Theoretical Studies on Artificial Water Splitting-Water Oxidation and Proton Transfer
Thesis for Licentiate Degree
Division of Theoretical Chemistry & Biology
School of Biotechnology
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To my family
Abstract

Encouragement Can Work Miracles

The present thesis is concerned with the theoretical studies on artificial water splitting process. As the quick development of research on utilizing of solar energy, which is a green, clean, and renewable energy source, many research groups focus their attention on artificial photo-synthesis systems inspired by the photosystem I and II. The overall reaction in these artificial systems is water splitting to oxygen and hydrogen. Artificial water splitting can generally be divided into two half reactions, catalytic water oxidation and catalytic proton reduction. There is an increasing interest and demand to understand the detailed mechanism of these two key parts. Since DFT (density functional theory) in particular, has proven to be a powerful and popular tool in exploring reaction mechanisms, B3LYP and M06 functionals were employed to provide a theoretical explanation of these two important reactions in this thesis.

For water oxidation reaction, many efficient Water Oxidation Catalysts (WOCs) based on Ru, Ir, etc., have been reported over the last several years. The discovery of mononuclear ruthenium WOCs carrying anionic ligands is one of the major breakthroughs recently. WOCs bearing anionic ligands are able to efficiently drive catalytic water oxidation with relatively higher Turnover Numbers (TON) and Turnover Frequencies (TOF). Therefore the influence of anionic ligands gained our attention. We decided to carry out a detailed investigation on this effect, and try to propose a full mechanism of this catalytic water oxidation as well. We found that 1) The anionic ligands exert a promoting influence on the ligand exchange between picoline and water, which facilitates the formation of aqua-Ru complex, 2) The anionic ligands facilitate the complex access to higher oxidation states, which is necessary for the OO bond formation, and 3) The work of OO bond formation is in progress.

For the proton reduction reaction, the transport or movement of protons is vital and interesting in many biological and chemical processes, including the hydrogen uptake/production, the reduction of CO₂ to formate, and the reduction of O₂ to water. It is often related to energy storage and utilization. However, the details of these processes are still ambiguous. In most natural hydrogenase enzymes or synthetic catalysts based on iron or nickel, the incorporation of a pendant amine is a frequently occurring feature. This internal amine base seems to facilitate this proton transfer by acting as a proton relay. Our calculated results
showed that the internal base allows for a splitting of one high enthalpy-high entropy barrier into two: one with a high enthalpy-low entropy barrier and the other with a low enthalpy-high entropy barrier, resulting in a low free energy of activation for proton transfer. Our results can serve as a guideline in the development of new catalysts, not only for proton reduction catalysts, but also for any process that involves proton transfer from a metal hydride to an external base, such as C-H activation and functionalization catalysts.

A thorough understanding on the mechanism of water splitting can help generate a strategy to enhance the catalytic performance on both water oxidation and proton reduction. We can tune or modify the synthetic complex by accelerating the slow step (rate-determining step) in the overall catalytic cycle, and can construct artificial water splitting systems with improved performance.
The work presented in the thesis was carried out at the Department of Theoretical Chemistry & Biology, School of Biotechnology, Royal Institute of Technology (KTH), Sweden.

List of papers included in the thesis

**Paper I.** Pendant Amine Bases Speed up Proton Transfers to Metals by Splitting the Barriers.

Ying Wang, Mei Wang, Licheng Sun, and Mårten S. G. Ahlquist.


**Paper 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.


**Paper III.** The Ligand Returns – Theoretical Evidence for Direct Involvement of a Dissociated Picoline in Catalyst Decay.

Ying Wang and Mårten S. G. Ahlquist.

(Manuscript)

**Comments on my contribution to the papers included.**

As the first author, I was responsible for the calculations and the writing of the first draft for Paper I. As the co-author, I was responsible for the theoretical calculations, discussion and revision of Paper II.
Abbreviations and acronyms

bpp  bis(2-pyridyl)-3,5-pyrazolate
bpy  bipyridine
dpp  2,9-dipyrid-2’-yl-1,10-phenanthroline
isoq  isoquinoline
pbn  2,2’-[4-(tert-butyl)pyridine-2,6-diyl]bis(1,8-naphthyridine)
pic  4-picoline
py   pyridine
tpy  2,2’:6’,2”-terpyridine
B3LYP  Becke, three-parameter, Lee-Yang-Parr
BLYP  Becke-Lee-Yang-Parr
CAES  Compressed Air Energy Storage
CCSD  Coupled Cluster Singles and Doubles
CI   Configuration Interaction
CpI  Clostridium pasteurianum I
DdH  Desulfovibrio desulfuricans Hildenborough
DFT  Density Functional Theory
GGAs  Generalized gradient approximations
OEC  Oxygen Evolving Complex
H2bda  2,2’-bipyridine-6,6’-dicarboxylic acid
H2hqc  8-hydroxyquinoline-2-carboxylic acid
H2pdc  2,6-pyridine-dicarboxylic acid
HF   Hartree-Fock
I2M  Interaction Between Two M-O Units
LDA  local density approximation
MCSCF  Multi-Configuration Self-Consistent Field
MPn  Many-body Perturbation theory
M06  Minnesota density functional
NHE  Normal Hydrogen Electrode
P680  Triad composed of a multimer of Chlorophylls
PBE  Gradient-corrected correlation functional of Perdew, Burke and Ernzerhof
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>PCET</td>
<td>Proton-Coupled Electron Transfer</td>
</tr>
<tr>
<td>TOF</td>
<td>TurnOver Frequency</td>
</tr>
<tr>
<td>TON</td>
<td>TurnOver Number</td>
</tr>
<tr>
<td>PRC</td>
<td>Proton Reduction Catalyst</td>
</tr>
<tr>
<td>PS-II</td>
<td>PhotoSystem II</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>Tyrz</td>
<td>D1-tyrosine 161</td>
</tr>
<tr>
<td>WNA</td>
<td>Water Nucleophilic Attack</td>
</tr>
<tr>
<td>WOC</td>
<td>Water Oxidation Catalyst</td>
</tr>
<tr>
<td>XC</td>
<td>Exchange-Correlation</td>
</tr>
<tr>
<td>ZPE</td>
<td>Zero Point Energy</td>
</tr>
</tbody>
</table>
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First of all, I would like to express my sincere gratitude to my supervisor Dr. Mårten Ahlquist, thanks a lot for his guidance, insightful suggestions, the work of this thesis would not have been completed without the great help of him and I really appreciated it. I really learned a lot of things which are new to me before.

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Chapter 1

Introduction

The sun will play an irreplaceable role in sustainable energy production, which is the original source of most of the energy we are using now. Energy consumption demand is predicted to rise significantly, up to 28-35 TW by 2050, from the present state of about 13 TW.\textsuperscript{[1,2]} Hence the access to sustainable energy will clearly be a crucial problem already in the next decades.

In order to solve the future energy supply problem, it is necessary to find and develop new technologies for generation of sustainable and environmentally benign energy. As solar energy, an abundant and sustainable form of energy, is gaining attention we need to find ways to store the energy efficiently.

To utilize the solar energy effectively, nature shows a perfect example, namely Photosynthesis.\textsuperscript{[3,4]} Photosynthesis, which occurs in plants and some algae, is a chemical process of converting the solar energy into chemical forms and storing it in the bonds of carbohydrates. The entire process needs the energy from sunlight, carbon dioxide and water, all of them are abundant and easy to fetch. The products of the photosynthesis are carbohydrates and oxygen, which are essential and vital to the survival and development of mankind.

Although photosynthesis takes place in many different ways in different environments, the key features of the process are similar.\textsuperscript{[5]} From these features we can make a general conclusion about this important process (Figure 1.1).

\begin{center}
\textbf{Figure 1.1} A Brief overview of Photosynthesis in nature.
\end{center}
Photosynthesis starts with the absorption of energy from the sunlight by the photosensitizer P680, which is a triad composing of a multimer of chlorophylls. Once the energy is absorbed, P680 reaches its excited state of P680* and it transfers electrons to a permanently bound plastoquinone molecule, QA, via a pheophytin molecule. By binding a plastoquinone molecule at the QB site, the transferring electrons finally go to the plastoquinone molecules in the membrane, where a two-electron reduction from plastoquinone to plastoquinol occurs, here QB functions as a two-electron gate. On the other side, after transferring one electron to the electron acceptor part, the oxidized P680+ becomes one of nature’s strongest oxidizing species, with a potential of 1.2V vs. NHE. It can oxidize the tyrosine residue Tyrz in a multiphasic process, and the oxidized Tyrz will be reduced by the manganese cluster quickly, which is the oxygen-evolving complex (OEC)\(^6,7\) of photosystem II. The oxidized manganese cluster which includes four manganese atoms can in turn oxidize the water nearby. By four successive charge separations the manganese cluster accumulates the four oxidizing equivalents, which are named as S\(_1\) to S\(_4\), (the subscript means the number of oxidizing equivalents it stored), and it is able to split two water molecules into oxygen and protons. In general, the electrons are originally from water.

Inspired by nature (Photosynthesis), many artificial photo-synthesis systems have been constructed recently\(^8-11\). The overall reaction in these systems is water splitting (Figure 1.2), which is breaking water into hydrogen and oxygen assisted by corresponding catalysts. The reaction of water splitting is typically separated into its two half reactions: catalytic water oxidation and catalytic proton reduction.

\[
\text{H}_2\text{O} \xrightarrow{\text{hv}, \text{WOC}} \text{H}_2 + \text{O}_2
\]

**Figure 1.2** Light-driven catalytic water splitting.

1) Catalytic water oxidation:

\[
2\text{H}_2\text{O} \xrightarrow{\text{hv, WOC}} \text{O}_2 + 4\text{e}^- + 4\text{H}^+
\]

This reaction is an essential part of water splitting, the net half reaction is water oxidation to produce oxygen, and electrons and protons are generated as “by-products”. This reaction can convert solar energy into chemical energy, and is
completed with an involvement of photo-sensitizer and Water Oxidation Catalysts. [Ru(bpy)$_3$]$^{2+}$ (bpy is 2, 2’-bipyridine) is often used as photo-sensitizer. After absorption of energy from sunlight, it reaches its excited state [Ru(bpy)$_3$]$^{2+*}$, a strong oxidant, it can oxidize the corresponding water oxidation catalysts (Ru, Ir, Co complexes), which complete water oxidation afterwards.

