Photo- and electro-catalytic hydrogen evolution by nickel complexes and DFT calculations for photoredox reactions

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2017

Shao, H.Y. (2017). Photo- and electro-catalytic hydrogen evolution by nickel complexes and DFT calculations for photoredox reactions. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69484>

<https://doi.org/10.32657/10356/69484>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**PHOTO- AND ELECTRO-CATALYTIC HYDROGEN
EVOLUTION BY NICKEL COMPLEXES AND DFT
CALCULATIONS FOR PHOTOREDOX REACTIONS**

SHAO HAI YAN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2016

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2016

Acknowledgement

I would like to express my deep gratitude to Nanyang Assistant Professor Soo Han Sen, my research supervisor, for his patient guidance, enthusiastic encouragement and useful critiques of my four years' research work.

I am grateful to Nanyang Technological University (NTU) for providing me the research scholarship and the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE) for providing the opportunity for me to attend many useful workshops and academic conferences.

I will also like to thank the colleagues in the Han Sen's group for making the pursuit of Ph.D. a vibrant and memorable journey. Specially thanks to Ho Xianliang for his help in photocatalytic proton reduction experiments when I got pregnancy in my last Ph.D. semester.

I would like to express my sincere gratitude to CBC Lecturer Dr Lu Yunpeng for his guidance and readiness in sharing his knowledge in DFT calculations. I also like to thank Associate Professor Xu Rong at SCBE for her professional help in CO₂ and proton reduction study. At the same time, I would like to thank Associate Professor Joachim Loo for his permission for me to work in Solar Fuels Lab in MSE and thank Dr Tran D. Phong for his help in electrocatalytic proton reduction.

I would like to thank Ms. Ee-Ling Goh in the NMR laboratory, Ms. Wen-Wei Zhu in the GC-MS laboratory, Dr Li Yongxin and Dr Rakesh Ganguly in XRD lab and all the other support staffs at CBC.

Finally, my deepest gratitude goes to my family especially my parents who love me more than anything in the world. Thank my husband Wu Bin for his limitless love, company and support. Most importantly, I want to thank my baby who will be born one month later. It is a wonderful period to finish this thesis together with you. Mom loves you!

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List of Abbreviations

ACN	acetonitrile
Ar	aryl (substituted aromatic ring)
<i>n</i> Bu	<i>n</i> -butyl
<i>t</i> Bu	<i>tert</i> -butyl
DFT	density functional theory
CV	cyclic voltammetry/cyclic voltammogram
CPE	controlled potential electrolysis
DLS	dynamic light scattering
DCM	dichloromethane
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
equiv	equivalent
Fc ⁺ / Fc	ferricenium / ferrocene redox couple
GC	gas chromatography
h	hour
HOAc	acetic acid
HRMS	high resolution mass spectrometry
Hz	hertz
LSV	linear sweep voltammetry
M	concentration (mol/L)
M ⁺	parent ion peak (mass spectrum)
Me	methyl
mg	milligram
MHz	megahertz

min	minute(s)
mL	milliliter
mmol	millimole
mol %	mole percent
nmol	nanomole
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
TEA	triethylamine
TEM	transmission electron microscopy
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TD-DFT	time dependent density functional theory
TOF	turnover frequency
TON	turnover number
UV-vis	ultraviolet-visible
XPS	X-ray photoelectron spectroscopy

Index of Symbols

δ	chemical shift (ppm)
$^{\circ}\text{C}$	degree centigrade
$i_{\text{pa}} / i_{\text{p}}^{\text{ox}}$	oxidative peak current (anodic)
$i_{\text{pc}} / i_{\text{p}}^{\text{red}}$	reductive peak current (cathodic)
ε	extinction coefficients
E_0	formal electrode potential
$E_{1/2}$	Half-wave potential
E_{pa}	Oxidative peak potential (anodic)
E_{pc}	Reductive peak potential (cathodic)
J	coupling constants
K_{eq}	equilibrium constant
m	multiplet
q	quartet
s	singlet
t	triplet
η	overpotential

Abstract

The usage of cleaner energy resources, such as hydrogen gas (H_2) derived from electrolysis of water, is an attractive solution for the over-reliance on fossil fuels. Currently, the most active catalyst for the hydrogen evolution reaction is platinum, although a number of Earth-abundant metal chalcogenides and phosphides are comparable in activity. Nonetheless, most of the reported catalysts function in organic solvents or under highly acidic aqueous solutions.

In this thesis, two sets of salicylaldimine nickel complexes with pendant, chelating ether groups were synthesized. The second-sphere ether functionalities on the periphery of the complexes can bind Lewis acid cations such as alkali metal cations to enhance the catalytic activity. One series of the catalysts possess sulfonate groups in the ligand periphery to improve water solubility and allow the complexes to function as highly active electrocatalysts for proton reduction in seawater, which has rarely been reported in the past decades. Another set of the nickel complexes is employed in photocatalytic H_2 evolution systems with a high TON of around 3800, together with an Ir dye as the photosensitizer and TEA as the sacrificial electron donor in water/methanol solution.

DFT calculations have been used for mechanistic investigations in the photoredox reaction. In the photocatalytic H_2 evolution reaction mentioned above, we confirmed that the Lewis acid cations chelated by the ether arms in close proximity to the Ni catalytic center direct protons to the transient metal hydride, resulting in efficient H_2 production. In another project, a previously reported photocatalytic fluorination reaction was studied, in which anthraquinone (AQN) is the light absorber and Selectfluor® is the electrophilic fluorine source. The elementary steps after irradiation have been elucidated by DFT calculations. Together with my colleague's time-resolved optical spectroscopy, an AQN-Selectfluor® triplet exciplex is observed in the photoirradiation and considered to be the predominant intermediate for initiating and sustaining the fluorination reaction.

Chapter 1. Introduction of Electro- and Photo-catalytic Hydrogen Evolution

1.1 Artificial photosynthesis

The growing issue of a global energy shortage has forced scientists to work on developing more sustainable energy resources in order to reduce our reliance on fossil fuels.¹ Among the renewable energy sources such as wind, solar, geothermal, tides, nuclear, biomass,² and others, solar energy dominates in availability and is the most likely long-term solution as the primary, carbon-neutral energy source.³ For example, a solar energy conversion device that collects and converts all of the sunlight striking just 2% of the Earth's surface for 8 h with an energy conversion efficiency of 12% would be sufficient to satisfy global energy consumption for two weeks.⁴ Thus, solar energy conversion seems to be the most promising approach to sustainable energy production.

In nature, photosynthesis plays a crucial role in converting solar to chemical energy. Simply, the process of natural photosynthesis can be broken down into three steps as shown in Scheme 1.1: (1) the initial light-harvesting process and charge separation in photosystem II (P680) and photosystem I (P700); (2) spatial charge separation through electron transfer between redox cofactors, and (3) fuel and oxygen formation at active sites.⁵

Scheme 1.1. Z-Scheme of natural photosynthesis.⁵

Inspired by nature, researchers have proposed at least two novel, solar energy utilization systems: (1) the solar-driven water splitting system, and (2) the solar cells system (photovoltaic devices and dye sensitized solar cells) to convert solar energy into fuels.⁶ However, solar cells are limited in converting solar radiation into electricity directly, and cannot store energy for subsequent use.⁷ On the other hand, a solar-driven water splitting system is able to store the energy in the form of fuel (H_2) and an oxidant (O_2). The storage of solar energy in the form of chemical bonds is also known as “artificial photosynthesis”. Artificial photosynthesis, by splitting water into H_2 (proton reduction) and O_2 (water oxidation), has been considered as one of the holy grails of 21st century chemistry.⁸ In other words, the artificial photosynthetic system is just a simplified model of the natural process, wherein the key structural elements and functions of natural photosynthesis are mimicked.⁹

Splitting of water is a highly desirable process, but running the reaction is challenging.

The equations of water splitting are shown as the following (Equation 1.1-1.3).

The water splitting involves two separate, multi-electron redox processes: a four-electron oxidation to produce O_2 (E 1.2) and a two-electron reduction to give H_2 (E 1.1). The reversible potential required for water splitting is 1.23 eV. However, the one-electron oxidation of water to form hydroxyl radicals is +2.80 eV, whereas the two-electron oxidation to form H_2O_2 is +1.78 eV. These intermediates are kinetically more likely since they involve fewer electrons, but the higher potentials required will increase the energetic barrier of water splitting.¹⁰ Metal-based catalysts are able to mediate the multi-electron redox processes instead to avoid formation of these energetic intermediates, thereby lowering the barriers for hydrogen evolution.¹¹ As illustrated in Scheme 1.2, metal catalysts are explored for H_2 evolution via the formation of a common metal-hydride. The catalytic conversion of protons to H_2 is the key fuel-generating transformation in the water-splitting reaction. Some of the biggest scientific challenges in converting protons to H_2 are the design and the implementation of efficient catalysts in H_2 evolution systems.

Scheme 1.2 Proposed mechanisms for H_2 evolution catalytic by metal catalysts.

1.2 Hydrogen evolution catalyst

At the moment, the best catalyst for H₂ evolution is undeniably platinum (Pt). It shows low overpotential (η), long durability, and high turnover frequency (TOF) in proton reduction reaction.¹² However, Pt is a precious metal, partly due to its relative scarcity in the earth's crust. In addition, catalysts based on Pt and other noble metals or metal oxides like Pd, Ir, and other members of the platinum group metals, are also robust proton reduction catalyst, but still suffer from their high cost and low abundance.¹³ Consequently, more Earth-abundant, heterogeneous catalysts have been sought as alternatives, including metal chalcogenides,¹⁴ carbides,¹⁵ phosphides,¹⁶ and hydroxides,¹⁷ and have been reported in attempts to produce H₂ at prices competitive with the production from fossil fuels. Unfortunately, the mechanistic studies of such heterogeneous systems remain challenging, since their performances are highly dependent on local variations in surface morphology and chemical reactivity. In contrast, molecular catalytic systems are often highly selective and active, more amenable to spectroscopic probes for elementary reaction steps, and may be systematically designed and improved through ligand modifications.

In nature, in terms of Earth-abundant iron and/or nickel metal centers, hydrogenases can reversibly interconvert protons to H₂ at low thermodynamic potentials with high efficiencies and activities. The structures of the active site of the hydrogenase enzymes are shown in Scheme 1.3. They are reported to produce 100–10,000 moles of H₂ per mole of catalyst per second.¹⁸ The application of hydrogenases in water splitting reactions has been reported and their catalytic mechanisms can be studied on a molecular level.^{18a,19} However, utilization of these macromolecular complexes still remains a challenge since

both the local density of active metal center and the relative stability under ambient conditions are quite low.^{19c,20} Inspired by hydrogenase enzymes, a great deal of work on the development of metallobiomolecules has been carried out, which was aimed at mimicking proton functionalities.²¹ In addition, a number of non-biomimetic systems show remarkable catalytic efficiency in H₂ evolution. Since the energy source can be electricity or sunlight directly, the catalytic systems can be classified as either electrocatalytic or photocatalytic, respectively. Examples of systems based on Earth-abundant later transition metal complexes will be discussed in detail below.

Scheme 1.3. Proposed structures of the active site of the [FeNi] and [FeFe] hydrogenase.

1.3 Electrocatalytic system

An electrochemical system uses electricity as the electron source. This method is considered as a convenient route to monitor the catalytic systems or to be used as a test bed for future integration into artificial devices. A number of molecules were found to be efficient H₂ evolution catalysts in aqueous or organic media.

Nickel complexes

In the 1980s, Ni tetraazamacrocyclic complex (**1**, Scheme 1.4) reported by Fisher and Eisenberg was one of the pioneering molecules in the field of electrocatalytic proton reduction, even though it was part of a competitive reaction in a CO₂ reduction system. However, the system functions only under a high potential of ca. -1.50 V vs. SHE in

water/acetonitrile (v/v: 2/1) mixtures with a mercury (Hg) electrode.²² Sauvage and co-workers later reported two related Ni(II) macrocyclic complexes ($[\text{Ni}(\text{cyclam})]^{2+}$, **2**) and ($[\text{Ni}_2(\text{biscyclam})]^{4+}$, **3**) showing higher catalytic activity of proton reduction in neutral water with a Hg pool electrode, probably via nickel hydride intermediates, which formed during the electrolysis.

Scheme 1.4. Structures of Ni catalysts **1-13**.

The most noteworthy examples of Ni catalysts are the mononuclear nickel-phosphine complexes (**4-11**) reported by DuBois and co-workers.²³ They usually show exceptional activity in proton reduction with high turnover numbers (TON) at low overpotentials. One of the most impressive catalysts, $[\text{Ni}(\text{P}_2\text{N}_2)_2]^{2+}$ (**10**), is able to catalyse H_2 production with

a turnover frequency (TOF) of more than $100,000\text{ s}^{-1}$ at -0.49 V vs. SHE in acetonitrile/water solution. This remarkable increase in catalytic activity was attributed to the key role of pendant amines that function as proton relays in the reaction.²⁴ Much effort has been invested to develop derivatives of Ni bis(phosphine) compounds that can carry out the proton reduction under water-compatible conditions.²⁵

Sarkar and co-workers reported a Ni(II) thiolene complex (**12**) which can catalyze proton reduction in aqueous solution with tosic acid as a proton source. The catalyst was coated on the surface of a glassy carbon working electrode, and the potential could be lowered to -0.5 V vs. SHE.²⁶ Crabtree *et al.* reported nickel complexes supported with pyridinediimine ligand (**13**) and also coated them on a carbon electrode. The modified electrode was used for H_2 evolution at -1.1 V vs. SHE with 95% Faradaic efficiency.²⁷

Cobalt complexes

In recent years, a significant number of cobalt complexes employed as electrocatalytic proton reduction catalysts have been developed. Examples are described below according to the ligand platforms.

