1}{[\text{Ru}^{II}]_0} \quad \text{(Equation 4.13)}
\]

Addition of 1 equivalent of CAN to the solution of [Ru$^{III}$(bpc)(bpy)OH$_2$]$^{2+}$ generated the [Ru$^{IV}=\text{O}$]$^+$ species (Equation 4.14) through a PCET process, according to the Pourbaix diagram of 32 (Figure 4.6). The reaction rate is first-order in either the concentration of the Ru$^{III}$-aqua species or that of CAN. Thus, the reaction follows the second-order rate law expressed in Equation 4.12 and 4.13 too. Rate constant of this Ru$^{III} \rightarrow$ Ru$^{IV}$ oxidation reaction, $k_2$, was calculated to be $2.2 \times 10^3$ M$^{-1}$s$^{-1}$ by monitoring and fitting the decay of absorbance at 310 nm in the time-resolved UV-vis spectrum (Figure 4.13).

\[
[\text{Ru}^{III}\cdot\text{OH}_2]^{2+} + \text{Ce(IV)} \rightarrow \text{Ru}^{IV}=\text{O}] + \text{Ce(III)} + 2\text{H}^+ \quad \text{(Equation 4.14)}
\]
Figure 4.12. Left: Spectral changes as a function of time after mixing 32 with one equivalent of CAN; conditions: $[32] = 0.05$ mM, pH 1.0 HNO$_3$. Right: Fitting of absorbance change at 457 nm according to the reaction rate law.

Figure 4.13. Left: Spectral changes as a function of time after mixing 32$^{2+}$ (trivalent) with one equivalent of CAN; conditions: $[32^{2+}] = 0.05$ mM, pH 1.0 HNO$_3$. Right: Fitting of absorbance change at 310 nm according to the reaction rate law.

After addition of another 1 equivalent CAN to the resulting [Ru$^{IV}$(bpc)(bpy)=O]$^+$ solution, two successive processes can be distinguished from the time-resolved spectra of UV-vis absorbance (Figure 4.14, a and b). They are proposed corresponding to the [Ru$^{IV}$=O]$^+$ $\rightarrow$ [Ru$^{V}$=O]$^{2+}$ ET step (Equation 4.15) and the subsequent water nucleophilic attack to the formally [Ru$^{V}$=O]$^{2+}$ species (Equation 4.16). The former step follows the same second-order rate law of Equation 4.13 and the latter a first-order law (Equation 4.17). Rate constants of these two steps, $k_3 = 1.7 \times 10^3$ M$^{-1}$s$^{-1}$ and $k_{O-O} = 1.1 \times 10^{-2}$ s$^{-1}$, were obtained by global fitting (performed with ReactLab) over
the full spectral scheme (300~600 nm) and the throughout reaction time (0~320 s). The calculated absorption profiles (from global fitting) for the \([\text{Ru}^{IV}=\text{O}]^{2+}\), \([\text{Ru}^{V}=\text{O}]^{2+}\) and \([\text{Ru}^{III}−\text{OOH}]^{+}\) intermediates and their time-dependent distributions are displayed in Figure 4.14, c and d.

$$\text{[Ru}^{V}=\text{O}]^{+} + \text{Ce(IV)} \xrightarrow{k_3} \text{[Ru}^{V}=\text{O}]^{2+} + \text{Ce(III)}$$  \hspace{1cm} (Equation 4.15)

$$\text{[Ru}^{V}=\text{O}]^{2+} + \text{H}_2\text{O} \xrightarrow{k_{O-O}} \text{[Ru}^{III}-\text{OOH}]^{+}$$  \hspace{1cm} (Equation 4.16)

$$\ln\left(\frac{A_0 - A_\infty}{A - A_\infty}\right) = k_{O-O} t$$  \hspace{1cm} (Equation 4.17)

Figure 4.14. Kinetics for the generation of Ru\(^{V}=\text{O}\) species and formation of O−O bond. (a) Spectral changes as a function of time after mixing \([\text{Ru}^{IV}(\text{bpc})(\text{bpy})\text{O}]^{+}\) with one equivalent of CAN; conditions: 0.05 mM complex in pH 1.0 HNO\(_3\). (b) Absorbance trace at 310 nm (blue dots) and the fitting line (green). (c) Calculated absorption spectra for the ruthenium-containing species based on global fitting. (d) Diagram of species distribution vs. time.
The rate constants $k_3$ and $k_{O-O}$ were measured at different temperatures (10~25 °C) and concluded in Table 4.1. The enthalpies and entropies of activation in respective steps (Table 4.2) could be estimated according to the Eyring equation\textsuperscript{xx} that correlates the rate constants with the temperature. Furthermore the Gibbs free energies of activation ($\Delta G^\ddagger$) for $[\text{Ru}^{IV}=\text{O}]^+ \rightarrow [\text{Ru}^{V}=\text{O}]^{2+}$ and $[\text{Ru}^{V}=\text{O}]^{2+} \rightarrow [\text{Ru}^{III}–\text{OOH}]^+$ steps were calculated to be 52.5 ± 1.9 kJ and 74.5+4.2 kJ respectively, at room temperature (293 K).