2) Catalytic proton reduction:

\[
2\text{H}^+ + 2\text{e}^- \xrightarrow{\text{hv, PRC}} \text{H}_2
\]

The generated protons from catalytic water oxidation are reduced to produce hydrogen using the reducing power of the electrons generated from catalytic water oxidation. The process is assisted by Proton Reduction Catalysts. Here [Ru(bpy)$_3$]$^{2+}$ can be also used as a photo-sensitizer, after being exposed to sunlight, it reaches its excited state [Ru(bpy)$_3$]$^{2+*}$ and is reduced to [Ru(bpy)$_3$]$^{1+}$ quickly by sacrificial electron donor such as ascorbate. After transferring electrons to proton reduction catalysts, such as hydrogenases, it returns to [Ru(bpy)$_3$]$^{2+}$ and the electrons transferred to the catalysts are used to reduce protons to produce hydrogen.

In this thesis, density functional theory is employed in mechanistic studies of these two key reactions:

1) Catalytic water oxidation using ruthenium based catalysts. In order to design water oxidation catalysts with higher efficiency, a thorough mechanistic understanding for water oxidation is necessary, and we need to provide an explanation for the promoting effects of anionic ligand.

2) Proton transfer in iron complexes. Since the proton transfer or movement in the complex is a vital part of the mechanistic study of hydrogen generation and uptake, a thorough understanding of the mechanism of proton transfer or movement could serve as a guideline for designing new catalysts for proton reduction.

This thesis is organized in the following manner. A brief introduction of the mechanism of photosystem-II and purpose of our research is given in this chapter, followed by a description of theoretical background and the adopted methodology in our calculations (chapter 2). An introduction to water oxidation catalysts and related basic concepts is given in chapter 3. Then a description about proton transfer or movement in natural and synthetic complexes is presented in chapter 4, accompanied with an explanation about the pendant base effect in iron complexes. A summary of included papers is presented at the end of this thesis.
Chapter 2

Theoretical Background

2.1 Brief Introduction of Quantum Chemistry

Quantum chemistry is usually taken as an important subfield of theoretical chemistry. It aims to calculate the various structures and properties of molecules, such as geometry, electronic energy, electric dipole moment, charge distribution, vibrational frequency, etc. by using the principles of theoretical chemistry and the tools of computer science. It aims at explaining the chemical problems specifically. Efficient computer programs are therefore indispensable to accomplish this target, and are constructed by theoretical chemists and physicists.

Since we focus on investigating chemical reactions, which include bond-forming and bond-breaking via transition states, a good description of the electronic distribution is necessary. Usually, quantum chemical methods, which are electronic structure methods ranging from ab initio to semi-empirical methods, are used to calculate the corresponding molecular properties. From ab initio methods, the solutions are obtained from purely theoretical calculations. It works well for small systems, however, the computational cost increases dramatically to get accurate results for large systems. On the contrary, semi-empirical methods reduce the computational demand for calculation of large systems, however, the accuracy becomes its limitation.

The time-independent Schrödinger equation\textsuperscript{[13,14]} is shown in Eq. 2-1.

\[ \mathbf{H} \Psi = E \Psi \] (2-1)

where \( \Psi \) is the wave function which determines the given physical system, \( \mathbf{H} \) is the Hamiltonian operator that represents the energy of the system, which includes kinetic and potential energy, and \( E \) is the energy of the given system obtained as an eigenvalue to the Hamiltonian.

The Hamiltonian of the time-independent Schrödinger equation within the non-relativistic approximation can be expressed in Eq. 2-2,

\[ H_{\text{tot}} = T + H_v \] (2-2)
where \[ T_n = \sum_a \frac{1}{2m_a} \nabla_a^2 \quad H_e = T_e + V_{ne} + V_{ee} + V_{nn} \]

Where \( T_n \) is the nuclear kinetic energy, \( H_e \) is the electronic Hamiltonian operator, \( T_e \) means the electron kinetic energy, \( V_{ne} \) denotes the attraction between nuclei and electron, \( V_{ee} \) is the electron-electron repulsion and \( V_{nn} \) is the nuclei-nuclei repulsion.

Employment of the Born-Oppenheimer approximation further reduces the computational cost of solving the time-independent Schrödinger equation. In this approximation the coupling interaction between the nuclei and electron is neglected. The electronic part of the Schrödinger equation is solved with the nuclear positions as parameters. The potential energy surface which results from electronic part solution is used as a basis to solve the nuclear movement. Hence, for a given set of nuclear coordinates, the large part of the computational cost will lie on the electronic Schrödinger equation solution (Eq. 2-3).

\[
H_e = T_e + V_{ne} + V_{ee} + V_{nn}
\]  \hspace{1cm} (2-3)

where

\[
T_e = \sum_a \frac{1}{2} \nabla_a^2 \quad V_{ne} = -\sum_a \sum_i \frac{Z_a}{|R_a - r_i|}
\]

\[
V_{ee} = \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|} \quad V_{nn} = \sum_a \sum_{b>a} \frac{Z_a Z_b}{|R_a - R_b|}
\]

The fundamental methodologies for investigating the properties of a system are divided into two main categories: wave-function based methods and electron density based methods, depending on the different bases.

2.2 Wave-Function Based Methods

Although we have adopted the Born-Oppenheimer approximation to solve the time-independent Schrödinger equation, the electronic Schrödinger equation is still too complicated to solve, since the interactions between electrons need to be considered.

In Hartree-Fock theory, \( [15] \) which takes the interaction between the electrons as an average, the electrons are assumed to move independently under a mean potential field generated by the remaining electrons. Their movements can be written as spin-orbital wave functions separately, and an expression of all the
occupied spin-orbital wave functions can be defined as the total electronic wave function for the system. The Hartree Fock theory includes the exchange interaction between two electrons, which comes from the anti-symmetric property of the wavefunction.

The HF equation can be described as in Eq. 2-4,

$$ F \varphi_i = \varepsilon_i \varphi_i $$

(2-4)

Where $F$ means the Fock operator, $\varepsilon_i$ means the energy of orbital, and $\varphi_i$ the Hartree–Fock molecular orbitals.

The Fock operator includes three terms, and can be expressed as in Eq. 2-5,

$$ F = h + \sum_i (J_i - K_i) $$

(2-5)

Where $h$ denotes the Hamiltonian of a single electron, which includes its kinetic energy and the attraction interaction with the nuclei, and $J$ and $K$ denote the Coulomb operator and exchange operator, respectively.

In general, the Hartree-Fock method cannot give satisfactory accuracy due to the lack of description of correlation interaction. The lack of this correlation interaction always results in a higher energy than the real one. The energy difference between the real energy and HF energy is defined as correlation energy. Although the correlation energy in a system is quite small, it is often important in a chemical reaction. This correlation interaction should be taken into account especially when calculating reaction barriers.

Therefore, many kinds of more accurate methods based on the Hartree-Fock method, usually referred as post-Hartree-Fock methods such as Configuration Interaction method\(^{16}\) (CI), Multi-Configuration Self-Consistent Field method\(^{17}\) (MCSCF), Many-body Perturbation theory method\(^{18}\) (MP\(_n\), etc. are developed to improve the performance. The correlation energy is considered in different ways with different methods, which improves the results systematically.

The computational cost of those accurate methods is usually huge, especially for large systems, which clearly sets a limitation for broad applications. Fortunately, taken as an improvement in HF method, the Density Functional Theory (DFT) method includes the correlation interaction part, and provides a better balance between computational cost and accuracy. It has therefore become popular in the chemical community in recent years.
2.3 Density Functional Theory (DFT)

As early as 1927, the first attempt of describing the property of a system with electron density was made by Thomas and Fermi. One year later, Dirac added one more term, which described the exchange energy between electrons. Therefore, the Thomas-Fermi-Dirac model is considered a breakthrough in the development of electron density based approaches.\textsuperscript{[19-21]} Different from the wave-function based methods, DFT incorporated the conception of electron density, which indicates that the electronic energy of ground state is determined by the electron density entirely. The relationship between the electron density and the energy for a given system is a one to one correspondence.

In fact, density functional theory (DFT) has become one of the most popular tools in investigation in chemistry and material science now. The Nobel prize in chemistry was awarded to Kohn and Pople in 1998 for their contribution to DFT and computational methods development, respectively.

A general description of its broad application\textsuperscript{[22]} is shown in Figure 2.1.

![Figure 2.1 Numbers of papers in Web of Knowledge from 2001 to 2011. (grey bar: “DFT” is searched as a topic; blue bar: B3LYP citations).](image)

2.3.1 Hohenberg and Kohn THEOREM

DFT is based on the proof by Hohenberg and Kohn,\textsuperscript{[23]} a theorem formulated in 1964 that is the basis of Density Functional Theory. The first theorem describes that an external potential $v_{\text{ext}}$ is uniquely determined by the electron density, therefore, the total energy of one system, specifically the ground state energy, can be written as a functional of the electron density. This theorem states that the electron density determines the properties of a system exclusively. The second theorem describes that we could calculate the electron density of one system by
using a variational method, which means we can obtain the true electron density \( \rho_0 \) of the system by finding the minimum of the energy functional \( E[\rho_0] \).