(I) Macrocyclic platforms

Following the initial report by Fisher and Eisenberg of cobalt(II) tetraazamacrocyclic catalysts²² with similar ligand frameworks as **1** in Scheme 1.4 for simultaneous electrocatalytic CO_2 and water reduction to produce CO and H_2 , various other works have started to focus on cobalt complexes with macrocyclic the ligand. Peters and co-workers established a series of Co(II) tetraazamacrocyclic complexes (**14-18** in Scheme 1.5) for electrocatalytic H_2 evolution. Some of these cobaloximes are active for the

electrocatalytic production of H_2 from pH 2.2 aqueous solutions at -0.69 V vs. SHE with 92% Faradaic efficiency on glassy carbon plate electrodes.²⁸ Cobalt chlathrochelates like boron-capped tris(glyoximato) cobalt(II) (**19-20**) reported by Bubnov *et al.* were able to reduce a strong acid like HClO_4 to H_2 in water/acetonitrile (v/v: 1/1) mixtures at an onset potential of around -0.19 V vs. SHE. Savnt and co-workers later demonstrated that a related tris(glyoximato) cobalt(II) complex (**21**) worked as a molecular precursor to form Co nanoparticles for H_2 evolution in pH 7 phosphate buffer at -0.75 V vs. SHE, with a 75 – 85% Faradaic yield.²⁹ More recently, Dinolfo's group reported a series of dicobalt complexes (**22, 23**) with bis(phenolate) tetrakis-Schiff base ligand, and used them for electrocatalytic production of H_2 from ACN solution containing acetic acid, with 94% Faradaic efficiency on a carbon paper working electrode.³⁰

Scheme 1.5. Structures of Co catalysts **14-23**.

(II) Pyridine-based platforms

Chang's group presented a series of cobalt pentapyridine complexes, $[\text{Co}(\text{RPY}_5\text{Me}_2)]^{2+}$ (**24-26** in Scheme 1.6), which are capable of reducing proton at -1.30 V vs. SHE in pH 7 phosphate buffer with 99% Faradaic efficiency on a Hg pool electrode. The prolonged stability of more than 60 h is one of the most exceptional features. A dinuclear Co complex with bis(pyridyl)pyrazolato and terpyridine ligands (**27**) was reported by Nam and co-workers.³¹ In an ACN solution with TFA, H_2 was generated by electrolysis with this catalyst at -1.1 V vs SCE. A Faradaic yield of 79% was obtained within 10 min. Sarkar and co-workers made a Co^{III} complex with a mesoionic pyridylcarbene ligand (**28**). This catalyst shows an efficient electrocatalytic activity for H_2 production at a very low overpotential (0.13 V) with high turnovers ($4 \times 10^2 \text{ s}^{-1}$) based on a foot-of-the-wave analysis and a Tafel plot.³²

Scheme 1.6. Structures of Co catalysts **24-31**.

(III) Thiolene-based platform

Eisenberg and Holland *et al.* recently reported that the bis(dithiolene) cobalt(II) complex (**29**) can reduce TFA to H_2 at -0.77 V vs. SHE in a water/acetonitrile (v/v: 1/1) solution, with a Faradaic efficiency of >99% on a glassy carbon electrode.³³ The subsequent work

focused on the modification of the benzene ring with either electron-donating or electron-withdrawing groups (**30-31**).³⁴ It was found that the complex with electron-withdrawing substituents caused a positive shift of the onset potential for catalytic H₂ evolution. In bulk electrolysis, the catalyst **31** can reduce TFA to H₂ at -0.71 V vs. SHE, with a TON of 6000 for 4 h in water/acetonitrile (v/v: 1/1) solutions using a glassy carbon electrode.

Iron complexes

Iron is regarded as the most abundant transition metal in nature and iron complexes show very good activity in proton reduction as well. The majority of Fe catalysts for H₂ generation have been focused on functional Fe-Fe hydrogenase biomimetic models, but most of them can only operate in organic solvents.^{18b,21a,21b,35} Besides these complexes, Savnt and co-workers reported a series of Fe porphyrin complexes (**32**, Scheme 1.7) that catalyse H₂ evolution at slightly more negative potential, around -1.5 V vs SCE.³⁶ Gray's group has found that iron complexes with a fluorinated ligand (**33**) can act as electrocatalysts for H₂ evolution at -0.9 V vs SCE with a TOF of 20 s⁻¹.³⁷ The corresponding monofluoroborated complex displayed an improved TOF of 200 s⁻¹ at -0.8 V vs SCE. More recently, two pentacoordinate mononuclear iron carbonyls of the form (bdt)Fe(CO)P₂ (**34**, **35**) were prepared and was shown to catalyse electrochemical proton reduction from acetic acid at a mild overpotential -0.17 to -0.38 V.³⁸ Iron complexes containing tetradentate monophenolate ligands (**36**) have been found to be highly active for the electrocatalytic reduction of protons to hydrogen gas. Catalysis occurs at -1.17 V vs SCE in acetonitrile solution with a turnover frequency of up to 1000 s⁻¹.³⁹

Scheme 1.7. Structures of Fe catalysts **32-36**.

1.4 Photocatalytic systems

A photocatalytic system uses solar energy as the energy source directly. The basic photocatalytic water reduction system involves a light-absorbing photosensitizer, a proton reduction catalyst, and a sacrificial reductant, which can be replaced by the challenging water oxidation half-reaction. Majority of the work done in this area is to explore transition-metal based proton reduction catalysts.

Nickel complexes

One of the typical DuBois' series nickel(II) molecular catalysts [Ni(P^{Ph}₂N₂^{Ph})₂](BF₄)₂ (**37**, Scheme 1.8) was utilized as the catalyst for photocatalytic H₂ generation from water/acetonitrile (v/v: 1/1) solution under visible light irradiation. A maximum TON of 2700 over 150 h was observed when Ru(bpy)₃²⁺ (bpy = bipyridine) or eosin Y was used as the photosensitizer and ascorbic acid as the sacrificial agent.⁴⁰ Sadly, the TOF was not high enough, in fact, it was only 18 h⁻¹. Durrant and Reisner's group modified the outer

coordination sphere of the NiP_2N_2 catalyst with phosphonic acid groups (**38**) and immobilized the catalyst on metal oxide semiconductors and a high TOF of 500 h^{-1} was obtained for photocatalytic H_2 evolution.⁴¹ Eisenberg and coworkers have presented seminal studies on Ni thiolates for the photogeneration of H_2 from aqueous-organic solvents.⁴² Notably, their recent Ni pyridinethiolate catalyst (**39**) displays a high TON (7300 in 30 h), with a proposed mechanism that works similarly to the natural hydrogenase enzymes.^{42b} A series of Ni(II) complexes with tetradentate macrocyclic N_4 , N_3S , and N_3P ligands (**40**) were synthesized, and their photocatalytic activity toward proton reduction has been investigated by an Ir dye and triethylamine as the sacrificial reductant. The highest TON of up to 5000 was found in THF/ H_2O (v/v: 9/1) solution. However, dynamic light scattering (DLS) and mercury poisoning experiments suggest that the Ni(I) intermediate is further reduced to Ni(0) nanoparticles, which are the real catalysts for H_2 production.⁴³

Scheme 1.8. Structures of Ni catalysts **37-40**.

Cobalt complexes

Cobalt bipyridine complexes were initially used as the catalysts for proton reduction, together with $\text{Ru}(\text{bpy})_3^{2+}$ or iridium based photosensitizers.⁴⁴ Later, the development of Co catalysts focused on cobaloxime complexes (**41-43**, Scheme 1.9).⁴⁵ Still, shortcomings like instability, air-sensitivity, and utilization of organic media for the cobaloxime complexes limited further studies at that time.⁴⁶ Du and Eisenberg later developed a Co(III) bis(dimethylglyoximate) complex **42** bearing an axial pyridine ligand, which could be used for visible light-driven water reduction in organic/aqueous media.⁴⁷ Soon after, the same group developed the first homogeneous system for visible light-driven H_2 production from water based exclusively on Earth-abundant elements. They used organic dyes (Eosin Y or Rose Bengal) as the photosensitizers, Co(III) dimethylglyoximate complexes as the catalysts and TEOA as the sacrificial donor. In 12 h of irradiation, a TON of 900 was obtained in this system.⁴⁸ Subsequently, a TON of up to 9000 was achieved when rhodamine dyes were used as the photosensitizers in further studies with the same system.⁴⁹ Recently, the second generation of cobaloxime catalysts, cobalt diimine–dioxime complexes, (**44**), were developed. These complexes display similar catalytic activities as cobaloximes, but are generally more stable against hydrolysis under strongly acidic conditions.^{45b}

Scheme 1.9. Structures of Co catalysts **41-48**.

The new cobalt complexes were also studied as catalysts for photocatalytic proton reduction. Cobalt dithiolene (**45**) reported by Holland and Eisenberg was found to generate H₂ in a 1:1 CH₃CN:H₂O system with Ru(bpy)₃²⁺ as the photosensitizer and ascorbic acid as sacrificial donor with a turnover number (TON) large than 2700.³³ The introduction of electron withdrawing groups (**46**) improved the system that exhibited the highest activity with turnovers up to 9,000 under the same condition.³⁴ Co complexes supported by tetradentate (**47**) or pentadentate ligands (**48**) were prepared subsequently, showing high activity in both photocatalytic and electrocatalytic proton reduction.⁵⁰

Another interesting approach is building molecular photochemical devices with the assembly of photosensitizer and cobalt complexes. For instance, cobaloximes have been studied when anchored with various Ru or Ir molecular photosensitizers.^{46b,51} However, these systems usually show low TONs and poor solubility in aqueous media.

Iron complexes

Iron complexes like [FeFe]-hydrogenases were first utilized for photocatalytic H₂ production in aqueous solution.⁵² A TON of 86 was found with Ru(bpy)₃²⁺ as the photosensitizer and ascorbic acid as the sacrificial electron source. When the photosensitizer was changed to an Ir dye, [Ir(ppy)₂(bpy)]⁺, and TEA as the sacrificial electron source, the TON increased to 466 with the same catalyst.⁵³ In addition, a series of iron carbonyl complexes was reported for light driven water reduction by Beller and co-workers. They include [{CpFe(CO)₂}]₂, [Fe(CO)₅], [Fe₂(CO)₉], [(cot)Fe(CO)₃] and [Fe₃(CO)₁₂].⁵⁴ Among these systems, [Fe₃(CO)₁₂] provided the highest activity with 510 TON in 6 h. An iron carbonyl hydride was proposed as the key reaction intermediate.

1.5 Aims of thesis research

Within the most active catalysts, a common feature has been the judicious customization of the second coordination sphere via the introduction of bioinspired H⁺ relays. Despite this, few studies have documented the effects of alkali metal ions in the second coordination sphere of molecular H₂ evolution catalysts, although copious amounts of alkali metal cations are found in seawater and biological systems. As a result, we have successfully developed the following catalytic systems:

(1) New salicylaldimine nickel complexes shown in Scheme 1.10 were developed for electrocatalytic H_2 evolution in aqueous media. The complexes are supported by salicylaldimine ligands with peripheral, chelating ether groups that can bind Lewis acids such as alkali metal cations. The second-sphere ether functionalities surrounding the complexes may enhance the electrocatalytic activity in the presence of alkali metal cations, such as Na^+ and K^+ . The electrocatalysts exhibit enhanced performances especially in the economical and sustainable seawater reaction medium.⁵⁵

Scheme 1.10. The structure and chelation function of salicylaldimine nickel complexes in electrocatalytic proton reduction.

(2) We have developed a more robust and active salicylaldimine nickel complex for photocatalytic H_2 evolution in methanol/water solution (Scheme 1.11). $\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})$ ($\text{ppy} = 2\text{-phenylpyridine}$; $\text{dtbbpy} = 4,4'\text{-di-tert-butyl-2,2'-bipyridine}$) was used as a photosensitizer for harvesting visible light, and TEA as the sacrificial electron donor. By introducing Lewis acid cations, we expected dramatically enhanced activity and selectivity for the H_2 production. Through my colleague's nanosecond time-resolved optical spectroscopy and my DFT calculation studies, we propose that the Lewis acid cations chelated by the ether arms in close proximity to the Ni catalytic center direct protons to the transient metal hydride, resulting in efficient H_2 production.⁵⁶

Scheme 1.11. Photocatalytic proton reduction diagram.

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Chapter 2. Experimental Methods

2.1 Summary of electrochemical methods

Electrochemistry is an important tool to supply useful current, potential and charge information in electrochemical systems.¹ Electricity is the electron source in these systems. Different electrochemical methods can be applied for the determination of the redox potentials, Tafel curves, anodic polarization curves, electrochemical impedance spectroscopy, and many other techniques.² In this research, the electrochemical experiments such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and controlled potential electrolysis (CPE) analyses will be used to determine each metal complex's redox potential and proton reduction potential, and as an electrolysis procedure to produce hydrogen gas.

2.2 Cyclic voltammetry

Cyclic voltammetry is usually abbreviated as CV and is the most commonly employed electroanalytical technique for characterizing electrode surfaces, studying properties of molecular electrocatalysts, and investigating reaction mechanisms.³

In cyclic voltammetry, the working electrode potential is ramped linearly versus time in cyclical phases. The potential is applied between the working electrode and the reference electrode, while the current between the working electrode and the counter electrode is recorded. In Figure 2.1, assuming there are analytes in the system, when the scan starts from t_0 to t_1 , an increasingly reducing potential is applied. The cathodic current will increase at the beginning until a reduction of the analytes is encountered in the system.

After the reduction potential of the analytes is exceeded, the cathodic current will decrease until the reduced analytes are depleted. If the redox couple is reversible, during the scan, from t_1 to t_2 , the analytes will be re-oxidized, and give an increased anodic current initially and then to the baseline.⁴

Figure 2.1. Cyclic voltammetry waveform.

The data produced during the scan is recorded as current (i) vs. potential (E), which is called a cyclic voltammogram (CV). A typical reversible CV is as shown in Figure 2.2.