**Table 4.1.** Rate constants measured in the temperature range of 10–25 °C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_3$ (M$^{-1}$s$^{-1}$)</th>
<th>$k_{O-O}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2</td>
<td>1142</td>
<td>0.78 × 10$^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td>1406</td>
<td>0.91 × 10$^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>1663</td>
<td>1.08 × 10$^{-2}$</td>
</tr>
<tr>
<td>24.9</td>
<td>1854</td>
<td>1.2 × 10$^{-2}$</td>
</tr>
</tbody>
</table>

**Table 4.2.** Enthalpies and entropies of activation for selected steps in catalytic water oxidation by 32.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}^{IV}=\text{O}] \rightarrow [\text{Ru}^{V}=\text{O}]$</td>
<td>19.0 ± 0.8</td>
<td>-113.7 ± 4.0</td>
</tr>
<tr>
<td>$[\text{Ru}^{V}=\text{O}] \rightarrow [\text{Ru}^{III}–\text{OOH}]$</td>
<td>16.9 ± 0.5</td>
<td>-196.6 ± 12.5</td>
</tr>
</tbody>
</table>

Table 4.3 concludes all measured rate constants that are involved in the catalytic cycle of water oxidation by 32. The values of $k_1$, $k_2$ and $k_3$ are significantly different in quantity but all larger than that of $k_{cat}$ in several order of magnitudes. Otherwise, the value of $k_{O-O}$ is smaller than but close to that of $k_{cat}$. Considering the overestimation of $k_{cat}$ aforementioned, we propose that the water-nucleophilic-attack (or ‘acid-base’) mechanism is the dominant

\textsuperscript{xx} The linear form of the Eyring-Polanyi equation is $\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \times \frac{1}{T} + ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}$, where $k$ is the rate constant, $T$ is absolute temperature, $R$ is gas constant, $k_B$ is Bolzmann constant, and $h$ is Plank’s constant.
pathway for water oxidation catalyzed by 32 and the O–O bond formation step ($k_{O-O}$ step) is the rate-determining step of the pathway.

Table 4.3. Rate constants of CAN-driven water oxidation catalyzed by 32, measured at room temperature (20 °C) in pH 1.0 HNO₃.

<table>
<thead>
<tr>
<th>Rate constant (20 °C)</th>
<th>Reaction description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{cat}$ = $2 \times 10^{-2}$ s⁻¹</td>
<td>Equation 1.3</td>
</tr>
<tr>
<td>$k_1$ = $2.0 \times 10^5$ M⁻¹s⁻¹</td>
<td>Equation 4.10</td>
</tr>
<tr>
<td>$k_2$ = $2.2 \times 10^3$ M⁻¹s⁻¹</td>
<td>Equation 4.14</td>
</tr>
<tr>
<td>$k_3$ = $1.7 \times 10^3$ M⁻¹s⁻¹</td>
<td>Equation 4.15</td>
</tr>
<tr>
<td>$k_{O-O}$ = $1.1 \times 10^{-2}$ s⁻¹</td>
<td>Equation 4.16</td>
</tr>
</tbody>
</table>

(4.6) Analysis of Intermediates by MS

After mixing 32 with 4~8 equivalents of CAN and injecting the sample into the mass spectrometer immediately, several Ru-containing species could be revealed in the mass spectrum besides the mass signal of [32 + H]+.

According to the mass of the signals from small to big, the first distinctive cluster of mass corresponds to [Ru(bpy)₂O]⁺ at m/z = 430.0963 (Figure 4.15, top), which generates via decarboxylation of the bpc ligand at Ru IV or Ru V state tentatively. This kind of Ru-catalyzed decarboxylation is known as a highly endothermic process¹²⁵ and thus favored at the high temperature of MS experiment conditions. This finding disclosed a possible way of decomposition of 32 during the catalytic water oxidation reaction. The second characterized mass signal at m/z = 474.0985 (Figure 4.15, middle) is assigned to [RuⅢ(bpc)(bpy)OH]⁺ that derives from [RuⅢ(bpc)(bpy)OH₂]²⁺. Even though the [RuⅢ–OH₂]²⁺ species is the preferred form for trivalent 32 in the pH 1.0 aqueous solution as concluded in the Pourbaix diagram of 32 (section 4.3). The aqua-RuⅢ complex tends to reduce its positive charge by losing one proton in the gas phase within mass spectrometer.
Figure 4.15. Observed and calculated mass spectra of assigned species after mixing 32 with 4–8 equivalents of CAN in pH = 2.0 HNO₃. (Top) [Ru(bpy)₂O]⁺; (middle) [Ru(bpc)(bpy)OH]⁺; (bottom) overlapped [Ru(bpc)(bpy)N₂]⁺ and [Ru(bpc)(bpy)O₂]⁺, the ideal spectrum was calculated with a ratio of [Ru(bpc)(bpy)N₂]⁺(pink)/[Ru(bpc)(bpy)O₂]⁺(grey) = 3/1.