According to these two theorems, the energy of ground state can be expressed as in Eq. 2-6,

\[
E[\rho] = F[\rho] + \int v_{\text{ext}} \rho dr
\]  

(2-6)

Where \( \rho \) means the electron density of system, \( E \) means the energy of ground state, \( F \) means the universal functional composed of electron-electron repulsion energy and electron kinetic energy, and \( v_{\text{ext}} \) means external potential.

### 2.3.2 Kohn-Sham Equation

The expression of Kohn-Sham equation is shown in Eq. 2-7,

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r)
\]  

(2-7)

\[
v_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{\text{xc}}(r)
\]  

(2-8)

The first term on the left hand side of Eq. 2-7 is the kinetic energy, \( v_{\text{eff}}(r) \) means effective local potential and \( v(r) \) means the external potential, including the electron-nuclei interaction. The second term on the right hand side of Eq. 2-8 is the electrostatic interaction between electrons, and \( v_{\text{xc}}(r) \) denotes the exchange-correlation potential.

The exchange-correlation (XC) energy is approximated in practical calculations. Different types of approximations have been introduced into this exchange-correlation term, therefore, many different density functional methods have been proposed and developed.

The simplest exchange-correlation energy approximation is the local density approximation (LDA),\(^{[24]}\) which was popular in the 1970s and 1980s. Generalized gradient approximations (GGAs)\(^{[25]}\) was introduced in the late 1980s, and it can be used well in chemical reactions with an acceptable accuracy. The most popular approximation in chemistry B3LYP currently was introduced by Becke in the early 1990s. He adopted the Hartree-Fock (HF) exchange instead of a fraction of GGA exchange. Recently, the Minnesota density functionals, especially the M06 family of functionals, were developed by Truhlar’s group, and it shows a broad
accuracy in many research fields.

### 2.3.3 Hybrid DFT Method-B3LYP.

There are many DFT methods available at present, the difference between them lies on the difference choice of functional form related to the exchange and correlation energy. B3LYP as one of the hybrid DFT methods has become very popular, due to its reliable performance.

The exchange-correlation term of B3LYP\(^{26,27}\) is shown in Eq. 2-9,

\[
E_{xc}^{B3LYP} = aE_{xc}^{HF} + (1-a)E_{xc}^{Slater} + bE_{xc}^{B88} + (1-c)E_{xc}^{VWN} + cE_{xc}^{LYP}
\] (2-9)

For the exchange part, it introduces exact Hartree-Fock exchange in the functional, Slater local functional and Becke 1988 nonlocal gradient correction. For the correlation it includes the Vosko-Wilk-Nusair (VWN) local functional, and the Lee-Yang-Parr local and nonlocal functional.

We have found that density functional theory (DFT) gives highly accurate results, and it can be used for the mechanistic studies in our projects. We adopted B3LYP and M06 to study the mechanism of our target reactions, namely water oxidation and proton transfer.

#### 2.3.3.1 Accuracy on Geometries

The errors in the calculation of geometrical parameters were analyzed by Charles W. Bauschlicher Jr.\(^{28}\) standard G2 are used as the benchmark, and consists of 55 molecules containing first and second row atoms. A series of 55 molecules including 71 bond lengths, 26 bond angles and 2 dihedral angles is tested for this purpose.

As shown in Table 2.1, comparing to other approaches the hybrid B3LYP functional has the lowest average error (0.013) when applied to the calculation of bond lengths. The error for B3LYP functional could be further reduced by using a large basis set.

The average absolute deviation on bond angles displays a similar trend, the hybrid functional B3LYP has the smallest error (0.62). Improving the basis set can slightly decrease the error (0.61) at the B3LYP level.
Table 2.1 The average absolute deviation for geometrical parameters.

<table>
<thead>
<tr>
<th></th>
<th>Bond length (Å) (average absolute error)</th>
<th>Angle (deg) (average absolute error)</th>
<th>Dihedral angle (deg) (average absolute error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF\textsuperscript{a}</td>
<td>0.020</td>
<td>1.16</td>
<td>1.92</td>
</tr>
<tr>
<td>MP2\textsuperscript{a}</td>
<td>0.015</td>
<td>0.67</td>
<td>1.24</td>
</tr>
<tr>
<td>BLYP\textsuperscript{a}</td>
<td>0.026</td>
<td>1.03</td>
<td>0.89</td>
</tr>
<tr>
<td>BP\textsuperscript{a}</td>
<td>0.020</td>
<td>0.91</td>
<td>0.27</td>
</tr>
<tr>
<td>BP86\textsuperscript{a}</td>
<td>0.022</td>
<td>0.96</td>
<td>0.24</td>
</tr>
<tr>
<td>B3P86\textsuperscript{a}</td>
<td>0.010</td>
<td>0.62</td>
<td>0.86</td>
</tr>
<tr>
<td>B3LYP\textsuperscript{a}</td>
<td><strong>0.013</strong></td>
<td><strong>0.62</strong></td>
<td><strong>0.35</strong></td>
</tr>
<tr>
<td>B3LYP (big)\textsuperscript{b}</td>
<td>0.008</td>
<td>0.61</td>
<td>3.66</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The 6-31G* basis set is used
\textsuperscript{b} The 6-311 + G(3df, 2p) basis set is used

Different from the bond angles and bond lengths, B3LYP does not have the smallest error when calculating dihedral angles, however, it is acceptable. Since the analysis only includes two dihedral angles, it is not likely to accurately describe the reliability of dihedral calculation using the approaches mentioned above.

2.3.3.2 Accuracy on Energies

In order to test the B3LYP accuracy on various energy calculations, which includes atomization energy, electron affinity, barrier height, etc., many reports have been published by various groups. One of them is the atomization energy calculations reported by Charles W. Bauschlicher Jr.

Table 2.2 The average absolute deviation for atomization energy calculation.

<table>
<thead>
<tr>
<th></th>
<th>Atomization energy (kcal/mol) (average absolute error)\textsuperscript{a}</th>
<th>Atomization energy (kcal/mol) (average absolute error)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>80.52</td>
<td>74.50</td>
</tr>
<tr>
<td>MP2</td>
<td>16.04</td>
<td>7.43</td>
</tr>
<tr>
<td>BP</td>
<td>8.21</td>
<td>11.81</td>
</tr>
<tr>
<td>BLYP</td>
<td>5.31</td>
<td>4.95</td>
</tr>
<tr>
<td>BP86</td>
<td>7.23</td>
<td>10.32</td>
</tr>
<tr>
<td>B3P86</td>
<td>5.87</td>
<td>7.82</td>
</tr>
<tr>
<td>B3LYP</td>
<td><strong>5.18</strong></td>
<td><strong>2.20</strong></td>
</tr>
</tbody>
</table>

\textsuperscript{a} The 6-31G* basis set is used
\textsuperscript{b} The 6-311 + G(3df, 2p) basis set is used

From Table 2.2, it is clear that the hybrid functional B3LYP demonstrates superior performance over other approaches. The average absolute error is 5.18
kcal/mol using a small basis set. Improving the basis set lead to a decrease to 2.2 kcal/mol.

In 2005 a new extensive set\cite{29} based on G3/05 containing a total of 454 energies was used to test for validation of quantum chemical methods. After comparison, B3LYP still stands out of other approaches within a mean unsigned error of 4.14 kcal/mol. Furthermore, the results indicate that B3LYP performs as well or even better than B98, which is considered as the most accurate functional in this G3/05 test set for smaller molecules.

2.3.4 Recently Developed Hybrid DFT Methods

Recently, many new approximate density functionals in the framework of Kohn-Sham density functional theory have been developed to improve the performance of DFT, such as the Minnesota density functionals, the family of “double-hybrid” density functionals, density functional theory including dispersion corrections, etc. These improved DFT methods meet the two fundamental conditions required by a good density functional approach. Firstly, they can produce a high accuracy for basic physical and chemical properties, such as geometry and energy. Secondly, these improved methods can be applied to a general research field (including organometallic chemistry, inorganic and organic chemistry, and biochemistry) and provide a better description.

2.3.4.1 The Minnesota Density Functionals

The Truhlar group has developed several approximate functionals, named as the Minnesota density functionals, or the M06 family\cite{30,31}. These functionals show a successful applications in many fields, such as organometallic, inorganic, organic and biological chemistry. Compared to B3LYP, M06 family shows a better performance for organic chemistry due to the improved treatment of medium-range correlation energy. We choose this method to give a more accurate electronic energy in our system.

10 functionals were tested against the dissociation energies of four 16T-isobutene complexes (four possible models of the dissociation of isobutene from 16T zeolite model cluster).\cite{32} Two of them (π-complex and tert-butyl carbenium ion) are non-covalent, while the other (tert-butoxide and isotutoxide) two are covalent. The results (Table 2.3) showed that, M05-2X and M06-2X gave the best performance, followed by M06-L and M06. All these four functionals gave a small MAD value. However, the other six functionals did not give an
acceptable result. The M06 family produces a satisfactory result for both covalent and non-covalent cases.

Table 2.3 A benchmark data of dissociation energies (kcal/mol) in four complexes involving the dissociation of isobutene from a 16T Zeolite cluster model.