Take a simple redox couple for example:

In E 2.1, O is the oxidized species in the reaction, R is the reduced species, and n is the number of electrons involved in the reaction. As the potential is scanned towards a negative direction, the O is reduced at the surface of the working electrode via ne^- to form R . The current increases as the cathodic potential approaches the formal potential of O , and eventually reaches a maximum current i_{pc} . When the potential is more negative than the reduction peak potential (E_{pc}), the current starts to decrease and give a characteristic peak-shaped voltammogram as a result. When the scan direction is

reversed after scanning past the switching potential, R starts to get oxidized and converted back to the starting material O .⁵ As shown in Figure 2.2, the oxidation peak current has a similar size as the reductive peak current, which is indicative of a chemically reversible process ($i_{pc}/i_{pa} = 1$) where i_{pc} is the reduction peak current and i_{pa} is the oxidation peak current. The peak current for such a process is also given by:⁶

$$i_p = 2.75 \times 10^{-5} n^{3/2} v^{1/2} C_0^* D_0^{1/2} \quad \text{E 2.2}$$

In E 2.2, v is the potential scan rate in $\text{V}\cdot\text{s}^{-1}$, C_0^* is the bulk concentration of the analytes in electrolyte solution in $\text{mol}\cdot\text{cm}^{-3}$, and D_0 is the diffusion coefficient in $\text{cm}^2\cdot\text{s}^{-1}$.

Figure 2.2. Typical CV.

2.3 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is another simple voltammetric technique that is similar to CV. The only difference is that the potential in LSV is only scanned in one direction without reversing.⁷

2.4 Electrochemical cell used in voltammetric experiments

A typical electrochemical cell used for CV and LSV in this research is shown in Figure 2.3. The electrochemical cell consists of three electrodes: glassy carbon as the working electrode (3mm in diameter), Pt wire as the counter electrode, and Ag/AgCl or another Pt wire as a (pseudo)reference electrode in water or anhydrous organic solvents. The reference electrode is placed in close proximity to the working electrode to minimize contributions of the Ohmic (IR) drop to the applied potential. The ohmic drop is associated with the uncompensated resistance of the solution and can be minimized by using a supporting electrolyte with a high conductivity. The potentials are reported with respect to NHE by adding 0.197 V to the experimental values when an Ag/AgCl electrode is used in aqueous solutions. Ferrocene (2 equiv. of catalyst, $E_{\text{Fc}^+/\text{Fc}}^0 = 0.69$ V vs. NHE) is added as an internal reference when using a Pt wire as the reference electrode in anhydrous organic solvents.

Figure 2.3. Electrochemical cell used in the research.

2.5 Controlled potential electrolysis

Controlled potential electrolysis (CPE) is also known as bulk electrolysis or

potentiostatic coulometry.⁸ The CPE experiment generally employs a three-electrode system which is similar to the CV measurements. In CPE, the working electrode is held at a constant potential and the current is monitored over time. Usually, the constant potential is approximately 0.1 – 0.2 V more positive or negative than the E_{pa} or E_{pc} value obtained by the CV measurements. In a properly conducted experiment, an analyte is quantitatively converted from its original oxidation state to a different oxidation state, either reduced or oxidized. As the substrate is being consumed, the current decreases and approaches zero when the conversion nears completion. The number of electrons transferred during the electrolysis process (n) is calculated from:

$$Q = \int_0^t i \, dt \quad \text{E 2.3}$$

$$N = Q / nF \quad \text{E 2.4}$$

In E 2.3 and E 2.4, i is the current in A, t is the duration of electrolysis in s, Q is the charge in C, n is the number of electron transferred during the reaction, N is the number of moles of the analyte, and F is the Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$).⁹

2.6 CPE set up for H₂ evolution experiment

Figure 2.4 shows a typical electrochemical cell used for each CPE experiment. The electrochemical cell is a customized, gas-tight, five-neck, one compartment, 63 mL electrolysis cell. Two of the necks are for the working electrode (carbon paper) and the Ag/AgCl reference electrode. A mercury pool at the bottom of the cell with a surface area of 1.13 cm^2 is also employed as the working electrode in certain cases. The reference electrode is placed in close proximity to the working electrode to minimize contributions of the ohmic drop to the applied potential. The IR drop is associated with the

uncompensated resistance of the solution and can be minimized by using a supporting electrolyte with a high conductivity. The counter or auxiliary electrode can be the Pt wire at the bottom. However, a carbon rod counter electrode through a side arm is used instead in this research to prevent the formation of H_2 gas, which happens on the surface of Pt wire during the electrolysis. The CPE experiments are conducted with the electrodes immersed in 25 mL electrolyte solution containing 0.1 M of different electrolytes and catalyst.

Figure 2.4. Photographs of the customized, one-compartment, five-neck CPE cell with a carbon paper electrode.

2.7 Photocatalytic setup for H_2 evolution experiment

Figure 2.5 shows a typical setup for a photocatalytic H_2 evolution reaction. This setup consists of a 27 mL Schlenk tube loaded with a magnetic Teflon-coated stir bar as the

reaction cell and a 300 W Xenon lamp as the light source. Before irradiation, the reaction solution is deoxygenated by bubbling with Ar for 20 mins and the Schlenk tube is stoppered and sealed with a septum. The visible light used in this research is supplied by a Xenon lamp with a 420 nm and a UV light cut-off filter. The gas generated during the reaction is analyzed by gas chromatography (GC, Agilent 7890A gas-chromatograph) with a thermal conductivity detector (TCD), a 5 Å molecular sieve column (2 mm × 5 m), and Ar as the carrier gas.

Figure 2.5. Typical photocatalytic H₂ evolution setup.

2.8 References

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Chapter 3. Enhancing Electrocatalytic Hydrogen Evolution in Aqueous Media by Nickel Salicylaldimine Complexes with Alkali Metal Ions

3.1 Introduction

The use of renewable energy for the electrocatalytic production of hydrogen gas from aqueous media, especially seawater, is an attractive solution for the generation of sustainable fuels.¹ Currently, the electrocatalyst with the lowest overpotential and highest activity for the H₂ evolution reaction is Pt,² but the high price and rarity of Pt have limited its further application. A number of Earth-abundant metal heterogeneous electrocatalysts have been exploited with similar performance, like chalcogenides³ and phosphides.⁴ In addition, homogeneous molecular complexes consisting of Earth-abundant elements (cobalt, nickel and iron) have received more and more attention as H₂ evolution electrocatalysts.⁵ Nonetheless, most of the reported electrocatalysts function in organic solvents or under highly acidic aqueous solutions. Only a few of the molecular electrocatalysts are active in aqueous media, ligated by scaffolds including the pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine (PY₅Me₂),⁶ *N,N*-bis(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine (DPA-Bpy),⁷ and hexakis(hydroxymethyl)tetradentate phosphine ligand (P₄N₂).^{5c,8} Among these active catalysts, the following common feature was observed. The second coordination sphere is customized with Lewis basic amine or Bronsted acidic alcohol groups in close proximity to the redox-active metal center to mimic natural enzymatic systems.⁹ However, few studies have documented the effects of alkali metal ions in the second

coordination sphere of molecular H₂ evolution electrocatalysts, despite the abundance of alkali metal cations in seawater and biological systems.

Our group prepared new nickel complexes supported by salicylaldimine ligands with pendant, chelating ether groups that were designed to bind Lewis acids such as alkali metal cations (Scheme 3.1). The alkali metal ion-binding capabilities of salen type ligands with peripheral ether arms have been reported by Floriani and co-worker.¹⁰ For instance, a cobalt salen complex was reported to bind CO₂ in bent form and to give reversible adducts, with additional stabilization of the oxygen atoms in CO₂ by the alkali metal ions. The introduction of ether functionalities in the second coordination sphere of the salicylaldimine Ni complexes was found to enhance the electrolysis of proton reduction in the presence of alkali metal cations, including sodium and potassium ions found in seawater. The catalyst exhibits much higher H₂ production rate with lithium ions in solution. Based on the analysis of the single crystal X-ray structure, we hypothesize that the peripheral ether arms would steer alkali metal ions and water molecules to the nickel active center, resulting in efficient proton delivery processes similar to the principles used in the recent studies by DuBois and others.^{8,11} We show that judicious selection of functional groups that target sodium ions can provide a viable approach to develop better electrocatalysts, which can produce H₂ fuel from seawater.

Scheme 3.1. Synthetic route for Ni complexes (**6**) with pendant ether groups.

3.2 Results and discussion

3.2.1 Preparation of nickel complexes

The preparation of Ni complexes (**6**) started from the modification of 2,3-dihydroxybenzaldehyde (**1**) by a methoxyethoxy group (Scheme 3.1). The purpose of the introduction of pendant ether arms is to impart the complex with the ability to stabilize alkali metals and their bound water molecules, and to improve the proton concentration close to nickel center. Subsequently, under the protection of benzaldehyde with aniline, sulfonate groups were introduced to make the salicylalimine compound soluble in water. The sulfonated salicylalimine compound (**5**) was obtained after the deprotection of aniline under basic conditions. Compound **5** was then condensed with diamines in the presence of nickel acetate in methanol or water to yield complexes **6** (diamine = *o*-phenylenediamine, **6a**; diamine = 2,3-dimethylbutane-2,3-diamine, **6b**).

3.2.2 Characterization of nickel complexes

Ni complexes **6a** and **6b**, together with other reaction intermediates, have been characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass

spectrometry (HRMS), and elemental analysis. The UV-vis spectrum in Figure 3.1 shows that **6a** has four absorption bands centered at 216, 312, 360, and 486 nm in water. From the Beer-Lambert law, $A = \epsilon Cl$ (A = absorbance; ϵ = molar extinction coefficient; C = concentration; l = pathlength of cell), the slopes of these plots give extinction coefficients of 29200, 10300, 11900, and 3130 $M^{-1}cm^{-1}$ at 216, 312, 360, and 486 nm respectively. These absorbance values will be used to gauge the concentration and stability of **6a** under the electrocatalysis conditions.

We intended to grow single crystals of **6a** but unfortunately, we were not able to obtain them despite numerous attempts. However, we successfully grew crystal of **6c** instead. Complex **6c** has a similar structure as that of **6a**, only without the sulfonate groups. From the single crystal structure of **6c** as shown in Figure 3.2a, we can see that **6c** is mononuclear,¹² which is unlike the numerous dimeric or polymeric Ni salen complexes reported.¹³ We can also see that the coordination geometry around Ni is square planar, in accord with a d^8 electronic configuration. The crystal structure in Figure 3.2b shows that the pendant ether arms in the complex bind a single K^+ cation (**6c** + KPF_6). This chelation to one alkali metal cation was also observed in previous reports on complexes containing 18-crown-6 and similar polyethers.¹²⁻¹⁴ It suggests that the ether arms typically bind single alkali metal cations and could direct solvent molecules to the Ni center.

Figure 3.1. (a) UV-vis spectra of **6a** at different concentrations in water. (b) Plots of absorbance at 216, 312, 360, and 486 nm respectively versus concentration of **6a** in water.

Figure 3.2. Molecular structure of (a) **6c** and (b) **6c** bound with KPF_6 (showing only one of the three disorder models for the labile PF_6 unit), with thermal ellipsoids drawn at the 50% probability level. Figure 3.2c shows the structure containing the entire disorder model for the PF_6 unit. Hydrogen atoms are omitted for clarity.

3.2.3 Electrochemical studies

(1) Cyclic voltammetry in organic solvents

The electrochemical properties of complex **6a** under reductive conditions were examined by cyclic voltammetry in *N,N*-dimethylformamide (DMF) solution purged with argon. Ferrocene was used as the internal reference. The cyclic voltamogram (CV) (Figure 3.3a) of **6a** in DMF features a quasi-reversible, one-electron reduction wave at -1.04 V vs. NHE, which is assigned to the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox couple. When the scan rate was increased up to $1.0 \text{ V}\cdot\text{s}^{-1}$, the ratios of the reductive peak current (i_{pc}) to the oxidative peak current (i_{pa}) became closer to 1 (Figure 3.3b, c). It suggests that the CVs appear increasingly reversible. The reasons of this behaviour could be that the reduced Ni^{I}

product may be metastable, due to the increased anionic charge of the complex, which results in reorganization of the coordination sphere around Ni. Alternatively, precipitation of the triply anionic transient species on the working electrode may occur during the cathodic scan, which can be avoided at high scan rates.¹⁵

Figure 3.3. CVs of 1.0 mM **6a** complex in 0.10 M *n*-Bu₄NPF₆ in DMF with a glassy carbon electrode (3 mm diameter) at (a) a scan rate of 100 mV s⁻¹; (b) different scan rates. (c) Plot of reductive peak current (i_{pc}) to the oxidative peak current (i_{pa}) ratios with different scan rate.

A comparison of the catalytic activity of **6a** and **6b** was carried out in DMF. As shown in Figure 3.4a, the Ni^{II}/Ni^I redox potential of **6b** was at -1.32 V vs. NHE, which is more negative than the reduction potential of **6a** at -1.04 V. It suggests that the overpotential for H₂ evolution electrocatalyzed by **6b** is expected to be larger than that of **6a** if the first reduction is coupled with the actual electrocatalysis. We propose that the electron donating nature of the aliphatic group in the structure of **6b** increase electron density at the Ni center, which results in a more negative reduction potential of **6b**. The hypothesis

was later verified by the controlled potential electrolysis (CPE) experiment (Figure 3.4b).

Consequently, all electrocatalytic measurements were conducted only with **6a**.

Figure 3.4. (a) CVs of 1.0 mM **6a** (red) and **6b** (blue) in 0.10 M $n\text{-Bu}_4\text{NPF}_6$ in DMF at a scan rate of 100 mV s^{-1} , with a glassy carbon electrode (3 mm diameter). (b). CPEs of 0.25 mM **6a** (red) and **6b** (blue) conducted in 0.10 M HOAc and 0.10 M Na_2SO_4 solutions at -1.0 V with a carbon paper working electrode, demonstrating that **6b** performs H_2 evolution similarly, but with a slightly lower activity.

The proton reduction behaviour in organic solution was carried out by adding acids as the proton sources. When the weak acid, acetic acid (HOAc), was added as a proton source in DMF, the cyclic voltammograms in Figure 3.5 show moderate current density increases, indicating that **6a** behaves as an electrocatalyst for H_2 evolution even with weak acids.

Figure 3.5. CVs of 1.0 mM of **6a** in 0.10 M $n\text{-Bu}_4\text{NPF}_6$ in DMF with different concentrations of acetic acid at a scan rate of 100 mV s^{-1} with a glassy carbon electrode (3 mm diameter).