The cluster of peaks appeared in the range from m/z = 479 to 492 are assigned as overlapped signals of [RuII(bpc)(bpy)N₂]⁺ and [RuIV(bpc)(bpy)O₂]⁺ (Figure 4.15, bottom). The [Ru⁴⁻O₂]⁺ species is assumed to generate from [RuIII(bpc)(bpy)-OOH]⁺ via a PCET process (Equation 4.18). A similar Ru⁴⁻-peroxo complex has been proposed as the critical intermediate involved in the catalytic cycle of water oxidation by 7 or
8. However, there is little directly experimental proof for its existence in the previous work. Meanwhile, [Ru$^{IV}$($bpc$)(bpy)$O_2$]$^+$ is proposed to liberate its ligated dioxygen easily and coordinate with one dinitrogen (Equation 4.19) in the intensive N$_2$ atmosphere of MS experiment conditions$^{xxi}$ albeit the very weak coordinative ability of N$_2$. Thus, the signal of [Ru$^{II}$($bpc$)(bpy)$N_2$]$^+$ was observed in the mass spectrum.

$$[\text{Ru}^{III}(bpc)(pic)_2\text{OOH}]^+ + \text{Ce(IV)} \rightarrow [\text{Ru}^{IV}(bpc)(pic)_2\text{O}_2]^+ + \text{Ce(III)} + \text{H}^+$$

(Equation 4.18)

$$[\text{Ru}^{IV}(bpc)(pic)_2\text{O}_2]^+ + \text{N}_2 \rightarrow [\text{Ru}^{II}(bpc)(pic)_2\text{N}_2]^+ + \text{O}_2$$

(Equation 4.19)

4.7. Description of Catalytic Cycle for the Ru-bpc WOC

According to the findings and discussions in sections 4.2~4.6, we propose a catalytic cycle of water oxidation by 32 as depicted in Figure 4.16. Under the pH 1.0 CAN-HNO$_3$ conditions, divalent 32 is oxidized to the [Ru$^{V}$=O]$^{2+}$ species through a sequence of oxidation reactions. Rate constant of each oxidation step has be determined ($k_1$~$k_3$ in Table 4.3) by tracking the change of absorbance in the time-resolved UV-vis spectra of the corresponding step. The following water-nucleophilic-attack to the [Ru$^{V}$($bpc$)(bpy)=O]$^{2+}$ species, which is also the O–O bond formation step, is believed to be the rate-determining-step for several reasons: (i) $k_{O-O}$ is smaller than but comparable with the overestimated rate constant of overall catalytic cycle, $k_{cat}$; (ii) the initial rate of CAN consumption is nearly irrelevant to the concentration of CAN under catalytic conditions; and (iii) the onset of catalytic current and the Ru$^V$/Ru$^{IV}$ redox event occur at almost same potential during the potential sweep measurements. The rate of further oxidation reaction, e.g. the [Ru$^{III}$–OOH]$^+$ → [Ru$^{IV}$–OO]$^+$ step, can’t be probed by the ‘stopped-flow’ method, but the formation of Ru$^{IV}$-peroxo species was corroborated by MS. After liberation of one O$_2$, the Ru$^{IV}$-peroxo returns to the initial Ru$^{II}$ complex (32).

$^{xxi}$ N$_2$ was used as carrier gas in the MS experiments.
Although the same WNA mechanism scenario in Figure 4.16 has been proposed for WOCs 7 and 8 that carrying tpy ligand, introduction of anionic tridentate bpc ligand instead of tpy almost influence every step of this catalytic cycle. While the $k_1$ and $k_3$ ET step for 32 is much faster than that for 7 or 8, the $k_2$ step of PCET for 32 is slightly slower than that for 7. It confirmed our previous conclusion in Chapter 3 that anionic ligands facilitate the ET process but compromise the PT process in comparison with neutral ligands. Unlike the catalytic pathway of water oxidation by 8, where $O_2$ release from the Ru$^{IV}$-peroxo species is proposed as the rate-determining-step, the $O_2$ liberation step in the catalytic cycle of 32 should be faster than the $k_{O-O}$ step ($k_{O-O} = 1.1 \times 10^{-2}$ s$^{-1}$) and thus significantly more rapid than $O_2$ liberation step (rate constant is $7.5 \times 10^{-4}$ s$^{-1}$) in the case of 8. In principle, the carboxylate donor enhances dissociation of $O_2$ from the Ru$^{IV}$ center in the same way that it enhances dissociation of pic from the Ru$^{III}$ center, as observed in the cases of 30, 31 and 33.

Other findings of this work point out auxiliary pathways that diverges from the dominant WNA pathway displayed in Figure 4.16: (i) $k_{\text{cat}}$ is larger than $k_{O-O}$; (ii) consumption of CAN is not exclusively irrelevant to the concentration of CAN in the experiment of determination of $k_{\text{cat}}$; and (iii) $k_{O2}$ is much larger than $k_{\text{cat}}$. While more work is definitely required to elucidate the auxiliary
pathway, our basic conclusion is that the path associates with CAN and doesn’t go through the water-nucleophilic-attack to [Ru-V=O]^{2+} step. Notably, rate constant of O\textsubscript{2} evolution, $k_{O2}$, is about eight times larger than $k_{cat}$. So the auxiliary pathway might overwhelm the water-nucleophilic-attack pathway when CAN is largely excess.

### 4.8 Summary

Two novel Ru WOCs (32 and 33) were prepared and characterized, which features with anionic bpc ligand. Kinetics of water oxidation and ligand exchange were examined in detail based on these two complexes. The effect of anionic ligand upon the catalytic cycle of water oxidation was elucidated by comparing 32 and 33 with representative [Ru(NNN)(NN)L] type of WOCs 7 and 8 which only bear neutral polypyridyl ligands.
5. Visible-Light Driven Water Oxidation

(Paper I, II and IV)

5.1 Introduction

In the past chapters, we described the design and preparation of mononuclear Ru WOCs that show promising catalytic performance. The goal of developing WOCs, however, is to apply them in artificial photosynthesis (APS), of which the diagram is illustrated in Figure 1.6. This chapter will discuss our attempts of integrating the WOCs and photosensitizers in a visible-light driven water oxidation system. In such a way, light energy is converted into chemical energy via the water to dioxygen reaction.