<table>
<thead>
<tr>
<th>method</th>
<th>( \pi )-complex (non-covalent)</th>
<th>ter-butyl carbenium ion (non-covalent)</th>
<th>tert-butoxide (covalent)</th>
<th>isotutoxide (covalent)</th>
<th>mean error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best estimate</td>
<td>15.1</td>
<td>-9.8</td>
<td>13.9</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>M05-2X</td>
<td>11.7</td>
<td>-8.1</td>
<td>14.9</td>
<td>14.0</td>
<td>1.6</td>
</tr>
<tr>
<td>M06-2X</td>
<td>12.7</td>
<td>-9.1</td>
<td>16.6</td>
<td>15.6</td>
<td>1.9</td>
</tr>
<tr>
<td>M06-L</td>
<td>14.4</td>
<td>-2.3</td>
<td>15.6</td>
<td>13.5</td>
<td>2.6</td>
</tr>
<tr>
<td>M06</td>
<td>13.3</td>
<td>-3.9</td>
<td>16.0</td>
<td>14.4</td>
<td>2.6</td>
</tr>
<tr>
<td>M06-HF</td>
<td>12.4</td>
<td>-12.5</td>
<td>18.6</td>
<td>18.8</td>
<td>3.7</td>
</tr>
<tr>
<td>PBEh</td>
<td>2.9</td>
<td>-15.6</td>
<td>4.7</td>
<td>4.7</td>
<td>9.1</td>
</tr>
<tr>
<td>PBE</td>
<td>3.2</td>
<td>-12.8</td>
<td>2.3</td>
<td>2.0</td>
<td>9.6</td>
</tr>
<tr>
<td>B97-1</td>
<td>3.9</td>
<td>-14.3</td>
<td>2.2</td>
<td>2.9</td>
<td>9.6</td>
</tr>
<tr>
<td>TPSSh</td>
<td>-0.9</td>
<td>-17.7</td>
<td>1.8</td>
<td>1.6</td>
<td>12.1</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-2.5</td>
<td>-20.7</td>
<td>-5.5</td>
<td>-4.8</td>
<td>16.6</td>
</tr>
</tbody>
</table>

\( ^{a} \) The 6-311+G (2df, 2p) basis set is used for all density functionals in this table. MAD denotes mean absolute deviation, and \( D_e-C_p \) denotes dissociation energy calculation with counterpoise correction.

2.3.4.2 The Family of “Double-Hybrid” Density Functionals

A new family of “double-hybrid” density functionals is proposed by Grimme in 2006,\(^{33}\) the performance of B2-PLYP (one of these new functionals) is assessed by the G2/97 standard benchmark test (including a suite of atoms, molecules and reactions). The accuracy of B2-PLYP for many vital aspects of chemistry (including transition-metal compound, reaction barriers and weakly bonded complexes) is satisfactory. B2-PLYP is taken as a reliable and efficient quantum chemical method for general purpose.

2.3.4.3 Density Functional Theory Including Dispersion Corrections

Non-covalent interactions, such as the ubiquitous attractive long-range van der Waals (dispersion) interactions, are playing an increasingly vital role in the theoretical description of chemical research, especially in organic chemistry, supramolecular chemistry and biochemistry. Several density functional
approximations have been developed to include this weak interaction. Density functional Theory- Dispersion (DFT-D), which means the developments of dispersion corrections in Kohn-Sham density functional theory, is one method and is applied successfully in various fields.

The common G3/99 set of heat of formation (HOF) is chosen by the Grimme group to test the general applicability. The G3/99 set includes relatively large molecules, therefore, intramolecular dispersion makes a significant contribution. Three density functionals (B3LYP, B2PLYP and mPW2PLYP) with and without the dispersion correction were adopted for comparison. The results with the dispersion correction improved remarkably for all three functionals. A statistical summary of their results is shown in Table 2.4.

### Table 2.4 Performance of three functionals (B3LYP, B2PLYP and mPW2PLYP) with and without the dispersion corrections. All values are in kcal/mol.

<table>
<thead>
<tr>
<th>Functional</th>
<th>MD</th>
<th>MAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>-4.6</td>
<td>5.6</td>
</tr>
<tr>
<td>B3LYP-D</td>
<td>-1.3</td>
<td>3.1</td>
</tr>
<tr>
<td>B2PLYP</td>
<td>-1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>B2PLYP-D</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>mPW2PLYP</td>
<td>-1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>mPW2PLYP-D</td>
<td>-0.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*a MD means the Mean Deviation.

*b MAD means the Mean Absolute Deviation.

### 2.4 Transition State Theory

Transition state theory, which was developed by Eyring and coworkers in 1935, has been proven to be a considerable success in the application of a wide variety of processes. This theory is generally used to calculate the reaction rates of chemical reactions, and describe qualitatively how a chemical reaction occurs, especially important for catalytic reactions.

As reactant A converting to product B in the reaction, a bond breaking and a new bond forming is often involved. The transition state forms or activated complex A* are usually assumed to exist as intermediate states during the reaction. (Figure 2.2).

\[
A \xrightarrow[K']{} A^* \xrightarrow[k]{} B
\]

**Figure 2.2**
The rate constant $k$ of a reaction can be described as follows,

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\neq}{RT}}$$

(2-10)

where $k_B$ denotes the Boltzmann’s constant ($1.38 \times 10^{-23}$ J/K), $h$ is Plank’s constant ($6.63 \times 10^{-34}$ J s), $\Delta G^\neq$ is the difference in Gibbs free energy between reactant and the transition state, $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$), and $T$ is the temperature in Kelvin.

From the formula above, we can derive that a rate of 1 s$^{-1}$, which indicates one unit of reaction per second, corresponds to a barrier of 17.4 kcal/mol at room temperature (298.15K). A change of 1.4 kcal/mol in activation barrier depicts an approximate raise or fall in reaction rate by one order of magnitude. These useful relationships can serve as a guideline for our mechanistic research, and help us assess the feasibilities of related reaction and compare different mechanistic proposals.

### 2.5 Solvation Model

In this thesis, the reactions we are interested in were carried out in a certain solvent, either in water or in dichloromethane. In order to describe solvated molecular systems we use a self-consistent reaction field method, here we choose a Poisson-Boltzman solver. To consider the solvation effect in our research, the solvation free energies corrections, which is the difference between the energy of optimized geometry in gas phase and the optimized geometry in a certain solvent, were calculated using Poisson-Boltzman Solvation Model.$^{[37]}$

### 2.6 Theoretical Studies

All Density Functional Theory (DFT) calculations were performed with Jaguar 7.6 program package of Schrödinger LLC. Becke’s three-parameter hybrid functional and the LYP correlation functional (B3LYP) was employed with the LACVP** core potential and basis set for geometry optimizations, frequency and solvation energy calculations, while the M06 functional using the LACV3P**++ basis set (augmented with two f-polarization functions on M (Fe or Ru) as suggested by Martin$^{[38]}$) was used for single point energy corrections. In order to confirm whether the geometries correspond to minima or first-order saddle points (transition states) or not on the potential energy surface (PES), frequency
calculations were performed using the optimized geometries. The expression for Gibbs free energies were presented as the following equation 

\[ G = E(M06/LACV3P**++ 2f on M) + G_{solv} + ZPE + H_{298} - TS_{298} + 1.9 \]

(1.9 denotes the concentration correction to the free energy of solvation from 1 M(g) → 1 M(aq) to 1 atm(g) → 1 M(aq)). The solvation model adopted was the Poisson-Bolzmann reactive field (PBF) implemented in Jaguar 7.6. For free energy of solvating proton, we chose the experimental number by Tissandier\(^{[39]}\) et al. of \(-264\) kcal mol\(^{-1}\) (for the free energy of 1M proton in water the value of \(-270.3\) kcal mol\(^{-1}\) was adopted).
Chapter 3

Experimental and Theoretical Studies on Water Oxidation Catalysts.

3.1 Brief Introduction

Searching and building a renewable and sustainable energy system is probably one of the greatest challenges facing the world. Trying to find a sustainable fuel to change our current energy consumption infrastructure is one of the key points in such a system. The conversion of solar energy into electricity or other forms of energy, which is one of the manners of energy storage, is a very promising way to solve this problem. Energy storage plays a critical role in balancing the supply and demand of energy and therefore securing our energy future. The development of storage technologies is therefore crucial to achieve this target. Generally, energy storage systems[40] can be categorized into four sectors, which are mechanical, bio-chemical, electrical and thermal forms.

1) Mechanical form. Compressed Air Energy Storage (CAES) system was constructed recently. In the form of compressed air it stores energy in a deep underground geological vessel or reservoir. Electricity from the grid powers compressors is used to drive air into the storage vessel underground during off-peak hours. When peak hours come, the stored air is released and heated with natural gas to expand its velocity. This air-gas mixture then can be used in a combustion turbine which can generate power for use.

2) Bio-Chemical form. Biofuels are gaining increased attention of both public and scientific recently. This kind of fuel is formed by biological carbon fixation and can be derived from biomass conversion. A considerable amount of solar energy is stored as chemical energy in this process, and the stored energy then can be released in a straightforward way. The widely utilization of biofuels such as bioethanol, biodiesel, biogas, etc., would increase energy security. This is the class of sunlight-to-bio-chemical energy storage.

3) Electrical form. Many kinds of rechargeable batteries such as Lead-acid, Carbon-zinc, Lithium-ion etc., are usually used to store spare electricity, and the stored electricity can be used at times when a demand comes. As the stored energy in battery is used up, it is easy to recharge.
4) Thermal form. This means the temporary storage of heat or cold for later use, ice-storage for air conditioning on hot summer days is one example, water is frozen into ice at night, when electricity consumption cost is lower, then the cool of the ice can be used in the afternoon to meet conditioning demand as well as reduce the electricity consumption in daytime when cost is higher. This ice storage is produced with a lower electrical utility rate.

Recently, much effort has been put to convert solar energy into electricity, and the discovery of the new type device showed that low cost materials can be used in the construction of solar cells. Another way to utilize solar energy is water splitting with production of molecular oxygen and hydrogen.[41]

The function of Photosynthesis sets an almost perfect example to solar energy utilization including solar capture, conversion and storage. This process provides energy for nearly all life on the earth. The generation of oxygen[42] from water takes place at an active site in Photosystem II (PS-II). This active center contains four manganese ions, which is a binuclear bis(μ-oxo) dimanganese unit.. This cluster containing four manganese ions is named the Oxygen Evolving Complex (OEC).[43,44]

![Figure 3.1 Proposed mechanism on water oxidation at the OEC in photosystem II.](image)

Many papers reported the possible mechanism[45] related to oxygen evolution at this active center. One general proposal is show in Figure 3.1. It is recognized that the release of oxygen from water takes place via a stepwise proton-coupled
electron transfer, resulting in the manganese complex from the sequentially oxidized state $S_0$ to $S_4$. At state $S_4$, $O_2$ is generated while two water molecules come in, and finally the complex returns to the state $S_0$.