After that, we added the stronger trifluoroacetic acid (TFA) as the proton donor. As shown in Figure 3.6, the CV current dramatically increases compared with the background. In addition, an anodic shift of the onset potential of the CVs was observed as the TFA concentration increases.

Figure 3.6. CVs of 1.0 mM of **6a** in 0.10 M $n\text{-Bu}_4\text{NPF}_6$ in DMF with different concentrations of trifluoroacetic acid at a scan rate of 100 mV s^{-1} with a glassy carbon electrode (3 mm diameter).

(2) Acid dependence study

An acid dependence study was carried out with **6a** in DMF. Figure 3.7 shows plots of the ratio (i_c/i_p) versus the TFA concentration at different scan rates (i_c is the catalytic current, and i_p is the peak current observed for the catalyst in the absence of acid.) According to Equation 3.1,¹⁶ Figure 3.7 reveals that during the CV measurements, the current ratio i_c/i_p of **6a** has a second order dependence relationship with the acid concentration.

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RT}{F}} \sqrt{\frac{k[H^+]^2}{v}} = 0.72 \sqrt{\frac{k[H^+]^2}{v}} \quad \text{E 3.1}$$

Figure 3.7. Plots of i_c/i_p versus trifluoroacetic acid concentration for 1.0 mM of **6a** in DMF with 0.10 M $n\text{-Bu}_4\text{NPF}_6$ at the indicated scan rates.

(3) Foot-of-the-wave analysis

The foot-of-the-wave analysis method has been reported by Sav éant and coworkers.¹⁷ It can be utilized to determine the turnover frequency (TOF) from the CV experiments. The electrocatalytic proton reaction was demonstrated to be a diffusion-controlled first-order reaction in the catalyst (Figure 3.10b). The method consists of using Equation 3.2 and the value of the turnover frequency k is calculated from the slope of the linear portion of a plot of i/i_p° vs. $1/[1 + \exp((F/RT)(E - E^\circ))]$, where $E^\circ = E_{1/2}(\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}) = -1.0$ V vs NHE. In Equation 3.2, i is the background-corrected catalytic current, i_p° is background-corrected current at $E = -1.0$ V in the absence of acid. R is the Ideal Gas Constant $8.314 \text{ J mol}^{-1}\cdot\text{K}^{-1}$, F is Faraday's constant 96485 C mol^{-1} , and T is the temperature 298 K.

$$\frac{i}{i_p^\circ} = \frac{22.4 \sqrt{\frac{RT}{Fv}} 2kC_H^+}{1 + \exp[\frac{F}{RT}(E - E^\circ)]} \quad \text{E 3.2}$$

The foot-of-the-wave analysis on H₂ evolution of **6a** was carried out in DMF solution in the presence of both TFA and acetic acid (Figure 3.8). However, the foot-of-the-wave analysis with TFA was not successful. As shown in Figure 3.8a, the curve indicates unexpected deviations from linear result. It could be due to the anodic onset shift at high TFA concentrations. The pK_a values for the protonation of phenoxide,¹⁸ arylether,¹⁹ alkylether,²⁰ and benzenesulfonic acid²¹ are approximately 9.6, -6.5, -2.0 to -4.0, and 0.70, respectively. This onset shift could be due to protonation of the phenoxide donor at high acid concentrations, which reduces the overpotential required for electrocatalytic H₂ evolution since protons will be positioned near to the Ni center.

On the other hand, the foot-of-the-wave analysis using acetic acid as the proton donor demonstrates the expected linear behaviour (Figure 3.8b), yielding a rate constant of 17.9 M⁻¹ s⁻¹ in 0.10 M acetic acid at a scan rate of 100 mV s⁻¹.

Figure 3.8. A foot-of-the-wave analysis of **6a** in (a) 0.10 M *n*-Bu₄NPF₆ in DMF in the presence of 19 mM TFA and (b) 0.10 M *n*-Bu₄NPF₆ in DMF in the presence of different concentrations of acetic acid with a scan rate of 100 mV s⁻¹.

(4) Cyclic voltammetry in aqueous solution

The CVs obtained in aqueous solutions with **6a** under argon indicated that **6a** has potential applications in proton reduction as well. The Ag/AgCl electrode was used as a

reference electrode in all the aqueous samples. As shown in Figure 3.9, the CVs were carried out in neutral deionized water with four different salts Li_2SO_4 , Na_2SO_4 , KPF_6 , and $n\text{-Bu}_4\text{NCl}$ as electrolytes. The CVs of **6a** all exhibit remarkable increases in the catalytic current at an onset potential of -1.05 V vs. NHE, corresponding to an overpotential of 590 mV. Gas bubbles were also observed around the glassy carbon working electrode in the electrochemical cell. The overpotential (590 mV) of **6a** is comparable to or slightly lower than other molecular electrocatalysts that contain first-row transition metals and function in neutral water with glassy carbon working electrodes.²² For instance, the overpotentials for Co complexes ligated by P_4N_2 ligands^{5c} or DPA-Bpy⁷ are about 550 and 780 mV respectively.

Figure 3.9. The current density increase in neutral deionized water with four different electrolytes with a glassy carbon electrode (3 mm diameter): (a) Li_2SO_4 , (b) Na_2SO_4 , (c) KPF_6 , and (d) $n\text{-Bu}_4\text{NCl}$. (e) The baseline corrected current density enhancement of Li_2SO_4 , Na_2SO_4 and KPF_6 as electrolyte compared to the current density with $n\text{-Bu}_4\text{NCl}$ as electrolyte.

From the CVs with $n\text{-Bu}_4\text{NCl}$, Li_2SO_4 , Na_2SO_4 , and KPF_6 as the electrolytes in neutral deionized water, we could also investigate the effects of the pendant ether on **6a**. The studies were carried out at an overpotential of 0.84 V. In Figure 3.9d, when $n\text{-Bu}_4\text{N}^+$ was utilized as the electrolyte, the current density increase is $0.702 \text{ mA}\cdot\text{cm}^{-2}$ compared to the background current density in the absence of **6a**. This indicates an appreciable, but slow H_2 evolution reaction. The reason for the low activity could be because $n\text{-Bu}_4\text{N}^+$ cations are bulky and hydrophobic and may hinder access to the Ni catalytic center by hydronium ions. It is similar to the proton-gated hangman iron porphyrins reported by Nocera and co-workers.²³ In contrast, with KPF_6 and Na_2SO_4 as the electrolytes, the current density is 4.4 and 8.3 times higher compared to the catalytic current density with $n\text{-Bu}_4\text{N}^+$ as electrolyte, respectively (Figure 3.9b and 3.9c). The highest electrocatalytic current is observed with Li^+ as electrolyte. It shows a 10.6 times increase compared to $n\text{-Bu}_4\text{N}^+$ as the electrolyte (Figure 3.9a). This dramatic increase in catalytic current

highlights the non-innocence of the electrolyte in our H₂ evolution system, and emphasizes the need for prudent management of second sphere effects around the catalytic center.

When 0.10 M acetic acid was added in 0.10 M Na₂SO₄ aqueous solution, the pH was changed from 7.7 to 2.8. The catalytic onset potential in Figure 3.9a shifts to -0.64 V. Compared with the onset potential in 0.10 M acetic acid in DMF solution (Figure 3.6), the shift is slightly larger than the expected Nernstian shift of about 0.24 V. A probable reason can be due to the increase of proton concentration by about four orders of magnitude. In addition, during the CV measurements, the potential was reversed at -1.3 V vs. NHE when TFA was the acid in DMF in Figure 3.5, but at -0.8 V vs. NHE in aqueous HOAc solution (Figure 3.10a). The current density in aqueous HOAc increased so rapidly that the cathodic and anodic return segments intersected. We attribute this observation to surface modification, possibly due to the formation of bubbles on the electrode surface or due to deposition of the reduced Ni catalyst and other electroactive materials on the electrode surface. Such behavior was not observed when we reversed the potential at -0.8 V when the CVs were conducted in water.

In addition, we tested the CV behaviors of different **6a** catalyst concentrations in 0.10 M HOAc solution. The catalytic current shows a first order dependence on the concentration of **6a** (Figure 3.10b), suggesting that H₂ evolution occurs via protonation of a mononuclear Ni intermediate, rather than bimolecular coupling of two highly anionic Ni complexes.

Figure 3.10. CVs of (a) 1.0 mM of **6a** in 0.10 M Na₂SO₄ solution with different concentrations of acetic acid and (b) different concentrations of **6a** in 0.10 M Na₂SO₄, 0.10 M HOAc solution at a scan rate of 100 mV s⁻¹ with a glassy carbon electrode (3 mm diameter).

The CVs in 0.10 M acetic acid solution in the presence of *n*-Bu₄NCl, Li₂SO₄, Na₂SO₄, and KPF₆ as the electrolytes were each conducted with a large surface area (6.9 cm²) carbon paper working electrode (Figure 3.11) since the differences are not obvious with normal glassy carbon electrodes. In 0.10 M acetic acid, the electrocatalytic current increase also follows the same sequence as described in neutral deionized water solution. The effect of the cations appears to be correlated to the charge density of the added element. Thus Li⁺ shows the fastest catalytic behaviour corresponding to the highest charge density, followed by Na⁺, K⁺, and *n*-Bu₄N⁺ cations.

Figure 3.11. The current density increase in 0.10 M acetic acid solution with four different electrolytes using a large surface area (6.9 cm²) carbon paper as the electrode: (a) Li₂SO₄, (b) Na₂SO₄, (c) KPF₆, and (d) *n*-Bu₄NCl.

(5) Controlled potential electrolysis

Controlled potential electrolysis (CPE) experiments were conducted with a mercury pool electrode in seawater and 0.10 M acetic acid solution with different electrolytes. The gas product was confirmed by gas chromatography. Seawater is abundant and sustainable. Since large amounts of alkali metal cations are contained in seawater (e.g. 1.0% of Na⁺, 0.13% of Mg²⁺, and 0.04% of K⁺ in mass), there is no necessity to add extra electrolytes for the CPE. However it is difficult to confirm which cation contributed most to the proton reduction. The seawater here was obtained from the coast of Singapore and filtered to remove the suspended particulate matter before use. The CPE studies were carried out at an overpotential of 0.84 V. As illustrated in Figure 3.12, the amount of H₂ produced from seawater increased dramatically compared to the blank solution in the absence of catalyst **6a**. The TON was 7.1 mol H₂ mol⁻¹ catalyst cm⁻² after 2 h (Table 3.1). It suggests that **6a** is indeed suitable as an H₂ evolution catalyst with seawater as the

medium. However, the Faradaic efficiency of H_2 production in seawater is only around 80%. Since the concentration of chloride is high in seawater (about 1.94% in mass), chloride oxidation can compete at the anode. In addition, the working electrode and the counter electrode are set quite close in the one-compartment cell and some of the O_2 produced at the anode could be re-reduced at the cathode (Figure 3.12b).

Figure 3.12. (a) The amount of H_2 evolved from seawater with 0.22 mM catalyst 6a (red line) and only seawater (black line) using a mercury pool working electrode. (b) Photograph of the customized, one-compartment, five-neck CPE cell with a carbon paper electrode.

To explore the effect of the cations in the electrolyte, CPEs were also conducted with $n\text{-Bu}_4\text{NCl}$, Li_2SO_4 , Na_2SO_4 , KPF_6 , and MgSO_4 as the electrolytes in 0.10 M acetic acid solutions (Figure 3.13). The CPE behaviors are different from the expected trend based on the CV results. The catalytic solution with KPF_6 as electrolyte shows the highest activity, probably because the poor solubility of Li and Mg salts led to catalyst precipitation during the CPE with a mercury pool working electrode.

Figure 3.13. The amount of H₂ evolved from 0.10 M HAc solution with 0.25 M Li₂SO₄ (red), Na₂SO₄ (blue), and Mg₂SO₄ (green), and 0.5 M KPF₆ (magenta) and *n*-Bu₄NCl (black) with catalyst **6a** using a mercury pool working electrode.

Table 3.1. Background-corrected TON and TOF calculations from CPE measurements using a mercury pool working electrode.

	Seawater	Li ₂ SO ₄	Na ₂ SO ₄	KPF ₆	<i>n</i> -Bu ₄ NCl	NiCl ₂
Charge (C)	10.8	0.575	3.55	6.57	1.67	1.53
Theoretical H ₂ (μmol)	55.8	2.98	18.4	34.0	8.65	7.93
Measured H ₂ (μmol)	44.4	1.55	14.8	19.1	4.56	3.37
Faradaic efficiency %	79.5	52.2	80.7	56.1	52.7	42.5
TON (mol H ₂ mol ⁻¹ 6a cm ⁻²)	7.14	0.249	2.34	3.06	0.733	0.542
TOF (mol H ₂ mol ⁻¹ 6a cm ⁻² h ⁻¹)	3.57	0.125	1.19	1.53	0.366	0.271

In addition, we also conducted CPEs with *n*-Bu₄NCl, Li₂SO₄, Na₂SO₄, KPF₆, and MgSO₄ as the electrolytes in 0.10 M acetic acid solutions and seawater with carbon paper as the working electrode (Figure 3.14). As expected, the TON with Li₂SO₄ as the electrolyte was the highest one in the CPE experiments, because the deposition of catalysts on the carbon paper electrode system would not result in the same deactivation observed with a

mercury pool electrode. The CPE measurements, the TON, and the TOF (Table 3.1 and 3.2) confirm that **6a** is an efficient catalyst for electrocatalytic proton reduction under almost neutral, highly saline aqueous conditions, even when mercury electrodes are used to suppress the activity of heterogeneous metallic nanoparticles.

Figure 3.14. (a) CPEs conducted in 0.10 M HOAc and 0.10 M of different electrolyte solutions with 0.25 mM **6a** (solid line) and without **6a** (dotted line) at -1.0 V, using a carbon paper working electrode. (b) CPEs of 0.25 mM **6a** conducted in 0.10 M HOAc and 0.10 M different electrolyte solutions after background subtraction.

Table 3.2. TON and TOF calculations from CPE measurements using a carbon paper working electrode.