A homogeneous system that consists of WOC, photosensitizer (PS), and sacrificial electron acceptor is employed to test the feasibility of visible-light driven water oxidation. Thermodynamically, water oxidation can’t happen in the system without assistant of light. When the PS is excited by light, the electron acceptor extracts one electron from the excited PS (PS*) leading to the formation of the oxidized PS (PS⁺) with high oxidation potential which makes water oxidation thermodynamically feasible. The difficulty of achieving this scheme is to keep electrons flowing efficiently and constantly along the multiple-step chain of electron transfer, \( \text{H}_2\text{O} \rightarrow \text{WOC} \rightarrow \text{PS} \rightarrow \text{electron acceptor} \). In this thesis work, we chose \([\text{Ru}^\text{II}(\text{bpy})_3]^2^+\) derivatives (Figure 5.1) as PSs and peroxodisulfate ion (\( \text{S}_2\text{O}_8^{2^-} \)) as an electron acceptor for the following reasons: (i) their redox potentials fulfill the energy profile of aforementioned light-driven water oxidation scheme (Figure 1.6, a); (ii) physicochemical properties of \([\text{Ru}^\text{II}(\text{bpy})_3]^2^+\) derivatives have been extensively studied; (iii) \([\text{Ru}^\text{II}(\text{bpy})_3]^2^+\) derivatives can be excited by visible light (> 400 nm) and have long lifetime at their excited state; (iv) the Ru\(^{\text{III}}\)/Ru\(^{\text{II}}\) redox potentials of \([\text{Ru}^\text{II}(\text{bpy})_3]^2^+\) derivatives can be easily tuned by installing different substituents at their bpy ligands.
Figure 5.1. Structures of [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} and its derivatives as photosensitizers.

When [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} is applied as a PS for instance, the electron transfer from [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} to S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} under light irradiation can be described by Equation 5.1 and 5.2.\textsuperscript{[126]} The generated [Ru\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} can oxidizing water thermodynamically under neutral and basic conditions (see section 1.6), while the presence of WOCs certainly accelerates the reaction rate (Equation 5.3). The net result of the light-driven water oxidation reaction is expressed in Equation 5.4.

\[
\begin{align*}
[Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+}\cdot + S_2O_8\textsuperscript{2−} & \rightarrow [Ru\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} + SO_4\textsuperscript{−} + SO_4\textsuperscript{2−} \\
[Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} + SO_4\textsuperscript{−} \rightarrow [Ru\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} + SO_4\textsuperscript{2−}
\end{align*}
\]

(Equation 5.1) (Equation 5.2)

\[
\begin{align*}
4 [Ru\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} + 2 H_2O \xrightarrow{WOC} & 4 [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} + 4 H^+ + O_2 \\
2 S_2O_8\textsuperscript{2−} + 2 H_2O \xrightarrow{hv} & 4 SO_4\textsuperscript{2−} + 4 H^+ + O_2
\end{align*}
\]

(Equation 5.3) (Equation 5.4)

5.2 Synthesis and Oxidation Potential of [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} Type Photosensitizers

[Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} is commercially available. Its analogues, [Ru\textsuperscript{II}(bpy)\textsubscript{2}(bcbpy)]\textsuperscript{2+} (34, bcbpy = 4,4’-bis(ethoxycarbonyl)-2,2’-bipyridine) and [Ru\textsuperscript{II}(bpy)(bcbpy)\textsubscript{2}]\textsuperscript{2+} (35), were prepared according to literatures.\textsuperscript{[127]} The synthesis rout of 35 is presented in Figure 5.2, and that of 34 is quite similar. The Ru\textsuperscript{II}/Ru\textsuperscript{III} redox potential of [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+} was measured as 1.26 V in pH 7.0 aqueous solution. The Ru\textsuperscript{II}/Ru\textsuperscript{III} redox potentials of 34 and 35 are higher
due to the electron-withdrawing effect of their ethoxycarbonyl substituents. $E^{1/2}(\text{Ru}^{II}/\text{Ru}^{III})$ potentials of all three PSs are listed in Table 5.1.

![Figure 5.2. Synthesis of [Ru$^{II}$bpy(bcbpy)$_2$]$^{2+}$ (35).](image)

**Table 5.1. Oxidation potential of photosensitizers.**

<table>
<thead>
<tr>
<th>Photosensitizer</th>
<th>[Ru$^{II}$bpy($^3$)]$^{2+}$</th>
<th>34</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^{1/2}(\text{Ru}^{II}/\text{Ru}^{III})$ vs. NHE*</td>
<td>1.26 V</td>
<td>1.37 V</td>
<td>1.50 V</td>
</tr>
</tbody>
</table>

* Measured in phosphate buffer (IS = 50 mM, pH = 7.0).