Inspired by the function of PS-II, many artificial photosynthesis systems aiming at producing oxygen by light-driven water splitting have been built recently. In order to mimic the function of the oxygen evolving complex (OEC) in PS II, much effort has been devoted to the development of molecular catalysts in order to be able to oxidize water. The design of qualified water oxidation catalysts\[46-54\] (WOCs) is one of the keys for an artificial photosynthesis system with high efficiency. However, only a few artificial bioinspired complexes display a satisfactory performance on catalytic $O_2$ generation from water. Several series of efficient WOCs based on the Ru, Ir and other transition metals, have been reported over the last years.

### 3.2 Introduction to Proton-Coupled Electron Transfer (PCET).

Charge separation is the basis of photosynthetic energy utilization which carried out in biological systems. The electron transfer, which occurs in the charge separation, is frequently accompanied with proton transfer, such as in Photosystem II (PS-II), and this is called as Proton-Coupled Electron Transfer (PCET) reactions\[55,56\]. The theory on PCET reaction has been developed over several years. It is depicted as\[57\] the nonadiabatic transitions between the reactant and product electron-proton vibronic states. Actually, this kind of reaction plays a vital role in a wide range of biological processes, such as respiration and photosynthesis.

In PS II, upon the absorption of a photon, P680 is excited and becomes strongly reducing and transfers an electron to the acceptor and form P680$^+$. Then a tyrosine group (Tyrz) donates one electron to the P680$^+$, and simultaneously dissociates its phenolic proton to a base nearby.

In order to mimic the proton coupled electron transfer function in PS II, Hammarström and coworkers used a synthetic compound\[58,59\] to investigate the electron transferring of tyrosine (Figure 3.2). They took ruthenium-tris-bipyridine (Ru(bpy)$_3$) as a photosensitizer, after exposure to sunlight, the Ru(bpy)$_3$ reaches its excited state and loses one electron. The oxidized Ru(bpy)$_3$ can receive one electron from the tyrosine, which transfers one electron and is deprotonated simultaneously.
In fact, PCET processes are important for oxygen evolution in artificial photosynthetic systems as well. Water is required to be oxidized to produce oxygen, however, this is not straightforward. The thermodynamic potentials decrease as the number of electrons transferred increase (Table 3.1). The required thermodynamic potential for oxygen evolution from water is 1.23 V vs. NHE at pH 1.0, and this water oxidation involves the loss of four protons and four electrons. The designed catalysts should have the property of multiple electron transfer. Therefore, transition metal complexes are considered as suitable candidates to perform this reaction in a catalytic manner since they often have many accessible oxidation states. Among them, ruthenium aqua complexes meet these requirements, since the Ru complexes has the ability of losing protons and electrons to reach their higher oxidation states.

**Table 3.1**

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>E, V (vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td></td>
</tr>
<tr>
<td>•OH + 1H⁺ +1e⁻ — H₂O</td>
<td>2.81</td>
</tr>
<tr>
<td>HO-OH + 2H⁺ +2e⁻—2H₂O</td>
<td>1.78</td>
</tr>
<tr>
<td>HOO• + 3H⁺ +3e⁻—2H₂O</td>
<td>1.51</td>
</tr>
<tr>
<td>O=O + 4H⁺ +4e⁻—2H₂O</td>
<td>1.23</td>
</tr>
</tbody>
</table>

(a) cis-[Ru⁺(bpy)₂(py)(H₂O)]²⁺ $\rightarrow$ 0.67 V cis-[Ru⁺⁺(bpy)₂(py)(OH)]²⁺ $\rightarrow$ 0.78 V cis-[Ru⁺⁺⁺(bpy)₂(py)(O)]²⁺ $\rightarrow$ V vs NHE, u=0.1M, pH=7

(b) cis-[Ru⁺⁺⁺(bpy)₂(Cl)]²⁺ $\rightarrow$ 0.0 V cis-[Ru⁺⁺⁺⁺(bpy)₂(Cl)]¹⁺ $\rightarrow$ 1.7 V cis-[Ru⁺⁺⁺⁺⁺(bpy)₂(Cl)]²⁺ $\rightarrow$ V vs NHE, 0.1M [N(n-Bu₄)PF₆/CH₃CN]

**Scheme 3.2** Oxidation potentials for two sets of ruthenium polypyridyl based redox couples.
Without involving high energy intermediates, the type of PCET provides a plausible reaction pathway to access the higher state for ruthenium aqua complexes.[62-64] The comparison in Scheme 3.2 provides an explanation for the advantage of ruthenium aqua complex. The redox potential difference between Ru(IV/III) and Ru(III/II) is only 0.11V for ruthenium aqua complex (Scheme 3.2 a), while this difference jumps to 1.7V for ruthenium chloride complex (Scheme 3.2 b). The smaller difference in oxidation of the ruthenium aqua complex indicates that the coordination of water stabilizes Ru(IV) dramatically. The main reason for this stabilization of higher oxidation state is the oxo formation. It also indicates that the conditions required for oxidation from Ru(II) to Ru(IV) are relatively mild for ruthenium aqua complexes.

One specific example[65] of PCET is for the “blue dimer”. The initial oxidation state $H_2O$-Ru$^{III}$-O-Ru$^{III}$-OH$_2$ also undergoes oxidative activation via proton-coupled electron transfer pathway, which means a sequential loss of protons and electron occurs. PCET is important for the blue dimer to build up multiple oxidative equivalents without increasing positive charge.

### 3.3 Water Oxidation Catalysts

#### 3.3.1 Ruthenium-Based WOCs.

##### 3.3.1.1 Dimeric Ruthenium-Based WOC.

![Figure 3.3 Structure of cis,cis-\{(bpy)$_2$(H$_2$O)Ru$^{III}$-O-Ru$^{III}$-(H$_2$O)(bpy)$_2$\}$^{4+}$](image)

Figure 3.3 Structure of cis,cis-\{(bpy)$_2$(H$_2$O)Ru$^{III}$-O-Ru$^{III}$-(H$_2$O)(bpy)$_2$\}$^{4+}$. TON and TOF values are given in parentheses, respectively.

Complex 3-1 cis,cis-\{(bpy)$_2$(H$_2$O)Ru$^{III}$-O-Ru$^{III}$-(H$_2$O)(bpy)$_2$\}$^{4+}$ (bpy = bipyridine) normally referred to as the blue dimer[66] due to its deep blue color, was first reported by Meyer’s group. The feature of this dimer is two Ru-OH$_2$ units are connected by a dianionic oxido ligand (Figure 3.3), which results in an electronic
coupling between the two metal centers, and therefore shows interesting electrochemical properties, such as redox behaviors and its catalytic property by extension.

The X-ray structure\[^{[67]}\] of this blue dimer is shown in Figure 3.4:

![Figure 3.4 X-ray structure of complex 3-1 cis,cis-\([(bpy)_{2}(H_{2}O)Ru^{III}-O-Ru^{III}-(H_{2}O)(bpy)]^{4+}\). Hydrogen atoms are omitted for clarity. (purple for Ru, grey for C, red for O and blue for N).](image)

When adding Ce\(^{IV}\) into the acidic solutions containing the blue dimer, the gas is released from the solution. After gas chromatographic and mass spectrometric measurements, the released gas was confirmed to be oxygen. The turnover number (TON) is around 13 and the turnover frequency (TOF) is 0.004 s\(^{-1}\). This ruthenium complex was taken as a landmark in water splitting since it is the first synthetic molecular catalyst for water oxidation. The mechanistic and kinetic studies of Ce\(^{IV}\) oxidation of this blue dimer will be discussed in detail later in this chapter.

Since the first water oxidation catalyst ‘blue dimer’ carries a dimeric structure. The two Ru fragments are connected via an oxo bridge that tends to cleave, which limits the lifetime of the catalysts. The discussion about the requirement for dimeric or higher order structures was in debate at that time until the discovery of monomeric ruthenium-based WOCs.

### 3.3.1.2 Monomeric Ruthenium-Based WOCs Carrying Neutral Ligands.

Several monomeric complexes based on Ru were presented by Thummel’s group.\[^{[68-70]}\] These complexes also displayed a good performance on catalytic water oxidation. This demonstrated that one site is enough for catalytic water oxidation. In fact, the discovery of mononuclear ruthenium WOCs is one of the
major recent breakthroughs.

In 2005, the hydrogen-bonded aqua complex 3-2 trans-[Ru(pbn)(4-R-py)2
(OH2)]2+ (pbn = 2,2’-[4-(tert-butyl)pyridine-2,6-diyl]bis(1,8-naphthyridine); py =
pyridine)71 (Figure 3.5), which contains only one Ru center was reported by
Thummel’s group. It was encouraging that this mononuclear catalyst also could
perform water oxidation, which provides a qualitative evidence for catalytic
activity of mono-nuclear catalyst.

Figure 3.5 Structure of complex 3-2, trans-[Ru(pbn)(4-Me-py)2(OH2)]2+. TON
and TOF values are given in parentheses, respectively.

![Figure 3.5](image)

Afterwards, a series of monomeric ruthenium WOCs were synthesized, as
shown in Figure 3.6. All those complexes, 3-3 Ru(tpy)(bpy)OH2 (tpy = terpyridine;
bpy = bipyridine), 3-4 Ru(tpy)(pic)3 (pic = 4-picoline) and 3-5 Ru(dpp)(py)2 (dpp
= 2,9-dipyrid-2’-yl-1,10-phenanthroline; py = pyridine) are active catalysts for

Figure 3.6 Molecular structures of mono-nuclear Ru (II) catalysts. TON and TOF
values are given in parentheses, respectively.