	Seawater	Li ₂ SO ₄	Na ₂ SO ₄	KPF ₆	<i>n</i> -Bu ₄ NCl
Charge (carbon paper, C) ^a	22.7	37.9	21.5	19.3	13.4
Theoretical H ₂ (carbon paper, μmol) ^a	118	196	111	99.9	69.6
Measured H ₂ (μmol) ^a	67.0	104	57.9	57.0	34.1
Faradaic efficiency % ^a	56.9	53.2	52.0	57.1	48.9
TON (mol H ₂ mol ⁻¹ 6a cm ⁻²) ^a	5.99	9.33	5.17	5.09	3.01
TOF (mol H ₂ mol ⁻¹ 6a cm ⁻² h ⁻¹) ^a	2.99	4.67	2.59	2.55	1.52

^a Due to visible roughening of the carbon paper electrode after each CPE experiment by the vigorous H₂ evolution, a fresh piece of carbon paper electrode was used in each new experiment because the surface area of the electrode has changed. The background current has not been subtracted from these measurements.

In order to determine whether **6a** is the genuine active catalyst for H₂ evolution electrocatalysis, or whether it is just a precatalyst that decomposes to Ni(0) nanoparticles

as the real catalyst, a series of standard electrochemical and spectroscopic experiments were performed. The UV-vis spectra, ^1H NMR spectra, and HR-MS (Figure 3.15a-e) before and after controlled potential electrolysis (CPE) indicate that **6a** remains intact in solution and has not been appreciably converted into a heterogeneous nanoparticulate catalyst. The UV-vis spectra in Figure 3.14a shows that the concentration of **6a** decreases to 90% and 78% after 1 h and 2.5 h, respectively. The charge passed during CPE were 37.6 C and 94.4 C at 1 h and 2.5 h, which was in much larger excess than the charge needed just to reduce Ni^{II} to Ni^{I} (0.120 C and 0.260 C for 10% and 22% **6a** respectively). We suspect that some of the **6a** was adsorbed on the carbon paper during the electrolysis process. In addition, there were no nanoparticles observed by dynamic light scattering (DLS) measurements in the electrolyte solution after CPE for 2.5 h (Figure 3.16). The DLS spectrum for majority of the samples indicated the absence of any particles, whereas a small number indicated the presence of the micron-sized materials, which could be contaminants from air or carbon dislodged from the electrode.

Figure 3.15. (a) UV-vis spectra during the CPE of 0.25 mM **6a** in 0.10 M HOAc solution over a 2.5 h period. ^1H NMR spectra of **6a** in DMSO- d_6 (b) before, (c) after the CPE in 0.10 M HOAc solution. The broad peak in (c) between 3.5 – 4.5 ppm is due to the acetic acid and water remaining in the NMR sample. HR-ESI-MS for **6a** (d) before and (e) after CPE, showing that **6a** remains intact after CPE.

Figure 3.16. DLS spectrum of **6a** in *one of the experiments* after CPE in 0.10 M HOAc solution, suggesting the presence of small amounts of *micron*-sized chunks.

To verify whether the loss of **6a** observed by UV- vis spectroscopy was due to catalyst adsorption on the carbon paper during the electrolysis process, the used carbon paper electrodes in a CPE measurement were rinsed thoroughly with water before being subjected to CPE again. From Figure 3.17 we can see that the used electrode still showed a small, but non-negligible amount of catalytic activity, although there was no observable deposits.

Figure 3.17. CPE experiments of 0.25 mM **6a** in 0.10 M HOAc and 0.10 M Na₂SO₄

solution at -1.0 V with carbon paper as the working electrode (red). After 5200 s of electrolysis, the carbon paper was rinsed with water and another CPE experiment was conducted under the same conditions in the absence of **6a** for 5200 s (blue). The CPE in the absence of **6a** was performed as a control experiment (black).

X-ray photoelectron spectroscopy (XPS) experiments were conducted on the used carbon paper electrode after the CPE experiment, with pristine samples of **6a** scanned as a reference for comparison. The data in Figures 3.18 and 3.19 indicate that the small amounts of deposited material on the carbon paper electrode after CPE have almost identical composition as **6a**. Based on the relative elemental compositions (Figure 3.15b, c and Table 3.3), we propose that some of the **6a** is adsorbed on the surface of the carbon paper working electrode by π -stacking between the aromatic rings and the carbon paper during the catalysis, and cannot be readily rinsed off.

Figure 3.18. XPS spectra of (a) pure **6a** adsorbed by drop-casting on carbon paper and secured with carbon tape (black), and carbon paper used as the working electrode after 2.5 h of CPE (red), demonstrating that **6a** remains mostly intact. XPS spectra of (b) Ni metal, (c) NiO, and (d) Ni(OH)₂ with data adapted from reference 21.²⁴

Figure 3.19. XPS spectra of **6a** adsorbed by drop-casting samples on carbon paper and securing the samples with carbon tape (black). The spectra for the carbon paper used as the working electrode after CPE with **6a** in 0.10 M acetic acid solution is shown in red.

Table 3.3. X-ray photoelectron spectroscopic data of **6a** and references.

Sample name	Ni ^{II} (2p _{3/2})	Satellite (2p _{3/2})	Ni ^{II} (2p _{1/2})	O 1s	N 1s	C 2p	S 2p
6a powder ^a	854.2	—	871.1	531.3	399.1	284.6	168.8
6a after CPE ^b	855.1	—	872.4	532.0	399.9	284.6	169.6
Ni metal ^c	852.6	858.6	—	—	—	—	—
Ni(OH) ₂ ^c	857.9	861.0	—	—	—	—	—
NiO ^d	853.5 856.1	861.5	—	—	—	—	—

^a Complex **6a** adsorbed by drop-casting the sample on carbon paper and secured it with carbon tape. ^b The carbon paper used as the working electrode after CPE with **6a** in 0.10 M acetic acid solution. ^c Reference data. ^d Reference data. ²⁵

A transmission electron microscopy (TEM) image (Figure 3.20) of the solution after CPE also exhibits little evidence of nanoparticle formation, and only shows large amorphous chunks of materials that may be crystallized electrolyte. The majority of the H₂ evolution electrocatalytic activity is still attributed to **6a** in homogeneous solution rather than

deposited or suspended nanoparticles.

Figure 3.20. TEM image of the electrolyte solution with **6a** after 2 h of CPE, indicating the presence of amorphous materials, such as the electrolyte residue for example.

3.2.4 Proposed mechanism

The influence of the alkali metal cations with the second coordination sphere around Ni in water during H₂ evolution catalysis was further verified by UV-vis spectroscopy. Before the measurements, the Na⁺ ions in **6a** were exchanged by dissolving 2 equiv. of *n*-Bu₄N⁺ for every equiv. of **6a** in water, removing the water *in vacuo*, followed by extraction of the residue with acetonitrile. The UV-vis spectra in Figure 3.21 show that the ion exchanged **6a** (0.020 mM) had different UV-vis absorptions with different concentrations of Li₂SO₄, Na₂SO₄, and KPF₆. The equilibrium constant K_{eq} for each exchange can be calculated by using Equation 3.3 if only *one* alkali metal cation is chelated by the ether arms.²⁶

$$K_{eq} = \frac{A/(\varepsilon_1 + \varepsilon_2)l}{\left([6a] - \left(\frac{A}{(\varepsilon_1 + \varepsilon_2)l}\right)\right)\left([M^+] - \left(\frac{A}{(\varepsilon_1 + \varepsilon_2)l}\right)\right)} \quad \text{E 3.3}$$

Equation 3.3 contains two unknowns, K_{eq} and $A/\varepsilon l$, where K_{eq} is the equilibrium constant of a single cation binding, A = absorbance at any wavelength that changes dramatically, ε_1 = molar extinction coefficient of **6a** (actual), ε_2 = molar extinction coefficient of **6a** after binding with the alkali metal cations, l = pathlength of cuvette, and $[M^+]$ = concentration of the alkali metal cations in mol l⁻¹. E 3.4 can be derived from E 3.3 as shown below.

$$\frac{A}{[\mathbf{6a}][M^+]} = \frac{A([\mathbf{6a}] + [M^+])K_{eq}}{[\mathbf{6a}][M^+]} + K_{eq}(\varepsilon_1 + \varepsilon_2)l \quad \text{E 3.4}$$

The value of the equilibrium constant K_{eq} is obtained from the slope of a fit to the plot of $A/([\mathbf{6a}][M^+])$ vs. $A([\mathbf{6a}] + [M^+])/([\mathbf{6a}][M^+])$. The plots (Figures 3.21b and 3.21d) of **6a** in Li₂SO₄ and Na₂SO₄ solution reveal linear fits, consistent with chelation to one cation in the concentration range we studied, but the behavior in KPF₆ is more complicated. These experiments clearly demonstrate the coordination of alkali metal salts during our electrocatalytic experiments. The equilibrium constants for binding Li⁺ and Na⁺ by **6a** are 27.9 and 53.6, respectively.

Based on the CVs, CPE results, and UV-vis spectroscopic study, we propose that a single Lewis acidic cation binds most effectively to the pendant ether arms and orientate water molecules and hydronium ions in close proximity to the catalytic Ni center, thus enhancing the H₂ evolution activity (Scheme 3.2). Since seawater contains copious amounts of Na⁺ cations, judicious selection of pendant chelating groups that (size)-select for Na⁺ may prove fruitful in improving the catalytic performance of **6a** and are being explored.

Figure 3.21. UV-vis spectra of 0.020 mM ion-exchanged **6a** in aqueous (a) 0.25 M Li_2SO_4 solution, (b) 0.25 M Na_2SO_4 solution, (c) 0.50 M KPF_6 solution, and (d) seawater. Plots of **6a** in aqueous (e) Li_2SO_4 , (f) Na_2SO_4 and (g) KPF_6 solutions were used to calculate each equilibrium constant of the alkali metal cation chelation by the pendant ether arm, derived by using the Beer-Lambert Law ($Y = A/([\mathbf{6a}][\text{M}^+])$) and $X = A([\mathbf{6a}] + [\text{M}^+])/([\mathbf{6a}][\text{M}^+])$; A = absorbance, M = Li, Na, K).

Scheme 3.2. Proposed catalytic cycle that illustrates how the alkali metal and other Lewis acid cations can potentially direct protons in close proximity to the catalytic Ni center. This cycle incorporates the insights from the crystal structures of the related **6c**, which has one K^+ cradled by the ether arms, and the labile PF_6^- anion has been replaced by a molecule of H_2O near the catalytic active site. This mechanism is also consistent with the operation of a mononuclear Ni catalyst with a first order dependence on [**6a**].

3.3 Conclusion

In conclusion, we have demonstrated that new mononuclear Ni complexes with salicylaldimine ligands can be used as electrocatalysts for the production of H_2 in both neutral and acidic aqueous solutions. The chelating ether groups in the structure can bind alkali metal cations, like sodium ions from seawater, to form Lewis acids and promote the proton reduction efficiency. Further studies will focus on modification of the Ni complexes with electron withdrawing substituents to reduce the overpotential and applying **6a** as in photocatalytic systems for H_2 evolution. The detail will be demonstrated in Chapter 4.

3.4 Experimental Section

3.4.1 Materials and Instruments

Chemicals were obtained from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Seawater was collected from a beach on the southern shore of Sentosa Island in Singapore (21 September 2014), and filtered before use. Unless otherwise noted, the commercial reagents were used as purchased.

All reactions involving air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under an argon (Ar) atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F₂₅₄ silica gel plates. UV-Vis absorption measurements were carried out on a Shimadzu UV-3600 spectrophotometer. The ¹H and ¹³C NMR measurements were recorded on Bruker AV-300 (300 MHz), BBFO-400 (400 MHz), and AV-500 (500 MHz) NMR spectrometers. The ¹H and ¹³C NMR spectra are reported in parts per million (ppm) downfield referenced to the residual protons of the deuterated solvents. High-resolution mass spectra (HR-MS) were obtained with a Q-TOF Premier LC HR mass spectrometer. Elemental analyses were performed with an Elementar vario MICRO cube analyser. X-ray photoelectron spectroscopy (XPS) profiles of **6a** intentionally drop-casted on carbon paper and the carbon paper used as the working electrode after controlled potential electrolysis in acidic water were obtained on a Phoibos 100 spectrometer (Specs, Germany) with monochromatic Mg X-ray radiation.

3.4.2 Syntheses

Compound 2-hydroxy-3-(2-methoxyethoxy)benzaldehyde (2).

The procedure has been adapted from published methods.² NaH (0.600 g of a 60% dispersion in oil, 15.2 mmol) was suspended in dry dimethyl sulphoxide (DMSO, 10 mL) in an oven-dried Schlenk flask equipped with a dropping funnel. The suspension was

cooled in an ice-bath. A solution of 2,3-dihydroxybenzaldehyde (1.00 g, 7.20 mmol) in dry DMSO (10 mL) was added dropwise to the mixture under a flow of Ar over the course of 1 h. Vigorous gas evolution occurred. After complete addition, the dark orange solution was stirred at ambient temperature and (2-methoxyethoxy)-*p*-toluenesulfonate (1.36 mL, 7.20 mmol) was added in one portion. The solution was then stirred for another 2.5 h. Water (50 mL) was slowly added to quench the reaction, and the solution was extracted with CHCl₃ (3 × 30 mL). The aqueous layer was acidified to pH 2 with 1 M aqueous HCl solution (15 mL) and the colour changed from dark orange to yellow. The aqueous layer was then extracted with CHCl₃ (3 × 30 mL). The organic layer was subsequently rinsed with 1 M HCl (2 × 30 mL), dried with anhydrous Na₂SO₄, and filtered. The solvent was removed *in vacuo* to afford an orange viscous oil. The residue was purified by silica gel column chromatography (hexane:ethyl acetate = 4:1) and 2-hydroxy-3-(2-methoxyethoxy)-benzaldehyde (1.19 g, 86.0%) was isolated as a pale yellowish-green solid. ¹H NMR (500 Hz, CDCl₃): δ = 3.41 (s, 3 H, -OCH₃), 3.75 (t, *J* = 5.0 Hz, 2 H, CH₂OCH₃), 4.17 (t, *J* = 5.0 Hz, 2 H, OCH₂CH₂OCH₃), 6.90 (t, *J* = 5.0 Hz, 1 H), 7.13 – 7.26 (m, 2 H), 9.90 (s, 1 H, CHO), 10.91 (s, 1 H, Ar-OH) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 59.2, 69.2, 70.9, 119.5, 121.0, 121.1, 125.3, 147.4, 152.2, 196.2 ppm. HR-MS calcd for C₁₀H₁₂O₄, [M+H]⁺ *m/z* = 197.0814, found 197.0805.