### 5.3 Visible-Light Driven Water Oxidation by Ru WOCs

#### 5.3.1 Visible-Light Driven Water Oxidation Involving Ru-pda WOCs

As discussed in Chapter 2, complexes 29a–c initiate catalytic water oxidation at around 1.2 V in pH 7.0 aqueous solution, less positive than the $E^{1/2}(\text{Ru}^{II}/\text{Ru}^{III})$ of [Ru$^{II}$bpy($^3$)]$^{2+}$. So the visible-light driven water oxidation mediated by 29a–c was examined in a WOC-[Ru$^{II}$bpy($^3$)]$^{2+}$-$S_2O_8^{2-}$ homogenous solution. A clark-type oxygen electrode was applied here to detect the O$_2$ evolution. When the three-component solution was irradiated by a 500 W xenon arc lamp (equipped with a 400 nm cut-off filter), obvious signals of O$_2$ generation were observed for all three cases (complexes 29a–c used as WOCs respectively) in comparison with the ‘catalyst-free’ control (Figure 5.3). However, the TONs attained are quite small, only 4–6.
Figure 5.3. Visible-light driven water oxidation catalyzed by 29a (red), 29b (blue) and 29c (green). Conditions: 2 mL phosphate buffer (20 mM, initial pH = 7.2) containing catalyst (5.0 μM), [RuII(bpy)3]2+ (0.25 mM) and S2O82− (5 mM).

5.3.2 Visible-Light Driven Water Oxidation Involving the Ru-hqc WOC

In neutral aqueous conditions (pH ≈ 7.0), the onset of water oxidation current catalyzed by complex 31 appears at about 1.1 V during the potential sweep (Chapter 3). In principle, [RuIII(bpy)3]3+, trivalent 34 and 35 are capable of oxidizing 31 to its high-valent state that triggers water oxidation. Figure 5.4 displays O2 evolving vs. time plots under irradiation, when complex 31 was assembled with S2O82− and the three PSs respectively in a three-component homogeneous light-driven system. Each point of O2-evolving data in the figure 5.4 was measured by GC. The 31-[RuII(bpy)3]2+-S2O82− homogeneous assembly hardly works because of small potential gap (or driving force for ET) between the catalytic potential of 31 and the oxidative potential of [RuIII(bpy)3]3+. The highest TON was found when PS 35 with the most positive oxidative RuII/RuIII redox potential was applied. The light-driven O2 evolution in the 31-35-S2O82− homogenous system got sluggish after 20 minutes reaction and almost stopped after 40 minutes. Meanwhile, the pH of the system dropped from 7.2 initially to about 3.5 after 50 minutes of the light-driven water oxidation, due to accumulation of protons during the reaction. Because the catalytic potential of 31 rises as the decrement of pH of
the reaction medium, the potential gap between the catalytic potential of 31 and oxidative potential of certain PS\(^+\) decreases as water oxidation is proceeding. Therefore, PS with higher oxidative potential is able to retain its function for a longer time during the light-driven water oxidation reaction. The light-driven O\(_2\) evolution for the resulting inactive 31-35-S\(_2\)O\(_8^{2−}\) system was recovered after its pH was adjusted from 3.5 to 7.2.

![Figure 5.4](image)

**Figure 5.4.** Light-driven water oxidation catalyzed by 31. All data were measured by GC. Condition: 10 mL pH 7.2 phosphate buffer (20 mM, initial pH = 7.2) containing catalyst (55.0 \(\mu\)M), photosensitizer (0.55 mM) and S\(_2\)O\(_8^{2−}\) (10 mM).

The photon-to-O\(_2\) generation quantum yield, defined as the number of oxidized H\(_2\)O molecules (half number of O\(_2\) molecules evolved) per photon absorbed, was measured to be 9% for the 31-35-S\(_2\)O\(_8^{2−}\) light-driven water oxidation system. While the number of O\(_2\) molecules could be calculated according the data from GC, the number of photons absorbed was calculated according to Equation 5.5, where \(n_p\) is the moles of photons absorbed, \(I\) is the radiant power of input light, \(I_o\) is the radiant power of output light (in our case \(I_o = 0\)), \(\lambda\) is the wavelength of the light, \(t\) is the irradiation time, \(h\) is the Planck constant, \(N_A\) is the Avogadro constant, \(c\) is the speed of light and \(\rho\) is the reflectance of the air/reaction vessel interface (measured as 9% in our experiment). It should be noted that a 445 nm laser was used as the light source for the determination of quantum yield, different from the light source
used in light-driven water oxidation experiments, because radiant power of the laser can be accurately measured.

\[
n_p = \frac{(1-\rho)(I-I_0)\epsilon\lambda}{N_Ahc}
\]

(Equation 5.5)

### 5.3.3 Visible-Light Driven Water Oxidation Involving the Ru$_2$-cpph WOC

When \( \text{trans-}[(\text{pic})_3\text{Ru}^\text{II}(\text{cpph})\text{Ru}^\text{II}(\text{pic})_3]^+ \) (5, \( \text{H}_2\text{cpph} = 3,6\text{-bis-(6'-carboxypyrid-2'-yl)-pyridazine} \)) was used as the WOC and 35 as the PS, a TON of 350 was attained by irradiating the homogeneous 5-35-S$_2$O$_8^{2-}$ three-component system. The rate of light-driven O$_2$ evolution maintained approximately 15 min$^{-1}$ in the first ten minutes of reaction. After the incipient 10-minute period, the O$_2$-evolving rate attenuated gradually. After about 60-minute reaction, the system lost its O$_2$ evolving activity totally. A severe drop of pH, from 7.0 to about 3.0, was observed in this case too. After 4 runs of repeated alkalization and irradiation of the same 5-35-S$_2$O$_8^{2-}$ sample, a combined TON of 1270 was obtained.