![Figure 3.6](image)
water oxidation, although their activities are different between different series.

### 3.3.1.3 Monomeric Ruthenium-Based WOCs Carrying Anionic Ligands

Recent research shows that the introduction of anionic (negatively charged) ligands\(^{[72-75]}\) as in complexes \(3-6\) Ru(bda)(pic)\(_2\) (H\(_2\)bda = 2,2’-bipyridine-6,6’-dicarboxylic acid; pic = 4-picoline) and \(3-7\) Ru(bda)(isoq)\(_2\) (isoq = isoquinoline), and \(3-8\) Ru(pdc)(pic)\(_3\) (H\(_2\)pdc = 2,6-pyridine-dicarboxylic acid; pic = 4-picoline.) (Figure 3.7), yields significantly improved catalytic activity compared to complexes bearing neutral ligands. This is because the introduction of negatively charged ligands results in destabilization of the filled d orbitals of ruthenium complexes with lower-valence, due to d\(_x\)-p\(_x\) repulsion. When the ruthenium complexes reach high-valent states, these negatively charged ligands provide stabilization by favorable interaction between the empty d-orbitals of the ruthenium and filled p-orbitals of the oxygen atoms.

![Molecular structure of complexes 3-6, 3-7, 3-8. TON and TOF values are given in parentheses, respectively.](image)

**Figure 3.7** Molecular structures of complexes 3-6, 3-7, 3-8. TON and TOF values are given in parentheses, respectively.

### 3.3.2 Iridium-Based WOCs

Several complexes based on iridium display water oxidation activity. The cyclometalated iridium-based complex \(3-9\) [Ir(5-F,4’-F-phenylpyridine)\(_2\)(OH\(_2\))\(_2\)]\(^+\) has been synthesized by Bernhard’s group.\(^{[76,77]}\)
Figure 3.8 Molecular structure of Ir catalyst. TON and TOF values are given in parentheses, respectively.

This kind of water oxidation catalyst (Figure 3.8) shows some impressive properties, such as robustness, high-efficiency, and easy-modification. However, the low catalytic rate limits its broad application. Usually it takes a long time (around one week) to complete the reaction.

3.3.3 First-Row Transition Metal Based WOCs

Artificial water oxidation catalysts using first row transition metals such as manganese, cobalt and so forth, usually suffers from both low turnover numbers and low turnover frequencies, even though a manganese cluster is central to the OEC in photosynthesis. Few of complexes based on the first-row transition metals have been reported as efficient water oxidation catalysts.

3.3.3.1 Manganese-Based WOCs

Synthetic water oxidation catalysts based on manganese have come into notice since complex 3-10 \([(tpy)(H_2O)Mn(\mu-O)_2Mn(tpy)(H_2O)]^{3+}\) (tpy = 2,2’:6’,2”-terpyridine) (Figure 3.9) was reported by Brudvig’s group.\(^7\) The TON reaches a moderate number of 17 using Ce\(^{IV}\) as an oxidant.

Figure 3.9 Molecular structure of \([(tpy)(H_2O)Mn(\mu-O)_2Mn(tpy)(H_2O)]^{3+}\), TON and TOF values are given in parentheses, respectively.
3.3.3.2 Cobalt-Based WOCs

Complex 3-11 Cobalt-based β–octa-fluoro hangman corrole was reported by Nocera’s group in 2011.\textsuperscript{[79]} It contains meso-pentafluorophenyl and β–octa-fluoro substituents (Figure 3.10), and shows a satisfactory performance on water oxidation. This complex is so far confirmed as the most active catalyst among cobalt corroles.

![Molecular structure of cobalt-based β–octa-fluoro hangman corrole.](---, 1 s⁻¹)

**Figure 3.10** Molecular structure of cobalt-based β–octa-fluoro hangman corrole. TON and TOF values are given in parentheses, respectively.

The TOFs per Co atom for 3-11 can approach around 1 s⁻¹ (at pH 7) when immobilized in Nafion films, which is higher than other cobalt-based water oxidation complexes.

3.4 A Hydrogen-Bonding Network Effect

Hydrogen bonds which are involving multiple peptide carbonyl groups to water form a network around the oxygen-evolving complex (OEC) in photosystem II. Some research results demonstrate that this hydrogen bonding network could be involved in the catalytic water oxidation and play a key role in this process.

The position of bound water molecules has been confirmed by the Kamiya research group.\textsuperscript{[80]} There are approximately 1300 water molecules per monomer of PS-II, four water molecules are proposed to be placed at the active reaction center OEC. Two of them were predicted to bind to manganese, and another two waters are bound to calcium (Figure 3.11). This structure confirmation suggests that at the OEC water forms wide hydrogen-bonding network.
Figure 3.11 Hydrogen bonding network at oxygen evolving complex, two of them were bound to manganese, and another two waters bound calcium. (Reprinted with permission from Nature Publishing Group).

In fact, this water hydrogen-bonding network at the OEC is necessary and important for water oxidation.\textsuperscript{[81]} Experiments show that disruption of this network destroys the steady state rate of S\textsubscript{1} to S\textsubscript{4} in water oxidation.

Hydrogen bonding networks are important in our calculated systems as well. In a realistic medium of water, the protic solvation effect is obvious and quite strong. In order to reproduce this effect accurately, we add two additional explicit water molecules to the aqua-Ru complex (L)(pic\textsubscript{2})Ru\textsuperscript{III}–OH\textsubscript{2} (L = hqc, pdc, H\textsubscript{2}hqc = 8-hydroxyquinoline-2-carboxylic acid) in our calculations.\textsuperscript{[82]} Two optimized geometries are shown in Figure 3.12:

Figure 3.12 Calculated geometries of [Ru\textsuperscript{III}(hqc)(pic\textsubscript{2}–OH\textsubscript{2})\textsuperscript{+}] (a) and [Ru\textsuperscript{III}(pdc)(pic\textsubscript{2}–OH\textsubscript{2})\textsuperscript{+}] (b) in aqueous medium. Hydrogen atoms except those bonding to oxygen atoms are omitted for clarity. (purple for Ru, grey for C, blue for N, red for O and green for H).
One of the water molecules serves as both a hydrogen-bond donor and acceptor at the same time, the other one acts only as a hydrogen-bond acceptor. This hydrogen-bonding network could function as a channel for proton transfer and facilitate the Proton-Coupled Electron Transfer (PCET).

3.5 OO Bond Formation (O₂ Evolution)

The O-O bond formation is one of the most important steps in the oxygen evolution mechanism. After a stepwise and simultaneous loss of electrons and protons, the complexes are able to reach their higher oxidation states, which is required for the OO bond formation.

Generally, there are two main proposals for the key O-O bond formation event. [83-85] One is coupling between one terminal oxo and the oxygen atom of the incoming water substrate or possibly a hydroxide ion (WNA). The other one is oxo-oxo coupling between two M=O units (I2M). The difference between these two pathways is whether a solvent water molecule is involved in the formation of OO bond or not. The two proposed OO bond formation pathways are shown in Table 3.2.

<table>
<thead>
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<th>Table 3.2</th>
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<td>WNA</td>
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<td>I2M</td>
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3.5.1 Water Nucleophilic Attack (WNA).

**Water attack on the oxo group to give a terminal peroxide in the key OO bond forming step**

When the transition metal complex reaches its higher oxidation state, it could undergo a water nucleophilic attack, forming a peroxidic intermediate, and finally release the oxygen while the empty position is coordinated by an incoming water. [86-89] The whole mechanistic proposal of WNA for water oxidation using Ru-based WOC is represented in Figure 3.13.
The complex Ru^{II}-OH_{2} undergoes a sequential removal of electrons and protons to form Ru^{IV}-O, and it can reach an even higher oxidation state Ru^{V}-O. Once the Ru^{V}-O is formed, which is a highly reactive species, it undergoes a nucleophilic attack from a solvent water, then forms the terminal hydroperoxidic complex Ru^{III}-OOH, which contains the key feature of the O-O bond. The formed Ru^{III}-OOH intermediate can lose one more electron accompanied with one proton loss to form Ru^{IV}-OO, then releasing oxygen and finally coordinate a solvent water molecule. This WNA route was identified to be feasible for the well-known blue dimer (Figure 3.14)\textsuperscript{[90]}

\[ \text{Ru}^{\text{II}}-\text{OH}_{2} \rightarrow \text{Ru}^{\text{III}}-\text{OH} \rightarrow \text{Ru}^{\text{IV}}-\text{O} \rightarrow \text{Ru}^{\text{V}}-\text{O} \]

The oxidation from H_{2}O-Ru^{III}-O-Ru^{III}-OH_{2} to O-Ru^{V}-O-Ru^{V}-O was completed by a stepwise electron-proton removal. This product is a reactive and
transient intermediate which is responsible for releasing oxygen when reacting with the solvent water. Once complex O-Ru\textsuperscript{IV}-O-Ru\textsuperscript{V}-O was generated, it underwent a water nucleophilic attack immediately to form HO-Ru\textsuperscript{IV}-O-Ru\textsuperscript{IV}-OOH intermediate. The following oxygen releasing step is dependent on the amount of Ce\textsuperscript{IV} oxidant.

If there is a stoichiometric amount of the Ce\textsuperscript{IV} oxidant, following path a HO-Ru\textsuperscript{IV}-O-Ru\textsuperscript{IV}-OOH intermediate generates oxygen and reforms the complex H\textsubscript{2}O-Ru\textsuperscript{III}-O-Ru\textsuperscript{III}-OH\textsubscript{2}, which is the initial form of blue dimer. However, the generation rate is relatively slow. If an excess of the Ce\textsuperscript{IV} oxidant is used, as path b shows, intermediate HO-Ru\textsuperscript{IV}-O-Ru\textsuperscript{IV}-OOH will be further oxidized to O-Ru\textsuperscript{V}-O-Ru\textsuperscript{IV}-OOH, which releases oxygen much more rapidly, and then forms H\textsubscript{2}O-Ru\textsuperscript{III}-O-Ru\textsuperscript{IV}-OH.