Compound 2-(2-methoxyethoxy)-6-((phenylimino)methyl)phenol (3).

Compound **2** (0.500 g, 2.50 mmol) was dissolved in ethanol (EtOH, 10 mL) in a 25 mL round-bottom flask. Aniline (0.35 mL, 3.8 mmol) was syringed in with vigorous stirring to give a bright orange solution. The solution was heated under reflux for 6 h, after which the solvent was removed *in vacuo*. The resulting dark orange oil was rinsed with hexane

(3 × 2 mL) to remove the excess aniline. The residue was dried under reduced pressure on a rotary evaporator to yield 2-(2-methoxyethoxy)-6-((phenylimino)methyl)phenol (0.643 g, 95% yield) as an orange oil.²⁷ ¹H NMR (400 MHz, (CD₃)₂CO): δ = 3.39 (s, 3 H, OCH₃), 3.73 (t, J = 4.6 Hz, 2 H, CH₂OCH₃), 4.21 (t, J = 4.7 Hz, 2 H, OCH₂CH₂OCH₃), 6.89 (t, J = 8.0 Hz, 1 H), 7.14 (d, J = 9.0 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 1 H), 7.34 (d, J = 6.0 Hz, 1 H), 7.41 – 7.50 (m, 4 H), 8.90 (s, 1 H, HC=N), 13.35 (s, 1 H, -OH) ppm. ¹³C{¹H} NMR (100 MHz, (CD₃)₂CO): 58.1, 68.9, 71.0, 118.0, 118.5, 121.3, 124.9, 126.9, 129.4, 147.7, 148.4, 152.1, 163.8, 204.9 ppm. HR-MS calcd. for C₁₆H₁₇NO₃, [M+H]⁺ m/z = 272.1287, found 272.1278.

Compound 4-hydroxy-3-(2-methoxyethoxy)-5-((phenylimino)methyl) benzenesulfonic acid (4)

Compound **3** (0.100 g, 0.370 mmol) was charged in a 50 mL Schlenk flask, and cooled with an ice bath. Concentrated sulfuric acid (0.500 g, 5.10 mmol) was then added under N₂ to give a clear brown solution. This solution was heated for 6 h at 45 °C, allowed to cool at -20 °C for 30 min, before crushed ice pieces were then added. The brown solution was extracted with CHCl₃ (3 × 10 mL), after which the aqueous phase was collected and cooled to -20 °C. The product 4-hydroxy-3-(2-methoxyethoxy)-5-((phenylimino)methyl) benzenesulfonic acid was isolated as a yellow powder by precipitation from the aqueous solution, with a yield of 0.0779 g (60%). ¹H NMR (400 MHz, D₂O): δ = 3.46 (s, 3 H, OCH₃), 3.90 (t, J = 4.8 Hz, 2 H, CH₂OCH₃), 4.33 (t, J = 4.8 Hz, 2 H, OCH₂CH₂OCH₃), 7.39 – 7.43 (t, J = 8.0 Hz, 2 H), 7.51 – 7.56 (t, J = 8.0 Hz, 3 H), 7.61 (d, J = 6.0 Hz, 1 H), 7.81 (d, J = 6.0 Hz, 1 H), 10.05 (s, 1 H, CH=N) ppm. ¹³C{¹H} NMR (100 MHz, D₂O): δ = 58.1, 68.3, 70.2, 115.9,

120.8, 121.7, 122.8, 129.2, 130.1, 134.5, 147.0, 152.4, 198.2 ppm. HR-MS calcd for $C_{16}H_{17}NO_6S$, $[M-H]^- m/z = 350.0698$, found 350.0714.

Disodium 3-(2-methoxyethoxy)salicylaldehyde-5-sulfonate (5).

Compound **4** (1.50 g, 4.30 mmol) was dissolved in 20 mL boiling water. Sodium hydroxide (0.341 g, 8.60 mmol) was added in small portions at room temperature. This mixture was then heated to its boiling point, during which N_2 gas was bubbled through the dark brown solution continuously to vapourize the aniline. The solution was heated until the vapour showed no alkaline response to pH paper, while the volume of the water was maintained by adding more water when needed. The aqueous solution was evaporated to dryness under reduced pressure to give the crude product, which was a mixture of disodium 3-(2-methoxyethoxy)salicylaldehyde-5-sulfonate and Na_2SO_4 . The yellow solid was suspended in methanol, filtered to remove Na_2SO_4 , and the filtrate was collected and concentrated to give disodium 3-(2-methoxyethoxy)salicylaldehyde-5-sulfonate (1.28 g, 93.0%) as a yellow powder.²⁸ 1H NMR (400 MHz, D_2O): δ = 3.45 (s, 3 H, OCH_3), 3.87 (t, J = 6.8 Hz, 2 H, CH_2OCH_3), 4.15 (t, J = 4.0 Hz, 2 H, $OCH_2CH_2OCH_3$), 7.20 (d, J = 4.0 Hz, 1 H), 7.60 (d, J = 4.0 Hz, 1 H), 10.09 (s, 1 H, CHO) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, D_2O): δ = 58.0, 67.1, 70.4, 112.7, 118.8, 122.6, 125.5, 152.6, 169.0, 193.6 ppm. HR-MS calcd. for $C_{10}H_{10}O_7Na_2S$, $[M-Na^+]^- m/z = 297.0045$, found 297.0041.

Complex 6a

To a solution of compound **5** (0.500 g, 1.56 mmol) and 1,2-diaminobenzene (0.0760 g, 0.780 mmol) in methanol (15 mL) was added $Ni(OAc)_2 \cdot 4H_2O$ (0.195 g, 0.778 mmol). The mixture was heated to reflux for 13 h. After cooling to room temperature, the solvent

was removed under reduced pressure. The crude dark orange product was washed with ethyl acetate followed by EtOH, and dried in *vacuo*. The complex **6a** (0.603 g, quantitative) was obtained as an orange powder. ^1H NMR (400 MHz, DMSO- d_6): δ = 3.36 (s, 6 H, OCH_3), 3.72 (t, J = 4.4 Hz, 4 H, CH_2OCH_3), 4.17 (t, J = 4.4 Hz, 4 H, $\text{OCH}_2\text{CH}_2\text{OCH}_3$), 7.22 (s, 2 H), 7.35 – 7.37 (m, 2 H), 7.71 (s, 2 H), 8.22 – 8.24 (m, 2 H), 9.17 (s, 2 H, $\text{HC}=\text{N}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ = 53.6, 61.1, 62.9, 99.0, 100.4, 102.0, 105.7, 109.9, 116.1, 120.9, 125.2, 131.3, 133.3 ppm. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{Na}_2\text{NiO}_{12}\text{S}_2 \cdot 6\text{H}_2\text{O}$ (%): C 37.47, H 4.35, N 3.51; found: C 37.00, H 4.08, N 3.07. HR-MS calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_{12}\text{S}_2\text{NiNa}_2$, $[\text{M}-\text{Na}^+]^- m/z$ = 701.0022, found 701.0021.

Complex 6b

Compound 2,3-diamino-2,3-dimethylbutane was prepared by a slight modification of reported procedures.²⁹ Compound 2,3-dimethyl-2,3-dinitrobutane (1.76 g, 10.0 mmol) was added to 12.0 M concentrated hydrochloric acid (30 mL) in a 100 mL round-bottom flask to produce a white suspension. Subsequently, Sn powder (10.0 g, 84.7 mmol) was added into the mixture in multiple portions with stirring over 1 h. Vigorous gas evolution was observed initially. The grey mixture was then heat to reflux for 3 h at 105 °C. After cooling to ambient temperature, aqueous NaOH solution (20 mL) was slowly added to the ice-cooled solution until the pH of the solution was above 12. Gray precipitate was filtered off and the filtrate was collected and saturated with NaCl. The solution was then extracted with dichloromethane (4 $\times$ 20 mL). The combined organic phases were dried with Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The residual oil was triturated with pentane (2 mL). Compound 2,3-diamino-2,3-dimethylbutane (0.695 g, 60%) was obtained as a colorless solid. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ =

1.05 (s, 9 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 25.9, 54.2 ppm. HR-MS calcd. for $\text{C}_6\text{H}_{17}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z = 117.1392, found 117.1385.

To a solution of compound **5** (0.0500 g, 0.156 mmol) and 2,3-diamino-2,3-dimethylbutane (0.0091 g, 0.078 mmol) in water (2 mL) was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.0194 g, 0.078 mmol). The mixture was stirred at room temperature for 1 h. After ethanol (1 mL) was added into the mixture, the yellow solution was stored for 24 h. The orange solution was then concentrated under reduced pressure. The crude product was washed with ethyl acetate followed by diethyl ether, and dried in vacuo. The complex **6b** (0.0494 g, 86.5%) was obtained as an orange powder. ^1H NMR (400 MHz, CD_3OD): δ = 1.40 (s, 12 H, CH_3) 3.33 (s, 6 H, OCH_3), 3.66 (t, J = 4.4 Hz, 4 H, CH_2OCH_3), 4.09 (t, J = 4.4 Hz, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$), 7.11 (s, 2 H), 7.45 (s, 2 H), 7.95 (s, 2 H, $\text{HC}=\text{N}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 36.3, 63.8, 71.2, 73.1, 75.4, 108.3, 112.5, 115.8, 125.7, 135.1, 139.9, 145.9 ppm. Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{N}_2\text{Na}_2\text{NiO}_{12}\text{S}_2 \cdot 6\text{H}_2\text{O}$ (%): C 37.11, H 5.27, N 3.33; found: C 36.82, H 5.24, N 2.97. HR-MS calcd. for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_{12}\text{S}_2\text{NiNa}_2$, $[\text{M}-\text{Na}^+]$ m/z = 709.0648, found 709.0624.

Complex 6c

To a solution of **2** (1.00 g, 5.10 mmol) and 1,2-diaminobenzene (0.276 g, 2.55 mmol) in ethanol (20 mL) was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.750 g, 2.55 mmol). The mixture was refluxed for 12 h. After cooling to room temperature, the precipitate was collected by filtration, washed with cold ethanol followed by diethyl ether, and dried in vacuum. Complex **6c** (1.26 g, 96%) was obtained as an orange powder. Single crystals were obtained by diffusion of diethyl ether into a methanol/dichloromethane (1:1) solution of **6c**. ^1H NMR (400 Hz, DMSO): δ = 3.32 (s, 6 H, $-\text{OCH}_3$), 3.65 (t, J = 4.0 Hz, 4 H,

CH_2OCH_3), 4.14 (t, $J = 4.0$ Hz, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$), 6.56 (t, $J = 8.0$ Hz, 2 H), 6.92 (d, $J = 8.0$ Hz, 2 H), 7.24 (d, $J = 8.0$ Hz, 2 H), 7.32 – 7.35 (m, 2 H), 8.14 – 8.18 (m, 2 H), 8.90 (s, 1 H, $\text{HC}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO): $\delta = 58.6, 68.6, 71.2, 115.1, 116.7, 118.9, 121.2, 127.0, 128.0, 142.9, 150.0, 157.0, 157.9$. Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_2\text{Ni}$ (%): C 59.92, H 5.03, N 5.37; found: C 59.70, H 4.86, N 5.40. HR-MS calcd for $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_2\text{Ni}$, $[\text{M}+\text{H}^+]$ $m/z = 521.1223$, found 521.1224.

Single crystals of **6c** bound with K^+ counterions were obtained by diffusion of diethyl ether into an acetone/dichloromethane (1:1) solution of **6c** and KPF_6 (1:1). Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_2\text{Ni KPF}_6$ (%): C 44.28, H 3.72, N 3.97; found: C 44.11, H 4.04, N 3.79.

3.4.3 Electrochemical Measurements

Cyclic Voltammetry

Cyclic voltammograms were obtained by using a Biologic SP-300 potentiostat in 0.10 M $n\text{-Bu}_4\text{NPF}_6$ in N,N -dimethylformamide (DMF) or 0.10 M Na_2SO_4 , KPF_6 , $n\text{-Bu}_4\text{NCl}$, or Li_2SO_4 in deionized water. Trifluoroacetic acid (TFA) or acetic acid (HAc) was added to achieve the different pHs. A standard three-electrode electrochemical cell was used with a glassy carbon working electrode (3 mm in diameter from BAS), a Pt wire as the counter electrode, and an Ag/AgCl electrode or another Pt wire as reference electrode. The potentials were reported with respect to NHE by adding 0.197 V to the experimental values when an Ag/AgCl electrode was used in aqueous the solution. Ferrocene (2 equiv. of catalyst, $E_{\text{Fc}^{+}/0} = 0.69$ V vs. NHE) was added as an internal reference when a Pt wire was used as the reference electrode in dry solvents. Before each experiment, the working electrode (glassy carbon) was polished using a 0.05 μm alumina solution on a polishing pad, followed by sonication in deionized water for 10 min, and dried in air. The saturated

Ar solutions were prepared by bubbling Ar through the solvents for 30 min.

Two methods are used to determine the onset potential in the CV curve of **6a** in neutral water with the different electrolytes. (1) The onset potential can be defined as the potential at which 10% of the current density at the peak potential was reached. For example, in the Figure 3.9c, the peak current density at -1.30 V is 6.64 mV cm^{-2} , so the onset potential is the potential at 0.664 mV cm^{-2} , which is -1.05 V. (2) Another method is to make a tangent to the cathodic peak and extrapolating the tangent to the X-axes, as shown in the Figure 3.9c (green line). The intersection is the onset potential, which is also -1.05 V.

Kinetics Studies

(1) Scan Rate Dependence Study.

In an electrochemical cell, 1.0 mM **6a** was dissolved in 0.10 M *n*-Bu₄NPF₆ in *N,N*-dimethylformamide (DMF, 5 mL). CV measurements were collected at various scan rates ranging from 50 mV s^{-1} to 1000 mV s^{-1} .