![Figure 5.5](image.png)

**Figure 5.5.** UV-vis spectra of the reaction mixture before (black line) and after (red line) 10 min irradiation. Conditions: Na$_2$S$_2$O$_8^{2-}$ (10 mM) and 35 (1 mM) in the presence (a) and absence (b) of 5 (38 mM). The spectra were measured after dilution of the sample.

The UV-vis absorption profile of 5-35-S$_2$O$_8^{2-}$ solution rarely changed after it was exposed to the irradiation for 10 minutes (Figure 5.5, a). In the absence of WOC (35-S$_2$O$_8^{2-}$ two-component system), however, significant bleach of
absorbance in the range of wavelength from 250 to 600 nm was observed after 10 minutes irradiation upon the system (Figure 5.5, b). It is referred that the PS is stable under irradiation in the three-component system as long as the WOC to PS electron transfer is efficient and effective. Otherwise, if the ET path from the catalyst to the PS was restrained, the trivalent Ru sensitizer is prone to decompose via ligand oxidation or other pathways.

5.4 Summary

Taking the advantage of low catalytic potential, Ru catalysts with anionic ligands (29a−c, 31 and 5) are capable of mediating visible-light-driven O₂ evolution in a three-component homogeneous system containing [Ru^{II}(bpy)₃]³⁺ type of photosensitizers and S₂O₈²⁻ as electron acceptor. The difference between catalytic potential of WOCs and oxidative potential of PSs influences the efficiency of the system. It was also found that increment of pH and decomposition of PS could cause inactivity of the light-driven O₂-evolving system.
6. Immobilization of Molecular WOC on Conductive Carbon Surface

(Paper v)

6.1 Introduction

Compared with heterogeneous WOCs, one advantage of molecular WOCs is that their properties and catalytic activity can be investigated explicitly in homogeneous system. That is exactly the way that Ru WOCs were studied in Chapter 2~5. In order to build an artificial photosynthesis device, however, molecular WOCs have to be immobilized on a conductive or semi-conductive surface.[42, 128] This chapter will describe the effort of building molecular WOCs in a model of electrocatalytic water-splitting cell.

Our strategy for immobilization of molecular WOCs is to couple acetylene-terminated catalyst and azide-modified carbon surface via copper-catalyzed azide-alkyne cycloaddition (so-called CuAAC or ‘click’) reaction (Figure 6.1). Advantages of this approach are: (i) the robust triazole linkage can resist to the harshly acidic water oxidation conditions; (ii) CuAAC is an efficient reaction even regarding heterogeneous coupling interface;[129] (iii) terminal acetylene group is facile to be installed to numerous kinds of molecular complexes; (iv) the azide group can be modified to various carbon materials.[130]

![Figure 6.1](image.png)

Figure 6.1. Scheme of immobilizing molecular Ru WOCs (36) on the conductive carbon surface.
6.2 Preparation of WOC Functionalized Carbon Electrode

6.2.1 Synthesis of the Ru-epc Complex

[Ru^{II}(epc)(pic)_3] (36, H_{2}epc = 4-ethynylpyridine-2,6-dicarboxylic acid) was designated as a model complex meant to be immobilized. It was developed on the base of well-defined mononuclear Ru WOC 30 and believed to have the same catalytic behavior with its precursor, complex 30. The synthetic rout of 36 was showed in Figure 6.1. The TMS group was introduced before the Ru-ligand chelating step and removed in the last step so as to avoid coordination between Ru center and the ethynyl group. The target product as well as intermediates involved in the preparation have been isolated and characterized unambiguously.

![Figure 6.2. Synthesis of [Ru^{II}(epc)(pic)_3] (36).](image)

6.2.2 Modification of Glass Carbon Surface

Glass carbon disk electrode (Ø = 3 mm) was employed as a conductive platform in this study, because it is the most widely used working electrode in electrochemical analysis. Azide groups were grafted to the glass carbon electrode by directly electrochemical reduction of 4-azidobenzene diazonium tetrafluoroborate salt ([N_{3}–C_6H_4–N_2]^+BF_4^-) in 0.1 M HCl (the procedure in the literature was followed). The electro-reduction was carried out in a typical three-electrode cell which is consisted of glass carbon working
electrode, SCE reference electrode and platinum wire counter electrode. The first CV scan in the acidic diazonium salt solution showed a broad irreversible wave at around –0.4 V vs. NHE corresponding to the reductive current of \([\text{N}_3\text{–C}_6\text{H}_4\text{–N}_2]^+\). Strength of this current significantly weakened in the subsequent CV sweeps, because the initially grafted organic compounds blocked the ‘active sites’ of glass carbon surface from further electro-reduction of diazonium salt.\(^{[130]}\) After modification, the glass carbon electrode was thoroughly rinsed with water and ethanol respectively to remove any physically adsorbed compounds.