### 3.5.2 Interaction Between Two M-O Units (I2M).

**Oxidative coupling of the two terminal oxo atoms of M=O.**

The OO bond formation from the interaction between two M-O complexes includes two different manners, 1) Intramolecular approach, which means two M-O units are situated in one complex; 2) Intermolecular approach, which indicates that it is a bimolecular process, each complex contains only one M-O unit. Both pathways using Ru-based WOCs can be concluded in Figure 3.15.

![Figure 3.15 General proposed OO bond formation mechanism based on interaction of two Ru-O units. (Both intramolecular and intermolecular pathways)](image-url)
3.5.2.1 Intramolecular Approach

For the complex in, in-\{[Ru^{II}(trpy)(OH_2)]_2(bpp)\}^{3+} (in, in- Ru-Hbpp) (trpy is 2,2':6',2''-terpyridine, bpp is bis(2-pyridyl)-3,5-pyrazolate),\[^{91}\] which contains two Ru-O units in one same complex, calculations show that the only OO bond formation mechanism occurring in this system is an intramolecular pathway (Figure 3.16), whereas the water nucleophilic attack manner is excluded.

![Figure 3.16 Potential water oxidation mechanism for the in, in-Ru-Hbpp complex, and the trpy ligands are omitted for clarity.](image)

The complex H_2O-Ru^{II}-Hbpp-Ru^{II}-OH_2 is stepwise oxidized by Ce(IV) up to O-Ru^{IV}-Hbpp-Ru^{IV}-O. It then generates a Hbpp-1,2-peroxo intermediate via an intramolecular interaction between two oxygen atoms, and this coupling reduces the Ru oxidation state from IV to III. A hydroperoxic intermediate HOO-Ru^{III}-Hbpp-Ru^{III}-OH is then formed when one water molecule enters and it release oxygen finally with one more water coming in.

3.5.2.2 Intermolecular Approach.

To the best of our knowledge, OO bond formation via intermolecular coupling proposal was first reported by Privalov and Sun in 2010.\[^{92, 93}\]
Figure 3.17 Structures of complexes 3-6 and 3-7.

Two different mono-ruthenium complexes 3-6 Ru(bda)(pic)$_2$ (H$_2$bda = 2,2’-bipyridine-6,6’-dicarboxylic acid; pic = 4-picoline) and 3-7 Ru(bda)(isoq)$_2$ (isoq = isoquinoline) were synthesized by Sun and coworkers (Figure 3.17). Especially complex 3-7 demonstrates superior catalytic performance on water oxidation using Ce$^{IV}$ as the oxidant. It reaches to an amazingly high reaction rate with a TOF of more than 400 s$^{-1}$. The performance of complex 3-7 is comparable to the oxygen-evolving complex in photosystem II, where the oxygen generation rate$^{[94]}$ in OEC is estimated at 100-400s$^{-1}$ (light-driven).

The kinetic studies provide insight into the mechanism of OO bond formation. The kinetics of the catalytic reaction for water oxidation was identified as second order, which indicates the reaction proceeds in a bimolecular manner. A radical coupling between two Ru-O units$^{[95-98]}$ was proposed to be involved in this key process.

Now we focus complex 3-6 for a detailed discussion. Normally the ideal angle for an octahedron configuration is 90º, however, for complex 3-6, the O-Ru-O angle is expanded to 122.99º. It therefore can generate a seven-coordinated complex by accepting one incoming water molecule. After reaching its high oxidation state, it forms a seven-coordinate Ru$^{IV}$ dimer μ-(HOHOH)-[Ru$^{IV}$(bda)(pic)$_2$]. The crystal structure of this dimer is shown in Figure 3.18.
Figure 3.18 Crystal structure of seven-coordinate Ru(IV) dimeric complex. Hydrogen atoms except those bonding to oxygen atoms are omitted for clarity. (purple for Ru, grey for C, red for O, blue for N, and green for H).

The calculated free energy barrier via a low-spin antiferromagnetic transition state is only 11.9 kcal/mol by taking the encounter complex as a reference. From the former computational study by Yang and Baik,[99] the dissociation of oxygen does not demand a high-energy ligand exchange from a peroxo intermediate. The general inter-molecular OO bond formation proposal is shown in Figure 3.19.

\[
\begin{align*}
2 \left[ \text{Ru}^{II} \right]_{\text{OH}_2} - 2e^- & \rightarrow 2 \left[ \text{Ru}^{III} \right]_{\text{OH}_2} - 2e^- - 2H^+ \\
2 \left[ \text{Ru}^{IV} \right]_{\text{OH}} - 2e^- & \rightarrow 2 \left[ \text{Ru}^{V} \right]_{O} - 2H^+ + 2OH_2 \\
\text{O}_2 & \rightarrow \text{Ru}^{IV}O\text{Ru}^{IV} + 2OH_2
\end{align*}
\]

Figure 3.19 General description of oxygen evolution with inter-molecular coupling pathway.

Both electronic and geometrical properties of bda ligand make a contribution on the formation of a seven-coordinate complex, which is essential for generation of seven-coordinate dimer afterwards. OO bond formation is proposed from the bi-nuclear coupling for the first time.
Chapter 4

Natural Hydrogenases and Synthetic Mimic Complexes

4.1 Brief Introduction

Providing a non-polluting, abundant and renewable energy source is one of the main scientific challenges we are facing. As an energy carrier and potential transportation fuel, hydrogen (H₂), a closed-shell molecule has been envisioned.\textsuperscript{100,101} Hydrogen is an ideal fuel, which can be generated from water, and the only product of the reaction is water when combustion of hydrogen is made with pure oxygen. It can therefore conform to the requirement of sustainability, energy security and environmental-benign character. Furthermore, hydrogen is one of the fuels which has highest specific energy. The energy density of hydrogen can reach 33.3 kWh/kg (30 MPa),\textsuperscript{102} this indicates it can release 33.3 kWh/kg of energy for every one kilogram. The energy density of hydrogen is much higher than that of gasoline (12.7 kWh/kg) which is frequently used in our daily life. However, gasoline (8.76 kWh/kg) shows a much better performance than hydrogen (0.75 kWh/kg, 30 MPa) if we compare these fuels in energy per unit volume. Finding new ways to store hydrogen is therefore one of the main targets we are facing now.

Hydrogen is also involved in several key chemical processes, such as hydrogenation of inorganic and organic compounds which affects our daily life greatly. For example, ammonia fertilizer is necessary for human society to survive and develop since we need to feed the growing population by increasing the production of agricultural products.\textsuperscript{103,104} In addition, there is a need to remove sulfur and nitrogen from hundreds of million tons of crude oil to keep a high quality,\textsuperscript{105} and hydrogen is used for this purpose.

Although hydrogen is playing and continues to play an important role in our daily life, the economical production or the uptake of molecular hydrogen is limited by the intrinsic kinetic properties. Usually hydrogen does not react with other chemicals at room temperature. It can react with oxygen to form water, however, this reaction is extraordinarily slow at ambient temperature. The hydrogen was even used as an “inert” gas in early air-free chemistry because of its stable chemical properties although it is now replaced by N₂ or Argon.
The following physical and chemical properties\textsuperscript{106} could provide part of the explanation for the unreactive property of hydrogen:

(1) Hydrogen is a completely nonpolar molecule;
(2) The bond between H-H is remarkably strong, and the required energy for homolytic cleavage of an H-H bond is 103 Kcal/Mol;
(3) Due to the high basicity of hydride (H\textsuperscript{-}) hydrogen is a poor acid.

Since the H-H bond is generally stronger than most new H-X bonds, chemists place the H-H bond into the strongest single bond category. The design of effective catalysts for hydrogen oxidation and proton reduction becomes a challenge. Because of the intrinsic thermodynamic limitations, molecular hydrogen production/uptake is currently only economically viable under high temperature condition or in presence of a platinum catalyst.\textsuperscript{107,108}

4.2 Hydrogeneases Enzymes

The natural hydrogeneases\textsuperscript{109-113} serve as good models for hydrogen uptake/production. Hydrogeneases are billion-year old redox enzymes and frequently present in microorganisms belonging to the Archaea and Bacteria domains of life, a few of them are found in Eukarya as well.\textsuperscript{114} They display a remarkable performance on the reversible inter-conversion between protons and hydrogen, since the purpose of hydrogeneases enzymes is to set a charge separation or combination. Consequently, synthetic catalysts with simpler structure based on these hydrogenease enzymes have been studied.

Most of the hydrogenease enzymes\textsuperscript{115} can be divided into two major classes by specifying the transition metal they carry: Ni-Fe and Fe-only hydrogeneases. Ni-Fe hydrogeneases are primarily used for hydrogen uptake, whereas the Fe-Fe hydrogeneases are usually used for proton reduction.

4.2.1 Ni-Fe Hydrogenases

The Ni-Fe hydrogeneases\textsuperscript{116,117} are mainly used for the heterolytic cleavage of hydrogen. The X-ray crystal structure of the oxidized form of Desulfovibrio gigas of a Ni-Fe hydrogenease was obtained at a resolution of 2.85 Å for the first time in 1995,\textsuperscript{118} and from then on X-ray crystal structures from other organisms have been obtained.\textsuperscript{119-121}
As shown in Figure 4.1, a nickel atom is situated in the active site, a chain of three iron-sulfur clusters consists of one [3Fe-4S] cluster and two cubane type clusters contain eleven iron atoms.\textsuperscript{[122]}

### 4.2.2 Fe-Fe Hydrogenase

Iron-iron hydrogenases\textsuperscript{[123-126]} are generally found capable of reducing protons, although some of them are used for hydrogen oxidation and bi-directional occasionally. For molecular structures of Fe-Fe hydrogenases, there are many different sources, scientists still found many structural similarities among them although the structures of them are even slightly different from each other under different crystallization states. The main structures were concluded from the X-ray crystallographic information of Desulfovibrio desulfuricans Hildenborough (\textit{DdH}) and Clostridium pasteurianum I (\textit{CpI})\textsuperscript{[127-129]} (Figure 4.2), which are hydrogen uptake and hydrogen production enzymes, respectively.