(2) Catalyst Concentration Dependence Study.

In an electrochemical cell, 0 – 2.5 mM **6a** were dissolved in 0.10 M *n*-Bu₄NPF₆ in DMF with 0.050 M HAc (5 mL). In aqueous solutions, 0 – 3.0 mM **6a** were dissolved in 0.10 M Na₂SO₄ in deionized water with 0.10 M HAc. CV measurements were collected at scan rates of 100 mV s^{-1} .

(3) Acid Dependence Study.

In an electrochemical cell, 1.0 mM **6a** was dissolved in 0.10 M *n*-Bu₄NPF₆ in DMF by adding 0 – 1.0 M HAc or 0 – 19 mM TFA (5 mL) at various scan rates. Plots of i_c/i_p versus [HAc] were used to determine the order with respect to the acid concentration at

the different scan rates. In the plot, i_c is the catalytic current and i_p is the peak current observed for the catalyst in the absence of acid. In aqueous solutions, 1.0 mM **6a** was dissolved in 0.10 M Na₂SO₄ in deionized water by adding 0 – 2.0 M acetic acid. CV measurements were collected at a scan rate of 100 mV s⁻¹.

(4) *Electrolyte Dependence Study.*

In an electrochemical cell, 1.0 mM **6a** was dissolved in 0.10 M electrolyte (Li₂SO₄, Na₂SO₄, KPF₆, MgSO₄, and *n*-Bu₄NCl) in deionized water or 0.10 M HAc solution (5 mL). CV measurements were collected at a scan rate of 100 mV s⁻¹.

(5) *Catalyst Dependence Study.*

In an electrochemical cell, 1.0 mM of **6a** or **6b** was dissolved in 0.10 M *n*-Bu₄NPF₆ in 5 mL DMF. CV measurements were collected at 100 mV s⁻¹.

(6) *Controlled Potential Electrolysis (CPE) Experiments*

Controlled potential electrolysis experiments were carried out with a Biologic SP-300 potentiostat in both neutral water and 0.10 M acidic solution with different electrolytes. A sealed 100 mL gas-tight cell was set with a 6.9 cm² surface area carbon paper as the working electrode, another piece of carbon paper as the counter electrode, and an Ag/AgCl reference electrode. The 50 mL electrolyte solution with 0.25 mM catalyst **6a** or **6b** was bubbled with Ar for 30 min prior to each experiment. CPEs were conducted at an applied potential of -1.3 V in neutral water or -1.0 V vs NHE in 0.10 M acetic acid solution with 0.10 M Li₂SO₄, Na₂SO₄, KPF₆, and *n*-Bu₄NCl as the electrolytes. Samples with the corresponding electrolytes without the catalyst were also run as the control.

Determination of Faradaic Efficiency, TON, and TOF

The CPE measurements performed to calculate the Faradaic efficiency of the catalyst

were performed on an Autolab PGSTAT-30 potentiostat with a customized gas-tight, five-neck, 63 mL electrolysis cell. A mercury pool with a surface area of 1.13 cm² was employed as the working electrode, while a carbon rod counter electrode and an Ag/AgCl reference electrode were placed in the electrolyte solution above the mercury pool. The solution with 0.22 mM catalyst **6a** was bubbled with Ar for 30 min before electrolysis. The electrolysis was carried out at an applied potential of -1.3 V (for seawater, containing around 0.60 M of salts, predominantly sodium chloride) or -1.05 V vs NHE (in aqueous solutions containing 0.50 M cations of the different electrolytes and 0.10 M HAc). The solution was constantly stirred during the electrolysis experiments. Gas samples were taken from the headspace of the cell and injected into an Agilent 7890A gas-chromatograph (with a thermal conductivity detector, a 5 Å molecular sieve column (2 mm × 5 m), and Ar as the carrier gas) at 30 min time intervals. The amount of H₂ was quantified by a GC calibration curve of H₂ samples of known concentration. The amount of H₂ generated from the electrolysis experiments and the amount of H₂ amount calculated from the consumed charge of each CPE experiment were calculated. The Faradaic efficiency data for the electrocatalytic H₂ production are summarized in Table 3.2.

$$\text{TON} = n_{\text{hydrogen}}/n_{\text{cat}} \text{ (mol H}_2 \text{ per mol catalyst)}$$

$$\text{TOF} = \text{TON}/(\text{duration of electrolysis}) \text{ (mol H}_2 \text{ per mol catalyst per hour)}$$

The n_{hydrogen} is the number of moles of H₂ generated from the electrolysis, and n_{cat} is the number of moles of catalyst used in the electrolysis experiment.

Single crystal X-ray structure of compounds

Complex 6c

A red plate-like specimen of $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NiO}_6$, with approximate dimensions 0.04 mm x 0.20 mm x 0.26 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 1.28 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 25084 reflections to a maximum θ angle of 28.28° ($0.75 \text{ \AA}$ resolution), of which 5710 were independent (average redundancy = 4.393, completeness = 99.9%, $R_{\text{int}} = 7.80\%$, $R_{\text{sig}} = 7.80\%$) and 3631 (63.59%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.4913(4) \text{ \AA}$, $b = 18.0722(7) \text{ \AA}$, $c = 22.1742(11) \text{ \AA}$, volume = $4605.0(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 2448 reflections above $2\sigma(I)$ with $5.816^\circ < 2\theta < 45.87^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.822. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8020 and 0.9650. The final anisotropic full-matrix least-squares refinement on F^2 with 318 variables converged at $R1 = 4.44\%$ for the observed data, and $wR2 = 15.83\%$ for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was $0.710 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.813 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.265 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.504 g/cm^3 and $F(000)$ was 2176 e^- .

Complex 6c + KPF_6

A red needle-like specimen of $\text{C}_{26}\text{H}_{26}\text{F}_6\text{KN}_2\text{NiO}_6\text{P}$, with approximate dimensions 0.12 mm x 0.14 mm x 0.42 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 0.96 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration

of the data using a monoclinic unit cell yielded a total of 58973 reflections to a maximum θ angle of 31.05° (0.69 Å resolution), of which 8845 were independent (average redundancy = 6.667, completeness = 99.8%, $R_{\text{int}} = 7.44\%$, $R_{\text{sig}} = 5.72\%$) and 6390 (72.24%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.4723(5)$ Å, $b = 18.6903(10)$ Å, $c = 15.7123(9)$ Å, $\beta = 96.0152(16)^\circ$, volume = $2766.4(3)$ Å³, are based upon the refinement of the XYZ-centroids of 8200 reflections above $2\sigma(I)$ with $4.358^\circ < 2\theta < 60.28^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.854. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6800 and 0.8900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P121/n1, with $Z = 4$ for the formula unit, $\text{C}_{26}\text{H}_{26}\text{F}_6\text{KN}_2\text{NiO}_6\text{P}$. The final anisotropic full-matrix least-squares refinement on F^2 with 519 variables converged at $R1 = 4.11\%$ for the observed data, and $wR2 = 8.42\%$ for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was $0.509 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.618 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.085 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.693 g/cm^3 and $F(000)$, 1440 e^- .

X-ray crystallographic coordinates for structures

Complexes **6c** and (**6c** + KPF_6) reported herein have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1435734 – 1435735. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.5 References

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Chapter 4. Visible Light-Driven Hydrogen Evolution Catalyzed by Nickel Salicylaldimine Complex

4.1 Introduction

The impending catastrophic consequence of global climate change has motivated the development of more sustainable energy resources to reduce the over-dependence on fossil fuels. The storage of solar energy in chemical bonds, also known as artificial photosynthesis, by splitting water into H_2 (proton reduction) and O_2 (water oxidation), has been explored as a potentially cleaner and carbon-free option.¹ Semiconductor materials such as metal chalcogenides and phosphides have emerged as cost-effective replacements for the unsurpassed platinum (Pt) as the photo- or electrocatalyst for proton reduction to H_2 .² Nonetheless, although such heterogeneous systems exhibit remarkably high H_2 production rates or even self-healing abilities, detailed mechanistic investigations on the solid phase chemical processes remain challenging. In contrast, molecular photocatalytic systems are often highly selective and active, more amenable to spectroscopic probes for elementary reaction steps, and can be systematically designed and improved through ligand variations. Typically, molecular photocatalytic H_2 evolution systems each consists of a light absorbing photosensitizer and a proton reduction catalyst, all of which can be independently optimized.³ Thus, some critical aspects of creating improved artificial photosynthetic systems include the development of affordable, efficient H_2 evolution catalysts and a thorough understanding of the light absorption and electron transfer events.⁴

Historically, integrated photocatalysts comprising platinum-group metals (PGMs) like

Pt,⁵ Rh,⁶ Ir,⁷ and Pd⁸ have exhibited modest performances for light absorption and H₂ evolution by the same molecule. However, new catalysts consisting of Earth-abundant, first-row transition metals are increasingly sought as more sustainable alternatives, due to the high price of PGMs.⁹ For instance, Co-containing cobaloxime catalysts have been combined with a variety of photosensitizers to produce H₂, although they have demonstrated low stability and turnover numbers (TON) thus far.¹⁰ DuBois and Bullock's team have reported Ni-N₂P₂ complexes of exceptional electrocatalytic H₂ evolution activity exceeding that of even enzymatic systems,¹¹ but they show surprisingly low turnover frequencies (TOF)¹² for photocatalytic proton reduction unless the outer coordination sphere has been modified with phosphonic acid groups and the catalyst is immobilized on metal oxide semiconductors.¹³ In addition, Eisenberg and coworkers have presented seminal studies on Co dithiolene¹⁴ and Ni thiolates¹⁵ for the photogeneration of H₂ from aqueous-organic solvents. Notably, their recent Ni pyridinethiolate catalyst displays a high TON (7300 in 30 h), with a proposed mechanism that is similar to the one in natural hydrogenase enzymes.^{15b}

In the previous chapter, a series of Ni salicylaldimine complexes have been discussed for their efficient electrocatalysis of H₂ production.¹⁶ The Ni salicylaldimine catalysts with pendant ether arms in the second coordination sphere are able to bind hydrated alkali metal cations and provide hydrogen-bonding stabilization for enhanced electrocatalytic H₂ evolution reactivity. In this chapter, attempts have been made to develop a more robust and active Ni salicylaldimine catalyst and integrated it with Ir^{III}(ppy)₂(dtbbpy)⁺ (ppy = 2-phenylpyridine; dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) for photocatalytic H₂ evolution by harvesting visible light.¹⁷ Water and methanol are used as the proton

sources. By introducing Lewis acid cations, dramatically enhanced activity and selectivity are expected for their H₂ evolution catalysis for the H₂ production. Through nanosecond time-resolved optical spectroscopy done by my colleague and DFT calculation studies done by the author,¹⁸ it is proposed that the Lewis acid cations chelated by the ether arms in close proximity to the Ni catalytic center direct protons to the transient metal hydride, resulting in efficient H₂ production.

4.2 Results and discussion

4.2.1 Preparation of nickel complex

The nickel complex **2** was synthesized over two steps from affordable, commercially available reagents with high yields (Scheme 1). Firstly, 2,3-dihydroxybenzaldehyde was modified with a pendant 2-methoxyethoxy ether arm to give 2-hydroxy-3-(2-methoxyethoxy)benzaldehyde (**1**). Subsequently, **1** reacted with 2,3-diamino-5-chloropyridine *via* a condensation reaction in the presence of nickel acetate in methanol to yield complex **2** as a deep orange powder. The electron-deficient chloropyridine group in **2** was expected to withdraw electron density from the Ni center and increase the reduction potential of the catalyst in the H₂ evolution reaction.

Scheme 4.1. Synthesis of Ni complex **2** with pendant ether groups.

4.2.2 Characterization of nickel complex

The nickel complex **2** was fully characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), elemental analyses, and UV-vis spectroscopy. The UV-vis spectrum of **2** in Figure 4.1 exhibits two absorbance peaks at 380 and 488 nm in methanol (containing 5% H₂O) with extinction coefficients of 18700 and 4820 M⁻¹cm⁻¹, which can be assigned to π - π^* transition of the salicyaldimine ligand and the ligand-to-metal charge transfer bands, respectively. The typical absorbance peak would be useful to gauge the stability of **2** under the catalytic conditions.

Figure 4.1. (a) UV-vis spectra of **2** at different concentrations in 5% H₂O in methanol. (b) Plots of absorbance at 380 and 488 nm versus concentration of **2** in 5% H₂O in methanol.

4.2.3 Electrochemical study

The electrochemical behavior of complex **2** under reductive conditions was examined by cyclic voltammetry (CV) in acetonitrile solution bubbled with argon. Ferrocene was used as an internal reference. The CV in Figure 4.2a shows three Ni-centered one-electron redox waves. The quasi-reversible oxidative wave ($E_{1/2}$) at 1.35 V vs. NHE is assigned to the Ni^{III}/Ni^{II} redox couple. The ratios of the reductive peak current (i_p^{red}) to the oxidative

peak current (i_p^{ox}) were calculated and listed in Table 4.1. The $|i_p^{\text{red}}/i_p^{\text{ox}}|$ ratios gradually increased to 1 when the scan rate was raised to $1.0 \text{ V}\cdot\text{s}^{-1}$, suggesting that the redox process was likely to be chemically reversible. The irreversible reduction wave at -0.84 V is attributed to the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox couple. It was observed that the peak shifted positively compared with the nickel salicyaldimine complex in Chapter 3, which is around -1.0 V vs. NHE. The anodic shift of the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox potential likely arises from the electron-withdrawing pyridine group in **2**, which can behave as a π -acceptor to distribute the anionic charge density around the complex. The quasi-reversible reduction wave at $E_{1/2} \sim -1.58 \text{ V}$ is likely due to the $\text{Ni}^{\text{I}}/\text{Ni}^0$ redox couple. The redox wave shows increasingly reversible behavior at higher scan rates (Figure 4.2d).

Table 4.1. $|i_p^{\text{red}}/i_p^{\text{ox}}|$ ratios at different scan rates for the redox wave at $E_{1/2}=1.35 \text{ V}$.