6.2.3 Coupling of Azide-Modified Glass Carbon and the Ru-epc Complex

Once the acetylene-terminated substrate \(36\) and azide-modified carbon electrode were readily attained, immobilization of the complex was conducted by simply immersing the modified electrode in a THF solution of \(36\) containing \([\text{Cu(CH}_3\text{CN})_4]^+\text{BF}_4^-/\text{TBTA}\) which was a typical catalyst-promoter combination for CuAAC reaction. After an incubation period of 12 hours, the resulting catalyst-functionalized glass carbon electrode was copiously washed with acetone and ethanol, and then sonicated in acetone and ethanol respectively (30 s for each solvent) in order to remove any physically adsorbed complexes.

6.3 Properties of WOC-Functionalized Carbon Surface

The CV curves of catalyst-functionalized glass carbon electrode recorded in \(\text{CH}_2\text{Cl}_2\) electrolyte evoked a reversible wave at 0.5 V (Figure 6.3) which is identical to the \(E^{1/2}(\text{Ru}^{II}/\text{Ru}^{III})\) of \([\text{Ru}^{II}(\text{pdc})(\text{pic})_3]\) \((30)\) under the same potential sweep conditions. The current is, however, much weaker than that recorded in the 1 mM \(\text{CH}_2\text{Cl}_2\) electrolyte solution of \(30\) (see Chapter 3). The control electrode, which is a pristine glass carbon electrode treated in the same procedure described in section 6.2.3, doesn’t evoke any redox wave in the potential sweep from 0.2~0.85 V. Furthermore, energy-dispersive X-ray spectroscopy (EDS) revealed a higher percentage of ruthenium weight on the
functionalized glass carbon surface than that on the pristine glass carbon surface. These experimental results indicate the target complex (36) is tethered on the glass carbon surface.

The effective density of WOC \((\Gamma_0, \text{mol/cm}^2)\) on the functionalized glass carbon surface was estimated according to the linear relationship between the peak current of \(E^{1/2}(\text{Ru}^{II}/\text{Ru}^{III})\) and the scan rate (Equation 6.1, where \(Slope\) is the ratio between peak current and scan rate, \(F\) is Faraday’s constant, \(A\) is surface area, \(R\) is ideal gas constant, and \(T\) is absolute temperature). An average concentration of \(1.2 \pm 0.4 \times 10^{-10} \text{mol/cm}^2\) was attained from three independent trials. The relatively dilute effective density is mainly ascribed to low activity and small specific surface of glass carbon surface.

\[
Slope = \frac{n^2 F^2 A\Gamma_0}{4RT} \quad \text{(Equation 6.1)}
\]

![Figure 6.3](image)

**Figure 6.3.** Left: CV curves of functionalized glass carbon electrode (red line) and control electrode (black dash); conditions: 0.1 M \(^n\text{Bt}_4\text{N}^+\text{PF}_6^-\) in CH\(_2\)Cl\(_2\), scan rate = 100 mV/s. Right: CV curves of functionalized glass carbon electrode (red) and pristine electrode (black); condition: phosphate buffer (pH = 7.0, ionic strength = 0.1 M), scan rate = 100 mV/s.

Under pH 7.0 phosphate buffer conditions, potential sweep upon functionalized electrode triggered catalytic current of water oxidation at around 1.25 V (Figure 6.3). This catalytic potential is consistent with that of water oxidation catalyzed of WOC 30 in homogeneous pH 7.0 solution.
Nevertheless, the CV curve of functionalized electrode doesn’t exhibit obvious waves of Ru$^{II}$/Ru$^{III}$ or other redox couples for two reasons: one is that the effective density of WOC ($\Gamma_0$) is quite low; the other is that pic/H$_2$O ligand exchange occurs in situ during the potential sweep, leading to ambiguity of current signals.xxii

6.4 Water Oxidation at WOC-Functionalized Carbon Surface

Bulk electrolysis of phosphate buffer (pH 7.0, IS = 0.1 M) was conducted in a standard three-electrode cell in order to evaluate the catalytic activity of functionalized glass carbon surface (Figure 6.4). Both the functionalized electrode and a pristine glass carbon electrode (control) are used as working electrode in this experiment. In either situation, chronoamperometric current was monitored under application of sequential potential steps (1.12~1.52 V, Figure 6.5, a). An appreciable catalytic current could be observed for the functionalized electrode at an overpotential 300 mV.xxiii This catalytic current became more and more salient as the applied overpotential increased from 300 to 700 mV. The molecular WOC retained its catalytic activity towards water oxidation after it was immobilized on the carbon surface.

![Figure 6.4](image_url)

**Figure 6.4.** Implementation of the functionalized glass carbon electrode in an electrochemical cell for water splitting.

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xxii This situation also happens during potential sweep upon homogeneous solution of 30. xxiii The thermodynamic potential of the water oxidation half-reaction is 0.82 V vs. NHE at pH = 7.0.
Figure 6.5. Electro-catalysis of water oxidation by functionalized glass carbon electrode. (a) Chronoamperometric current density measured in phosphate buffer (pH 7.0, IS = 0.1 M) at functionalized glass carbon electrode (red trace) and the pristine glass carbon electrode (black trace) under application of ascending potential steps. (b) TOF plot of functionalized glass carbon electrode as a function of overpotential \( \eta \). The inset is a Tafel plot showing current density functionalized electrode vs. \( \eta \).