**Figure 4.1** The crystal structure of nickel-iron hydrogenases purified from \textit{D. gigas}. (Reprinted with permission from ACS Publications)

**Figure 4.2** The crystal structure of \textit{Clostridium pasteurianum I (CpI)} iron-iron hydrogenase. (Reprinted with permission from ACS Publications)
The consensus structure\textsuperscript{[130]} of the active site of Fe-Fe hydrogenase is shown in Figure 4.3,

\begin{center}
\begin{tikzpicture}
\node (4Fe-4S) at (0,0) {4Fe-4S};
\node (Cys) at (0.5,0.5) {Cys};
\node (CO) at (1.5,0) {CO};
\node (NC) at (1.5,-0.5) {NC};
\node (L) at (-0.5,0.75) {L};
\node (S) at (-0.25,0) {S};
\node (X) at (0,1) {X};
\draw (4Fe-4S) -- (Cys);
\draw (4Fe-4S) -- (CO);
\draw (4Fe-4S) -- (NC);
\draw (4Fe-4S) -- (L);
\draw (4Fe-4S) -- (S);
\draw (4Fe-4S) -- (X);
\end{tikzpicture}
\end{center}

\textbf{Figure 4.3} The consensus structure of the active site of Fe-Fe Hydrogenase.

Furthermore, the Fe-Fe hydrogenases are well known for their abilities to reduce protons to hydrogen, at nearly Nernstian potentials the turnover frequencies of Fe-Fe hydrogenase enzymes can reach a value of around 6000 mol of H\textsubscript{2}/mol per hydrogenase enzyme per second. Many scientists are inspired by the amazing catalytic performance of proton reduction/hydrogen uptake with hydrogenases. Therefore, many variations of electrochemical and photochemical hydrogen production/uptake systems based on Fe-complexes have been created. Numerous studies both experimentally and theoretically focus on these artificial systems.

\textbf{4.3 Homogeneous Light-Driven Catalytic Systems}

After studying the structures of hydrogenase enzymes, we found that the first-row transition metals, such as iron and nickel, are usually present in catalysts for a catalytic hydrogen uptake/production. This discovery results in a fast development of hydrogenase modelization, therefore many studies have been devoted to synthesize much smaller molecular complexes to mimic the structure and function of these hydrogenase enzymes.

In addition, hydrogen generation using renewable energy such as solar energy could be an ideal method for sustainable production and storage of energy, and many scientific groups has focused their attention on water splitting during last 30 years.\textsuperscript{[131-138]} It is important to emphasize that most of work in this field was devoted to heterogeneous photocatalytic systems,\textsuperscript{[139-141]} while homogeneous ones were poorly developed. However, during the past few years much progress has been achieved in developing and understanding homogeneous photocatalytic systems.\textsuperscript{[142-146]}

Recently, Mei Wang and coworkers designed a system\textsuperscript{[147]} (Figure 4.4) comprising of 1) Photosensitizer, usually based on the ruthenium tris-bpy moiety;
2) A catalytic center based on a transition metal complex; 3) A redox mediator.

![Chemical structure of a catalytic center based on a transition metal complex and a redox mediator.](image)

(a) reductive quenching; (b) intermolecular ET; (c) catalytic proton reduction

**Figure 4.4** *Homogeneous light-driven catalytic systems based on Fe for hydrogen production using ruthenium-polypyridine as photosensitizer.*

However, homogeneous light-driven catalytic systems for hydrogen production remain relatively rare in experimental phase. A practical technology for hydrogen generation derived from solar energy remains a goal to be achieved.

**4.4 Effect of the Pendant Base in Iron-Complexes.**

The transport or movement of proton is vital\textsuperscript{[148-151]} in many biological and chemical processes including the hydrogen oxidation/production, the reduction of CO\textsubscript{2} to formate and the reduction of O\textsubscript{2} to water. It is often related to energy storage and utilization, however the details of these processes are still ambiguous. Internal amine base is a reoccurring feature of hydrogenases. It is likely to facilitate the proton transfer to the metal center. For natural hydrogenase enzymes or synthetic catalysts based on iron or nickel, we found that the incorporation of a pendant amine is a frequently occurring feature, the pendant amine base is located in proximity of the metal and forms a weak interaction with the metal since it is too far away to form a strong bond.\textsuperscript{[152]} Many research groups have also reported aza and oxadithiolates as probable proton relays\textsuperscript{[153-158]} in functional models for the Fe-Fe hydrogenases, and are dedicating their efforts to this process, aiming at providing understanding for their functions.

**4.4.1 Pendant Base Effect on Proton Transfer in Iron-Complex**

Three complexes 4-1 \(\text{Fe}_2(\text{pdt})(\text{CO})_2(\text{dpvv})_2\), 4-2 \(\text{Fe}_2(\text{adt})(\text{CO})_2(\text{dpvv})_2\) and 4-3 \(\text{Fe}_2(\text{odt})(\text{CO})_2(\text{dpvv})_2\) (dpvv = cis-1,2-bis(diphenylphosphino)ethylene; pdt = 1,3-propanedithiolate; adt = 2-azapropene-1,3-dithiolate; odt =
2-oxopropane-1,3-dithiolate) were synthesized, and all these complexes are with a dithiolate moiety which acts as a bridge between the two iron subunits.\textsuperscript{159} Rauchfuss and coworkers proposed that the functionality of amine in complex 4-2 could act as a proton relay that transfers the proton from and to the bridging site between the two Fe atoms.

\begin{scheme}
\begin{align*}
\text{Scheme 4.1} & \text{ Proton relay effect of heteroatom in the dithiolate.}
\end{align*}
\end{scheme}

Scheme 4.1 demonstrates how a heteroatom in the dithiolate shuffles proton to and from the metal iron. All these complexes 4-1, 4-2 and 4-3 were found to be protonated with a strong acid \([\text{H(Et}_2\text{O)}_2]\text{BAr}_4\) quickly at -90°C, however, only complex 4-2 can be protonated if a billion-fold weaker acid \([\text{HPMe}_2\text{Ph}]\text{BF}_4\) was used instead, even though these diiron complexes have similar basicities. This difference indicates that the presence of a heteroatom N exerts a strong effect on the rate of protonation. Their results suggested that in complex 4-2 the protonation initially happens at the amine base, then transfers to the terminal site, and finally reaches the bridging site. In contrast, for complex 4-1 that contains nonbasic propanedithiolate or complex 4-3 with a weakly basic oxadithiolate, the initial protonation on the internal base is blocked.

They also compared the deprotonation of all terminal hydride complex \([4-1(t-H)]^+\), \([4-2(t-H)]^+\), \([4-3(t-H)]^+\). For complex \([4-1(t-H)]^+\), even at room temperature it is impossible deprotonate using any organic base, and it isomerizes to bridging complex eventually. For complex \([4-3(t-H)]^+\), it is inert toward base at -78°C, however it will generate two products 4-3 and \([4-3(\mu-H)]^+\) slowly when the
temperature increase to around 0°C. Neither the concentration nor the pKₐ of the base has any influence on the proportion of these two products. It is quite different in the case of [4-2(t-H)]⁺, the deprotonation of it occurs immediately with a base of PBu₃[HPBu₃] BF₄ even at a rather low temperature of -90°C, and the only observed product is complex 4-2.

Since there is almost no difference in the νₐCO region among these three complexes in the IR spectra, the thermodynamic acidities of them should be the similar. This demonstrates that the big difference of the deprotonation rate among them lies in the presence of the heteroatom.

In summary, complex 4-2 shows that the heteroatom N facilitates the protonation and relay the proton to Fe immediately, and complex 4-3 which contains a relatively weakly basic oxadithiolate shows a moderate performance although inferior of complex 4-2. Complex 4-1 with non-basic propanedithiolate is inert to both protonation and deprotonation.

4.4.2 Pendant Amine Base Effect on Heterolytic Activation of Hydrogen in Iron-Complex

The pendant amine base is not only involved in the intramolecular proton transfer but also related to the heterolytic activation of hydrogen. Computational and experimental studies were used to provide insight into the details of heterolytic splitting of hydrogen, which takes place at the incorporated pendant amine and the metal core (Scheme 4.2).

Scheme 4.2 The pendant amine base facilitates the heterolytic activation of hydrogen.
Complex $4\text{H}^2[160]$ Fe$_2[(SCH_2)_2NBn](CO)_3-(dppv)(PMe_3)$ first loses one electron to generate $[4\text{H}]^+$ to the mild oxidant $[Fe(C_5Me_5)_2]^+$, then $[4\text{H}]^+$ participates in the heterolytic activation of hydrogen, one situated at the pendant amine base N position, while another one is located at the Fe atom. This internal base makes a contribution to the stabilization of the heterolytically splitted species. The cleavage first generates a terminal hydride intermediate, which isomerizes to a more stable form the bridging hydride complex $[4\text{H}]^2$. The proton at the N site is trapped by P(o-tol)$_3$, and yields $[4\text{H}]^+$ as the final product.

The two cases we described above indicate that pendant amine bases are important in proton transfer or movement. In fact, this proton transfer or movement in complex is a vital part of the mechanistic study of hydrogen generation and uptake, and pendant amine base plays an important role in this kind of proton movement or transfer. It is worth for a detailed investigation. However, the need for this proton relay function has not been clearly explained. It is therefore necessary for us to study and provide further explanation on the role the pendant base. We believe that a thorough understanding of proton relays will be crucial for developing efficient hydrogen production and hydrogen oxidation catalysts.
References

47, 11763-11773.