The TOF of tethered catalysts were estimated according to Equation 6.2, where subtraction between integrated charge through a functionalized electrode \( (Q_c, \text{C/cm}^2) \) and that through a control electrode \( (Q_p, \text{C/cm}^2) \) equals to the quantity of electrons involved in the anodic water oxidation half-reaction at the given integration time \( (t = 360 \text{ s}) \) and overpotential. The
attained TOF values increase from 0.037 s\(^{-1}\) to 1.6 s\(^{-1}\) in the 300~700 mV overpotential range and exhibit Tafel behavior, as showed in Figure 6.5, b. It implied a rate-determining step of electron transfer in the anodic reaction.

\[
\text{TOF} = \frac{1}{4} \times \frac{1}{t} \times \frac{(Q_c - Q_p)}{F \Gamma_0} \quad \text{(Equation 6.2)}
\]

### 6.5 Summary

In summary, a target Ru WOC was successfully immobilized on glass carbon surface via a robust covalent linkage. The WOC-functionalized electrode showed significantly enhanced catalytic performance for water oxidation in comparison with a pristine glass carbon electrode. In principle, the approach we provided here can be facially applied in other carbon surfaces and molecular WOCs. Moreover, it is expected that the density of catalytic would increase in orders of magnitudes if one kind of engineered carbon material with high specific surface is used as a platform.
7. Concluding Remarks

The former half of this thesis described our effort of developing molecular Ru WOCs which have intrinsic relations within themselves as well as with previous examples. Comparative studies about Ru-pda (29a–c) and Ru-bda (21) WOCs illustrate that the rigidity of ancillary ligands may influence the reorganization of the structures of WOCs during catalytic water oxidation and thus determine their catalytic pathways. It is also found that the tetradentate anionic pda ligand plays a similar role with tridentate anionic pdc and hqc ligands in the catalytic performance of mononuclear Ru WOCs. All these anionic ligands are able to facilitate the access of high-valent Ru species and lower the catalytic overpotential of Ru WOCs. Meanwhile, these ancillary ligands significantly enhance the dissociation of monodentate ligand from the Ru center in aqueous medium. Ru WOCs carrying dianionnic ligand usually suffer from deficient solubility in water. Ru-bpc complexes (32 and 33) were designed and prepared to overcome this disadvantage. They share the same coordinative motif with Ru-pdc (30), Ru-hqc (31) and well-studied Ru-tpy WOCs. Kinetic studies of water oxidation catalyzed by Ru-bpc complexes revealed details about how carboxylate donors are involved in every step of the catalytic cycle.

The latter half of this thesis described our attempts of applying the aforementioned Ru WOCs in the artificial photosynthesis device. On one hand, visible-light driven O₂ evolution was achieved in a three-component homogenous system. It indicates the potential feasibility of assembling given Ru WOCs in an operative water-splitting device. One the other hand, a strategy was developed to immobilize molecular WOCs on the conductive carbon surface. This method is not limited by the catalyst or carbon substrate.

The work in the thesis broadens the understanding of molecular water oxidation catalysts and provides insight in the design of an artificial photosynthesis device.
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My family. Your love is always my motivation!
Appendices

Appendix A. Structures of Selected Ancillary Ligands

\[
\begin{align*}
\text{py} & \quad \text{Me} & \quad \text{pic} & \quad \text{bpy} & \quad \text{bpm} \\
\text{pyridine} & \quad \text{4-picoline} & \quad \text{2,2'-bipyridine} & \quad \text{2,2'-bipyridine} \\
\text{EtO}_2\text{C} & \quad \text{CO}_2\text{Et} & \quad \text{H}_2\text{pdc} & \quad \text{H}_2\text{hqc} \\
\text{bcbpy} & \quad \text{2,6-pyridinedicarboxylic acid} & \quad \text{8-hydroxyquinoline-2-carboxylic acid} \\
\text{H}_2\text{bpc} & \quad \text{H}_2\text{epc} & \quad \text{H}_2\text{bda} \\
\text{2,2'-bipyridine-6-carboxylic acid} & \quad \text{4-ethynylpyridine-2,6-dicarboxylic acid} & \quad \text{2,2'-bipyridine-6,6'-dicarboxylic acid} \\
\text{H}_2\text{pda} & \quad \text{tpy} & \quad \text{H}_2\text{cpph} \\
\text{1,10-phenanthroline-2,9-dicarboxylic acid} & \quad \text{2,2',6',2'-terpyridine} & \quad \text{3,6-bis-(6'-carboxyguanidino-2'-yl)-pyridazine}
\end{align*}
\]
Appendix B. Apparatus Used to Detect O$_2$ Evolution

Name: Oxygraph System (Clark electrode)
Producer: Hansatech Instruments
Remarks: Including S1 Clark type oxygen electrode disc and DW1/AD electrode chamber.

Name: Oxygen Sensor
Producer: Ocean Optics
Remarks: Including Ocean Optics FOXY-OR125-G probe and Ocean Optics MFPF-100 fluorimeter.

Name: 3000A micro Gas Chromatography
Producer: Agilent Technologies
Remarks: Equipped with thermal conductive detector and 5 Å molecular sieve column. Using He as carrying gas.

Name: Pressure Transducer (PX138-030A5 V)
Producer: Omega
Remarks: Data acquired by Omega OMB-DAQ-2416.

Name: Gas Chromatography-2014
Producer: SHIMADZU
Remarks: Equipped with thermal conductive detector. Using He as carrying gas.

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xxiv Pictures of apparatus are from the websites of corresponding companies.
References