Scan rate	$ i_p^{\text{red}}/i_p^{\text{ox}} $
50	0.79
100	0.82
400	0.85
700	0.94

Figure 4.2. CV of 1.0 mM **2** in 0.10 M *n*-Bu₄NPF₆ in ACN with a glassy carbon electrode (3 mm diameter) at (a) a scan rate of 100 mV s⁻¹ (b), (c), and (d) increasing scan rates in different ranges.

4.2.4 Standard conditions for photocatalytic H₂ evolution

A series of photocatalytic H₂ production experiments were performed by using a solution of **2** as the H₂ evolution catalyst, Ir^{III}(ppy)₂(dtbbpy)⁺ [Ir]⁺ as the photosensitizer, and triethylamine (TEA, 0.10 M) as the sacrificial electron donor in methanol (containing 5% H₂O) under *visible light* irradiation. The amount of H₂ built up in the headspace was quantified every one to two hours by GC analysis (Table 4.2), and calculated by subtracting the H₂ produced from control experiments that were conducted in the absence of **2**. H₂ was produced in the solution even without catalyst **2**, which could be due to IrO₂ catalyst formation during the irradiation. Among the various solvent systems tested, 5% H₂O in methanol gives the highest TON, and TEA is a much better sacrificial reductant than triethanolamine (TEOA) and 1-benzyl-1,4-dihydronicotinamide (BNAH) (Table 4.2). We have also tried to use [Ru(bpy)₃]Cl₂ [Ru] and Cu(dap)₂Cl [Cu] as photosensitizers, but a much lower amount of H₂ (0.52 μmol) was observed for [Ru] and no H₂ was produced when [Cu] was used.

The H₂ vs. time profiles with different catalyst concentrations ranging from 1.0 to 10.0 μM are displayed in Figure 4.3a. All experiments were repeated at least three times. The amount of H₂ produced increases as the catalyst concentration increases. However, the highest TON of 3880 was achieved with 2.0 μM of **2** in the system (Figure 4.3b). When 1.0 μM of **2** was used, the TON was comparable with results from the experiments with 2.0 μM of **2** for the first 2 h of irradiation. However, the TON (for 1.0 μM of **2**) decreased dramatically after the initial 2 h and finally reached a value after 6 h between experiments with 5.0 μM of **2** sample and 10.0 μM of **2**, probably because **2** (5.0 nmol) had become catalytically inactive after the first two hours. Our experiments indicated that

at concentrations of **2** above 2 μM , the H_2 evolution performance per unit catalyst is lower. We hypothesize that complex **2** may have reacted with deligated Ni^{II} cations or another equivalent of **2** to form binuclear or polynuclear salicylaldimine complexes in solution.¹⁹ A similar phenomenon was also observed by Zhao and co-workers with their Co complex ligated by DPA-Bpy.²⁰ In addition, a control experiment with 2.0 μM of **2** conducted in anhydrous methanol solution under otherwise identical conditions (Table 4.2, entry 5) revealed that the TON was almost halved to 1900, which suggested that H_2O was a more effective proton source, albeit not the only one in this photocatalytic system.

Table 4.2. Summary of the photocatalytic H_2 evolution experiments conducted.

Entry	Conditions	Solvent	Time(h)	TON
1 ^a	10 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH (5 % H_2O)	6	1660
2 ^a	5.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH (5 % H_2O)	6	2370
3 ^a	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH (5 % H_2O)	6	3880
4 ^a	1.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH (5 % H_2O)	6	2100
5	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH only	6	1900
6	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEOA	MeOH (5 % H_2O)	4	0
7	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M BNAH	MeOH (5 % H_2O)	4	64
8	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	Acetone (5 % H_2O)	4	660
9	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$, 0.10 M TEA (In dark)	MeOH (5 % H_2O)	6	0
10	2.0 μM 2 , 0.10 mM $[\text{Ir}]^+$	MeOH (5 % H_2O)	6	0
11	0.10 mM $[\text{Ir}]^+$, 0.10 M TEA	MeOH (5 % H_2O)	6	-
12	2.0 μM 2 , 0.10 M TEA	MeOH (5 % H_2O)	6	0
13	2.0 μM 2 , 0.50 mM $[\text{Ru}]$, 0.10 M TEA	MeOH (5 % H_2O)	6	52
14	2.0 μM 2 , 0.50 mM $[\text{Cu}]$, 0.10 M TEA	MeOH (5 % H_2O)	4	0
15 ¹²	0.14 mM $[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}_2^{\text{Ph}})_2](\text{BF}_4)_2$, 0.10 mM $[\text{Ru}]$, 0.10 M ascorbic acid	ACN (50 % H_2O)	150	2700
16 ¹³	NiP-RuP (TiO_2), 0.1 M ascorbic acid	aqueous solution	2	723 $\pm$ 171
17 ^{15b}	4.0 μM $(\text{Et}_4\text{N})\text{Ni}(\text{X-pyS})_3$, 2.0 mM fluorescein, 0.36 M TEA	EtOH (50 % H_2O)	30	7300

18²¹ 0.010 mM [Ni(L₄)]₂⁺, 1.0 mM [Ir]⁺, 0.6 M TEA THF (10 % H₂O) 70 5000

^a Experiments repeated at least three times; the data have been reported as the average of multiple runs.

Figure 4.3. 0.10 mM [Ir]⁺ and 0.10 M TEA under 6 h visible light irradiation. The amounts of H₂ generated were obtained as an average of at least three independent measurements.

4.2.4 Stability study of the photocatalytic system

The production of H₂ was observed to slow down drastically after 6 h of visible light irradiation, prompting us to perform further experiments to identify the causes. Since TEA was present in large excess, it was unlikely to be the limiting reagent. Thus, we examined if the other components were responsible for the loss in activity by adding [Ir]⁺

or **2** separately after 6 h to probe if H₂ production could resume. When the same amount of [Ir]⁺ was added in the photocatalytic reaction, no significant additional H₂ was detected, suggesting that the photosensitizer was not the main culprit for the termination of H₂ evolution. On the other hand, a second equivalent of **2** added reactivated the catalysis, leading to an 80% recovery of H₂ production in the next 6 h (Figure 4.4).

Figure 4.4. Changes in H₂ evolution with irradiation time before and after adding an additional 2.0 μM of **2** to the photocatalytic system containing 2.0 μM of **2**, 0.10 mM [Ir]⁺, and 0.10 M TEA in methanol (5 % H₂O) solution under visible light irradiation.

Recent work²² has indicated that zero-valent nickel nanoparticles are effective during photocatalytic H₂ evolution. In order to determine whether **2** is an active species or just a precatalyst that decomposes into heterogeneous Ni catalysts, a series of standard electrochemical and spectroscopic experiments were conducted. Dynamic light scattering (DLS) experiments after 6 h of photocatalysis suggested that no nanoparticles had formed during the reaction (Figure 4.5). A transmission electron microscopy (TEM) image (Figure 4.6) of the solution after irradiation also exhibits little evidence of nanoparticle formation, and only large amorphous chunks of materials that could be

by-product salts of TEA. These measurements verified that **2** was likely to be the molecular H₂ evolution catalyst in our photodriven system.

Figure 4.5. Particle distribution determined by DLS measurements before and after 6 h photoirradiation of a methanol (5% H₂O) solution containing 2.0 μ M of **2**, 0.10 mM [Ir]⁺, and 0.10 M TEA.

Figure 4.6. TEM image of an aliquot of the reaction mixture after 6 h photoirradiation of a methanol (5 % H₂O) solution containing 2.0 μ M of **2**, 0.10 mM [Ir]⁺, and 0.10 M TEA.

4.2.5 Time-Resolved Studies

To gain mechanistic understanding of the elementary reaction steps during the photocatalysis, nanosecond transient absorption spectroscopic (TAS) experiments were conducted. There are two generally accepted pathways for single photon-electron transfer

in photocatalytic systems. In one route, the photosensitizer absorbs light, after which its excited state is reduced by a sacrificial electron donor. The reduced photosensitizer then recovers by transferring an electron to the catalyst enroute to producing H₂. Alternatively, the photosensitizer absorbs light, forms a transient excited state species, and transfers an electron to the catalyst directly. The oxidized photosensitizer is then reduced to its original oxidation state by the sacrificial electron donor. To distinguish these plausible routes, transient emission spectroscopy was carried out by 355 nm pulsed irradiation of 0.10 mM [Ir]⁺. The excited [Ir]^{+*} at 570 nm decayed back to its ground state with a lifetime τ_0 of $3.92 \pm 0.04 \mu\text{s}$ (Figure 4.7). Subsequently, we measured the lifetimes and TAS of the photoexcited [Ir]^{+*} in the presence of different concentrations of TEA and **2**. The Stern-Volmer plots (Figures 4.8) were obtained from the decay lifetimes of the isolated signal at 570 nm arising from [Ir]^{+*}, yielding quenching rate constants, k_q , of $5.66 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of TEA only which is close to the reported value ($1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$),⁸ and $7.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of **2** only. The concentrations of TEA exceed that of **2** by at least 10,000 times, whereas the bimolecular rate constant of **2** is only 1300 times higher. Consequently, the quenching rate constants demonstrated that in our three component photocatalytic system, the excited [Ir]^{+*} would be predominantly quenched through reduction by TEA, before transferring an electron to complex **2** and reduce Ni^{II} to Ni^I.

Figure 4.7. Transient emission spectroscopic signal at 570 nm after 355 nm pulsed irradiation of 0.10 mM of $[\text{Ir}]^+$. The black line is the data and the red line is the mono-exponential fit for the decay.

Figure 4.8. Stern-Volmer plot for quenching the transient emission spectroscopic signal of $[\text{Ir}]^{+*}$ at 570 nm by varying concentrations of (a) TEA and (b) **2**.

More detailed mechanistic understanding was derived from nanosecond transient absorption measurements. The initial photoinduced step of the reaction mixture has been identified as the reduction of excited $[\text{Ir}]^{+*}$ to $[\text{Ir}]$ by TEA. $[\text{Ir}]$ is a highly reducing species that has a reduction potential of -1.45 V vs NHE that can reduced Ni^{II} to Ni^{I} . The transient absorption spectra of $[\text{Ir}]^{+*}$ with TEA in the absence and presence of **2** in MeOH/ H_2O solution upon laser excitation at 355 nm were recorded in Figure 4.9. In

Figure 4.9(a), the characteristic absorption wavelength of $[\text{Ir}]^{+*}$ at 380, 480, and 610 nm were monitored over time. The disappearance of the $[\text{Ir}]^{+*}$ in the two component system resulted in the formation of a transient reduced species $[\text{Ir}]$, which can be fitted into a mono-exponential decay of 324 ns in the absence of **2** (Figure 4.10a). The spectral signature appeared at 530 nm (Figure 4.9c) confirmed the formation of $[\text{Ir}]$ through the reductive quenching of $[\text{Ir}]^{+*}$.

Figure 4.9. Transient absorption spectra of $[\text{Ir}]^{+*}$ upon 355 nm pulsed irradiation of 0.10 mM $[\text{Ir}]^{+}$ with 0.10 M TEA (a) in the absence of **2**, (b) in the presence of 40 μmol **2** at different times, (c) from 3 to 90 μs in the absence of **2**, (d) from 3 to 90 μs in the presence of 40 μmol **2**.

In the presence of **2** (Figure 4.9b), a second transient species was observed following the disappearance of $[\text{Ir}]^{+}$. A bi-exponential curve with lifetimes of 350 ns and 13.0 μs were detected (Figure 4.10b). The band centered at 380 nm shifted to 420 nm whereas the signal at 380 nm became a bleach (Figure 4.9d). Through the absorption spectra comparison of $[\text{Ir}]^{+*}$ upon 355 nm pulsed irradiation in the absence and presence of **2** at

90 μs in Figure 4.11, we can see there is a broad absorption from 560 nm to 750 nm when **2** was present in the system. This indicates that Ni^{I} species is formed and the reduced $[\text{Ir}]$ may be oxidized back to $[\text{Ir}]^+$ at the same time. The spectral signature at 530 nm in Figure 4.9d decreased with time, which also verified the decay of the $[\text{Ir}]$ species. However, the spectrum did not return back to the original state even at 90 μs , which may be due to the absorption of the reduced Ni^{I} species in the same wavelength domain.

Figure 4.10. Transient emission spectroscopic signal at 380 nm after 355 nm pulsed irradiation of 0.10 mM of $[\text{Ir}]^+$ with 0.10 M TEA (a) in the absence and (b) in the presence of 40 μmol **2**. The black line is the data and the red line is the mono-exponential fit for the decay.

Figure 4.11. Comparison of transient absorption spectra of $[\text{Ir}]^{+*}$ upon 355 nm pulsed irradiation of 0.10 mM $[\text{Ir}]^+$ with 0.10 M TEA at 0 ns (black line), in the absence (red line) and in the presence of **2** (blue line) at 90 μs .

Based on the nanosecond transient absorption results observed above, the rate constant for the electron transfer from the reduced [Ir] to the Ni^{II} catalyst could be evaluated. A Stern-Volmer plot with a rate constant of $3.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} (\pm 0.10)$ was obtained at different concentration of **2** in the presence of TEA. Since [Ir] is a long-lived species, the Stern-Volmer equation can be simplified as:

$$\frac{1}{\tau} \approx k[\mathbf{1}]$$

where τ is the lifetime of [Ir] in the presence of **2** and k is the corresponding bimolecular electron transfer rate constant from [Ir] to **2**.

Figure 4.12. Stern-Volmer plot for quenching the transient emission spectroscopic signal of $[\text{Ir}]^{+*}$ at 570 nm by varying concentrations of **2** with 0.10 M TEA.

4.2.5 DFT calculations

The detailed photocatalytic H_2 evolution reaction mechanism by **2** was further investigated with DFT calculations by using the UM06 functional and the def2SVP basis set with the Gaussian 09 software. This combination of functional and basis set provided a possible mechanism for the photocatalytic H_2 evolution reaction. Two sets of calculations were performed, one in the absence and the other in the presence of

potassium cations. As illustrated in Figure 4.13, complex **2** in **RC1** converged to a stable Ni^{I} intermediate after one electron reduction by the photoexcited $[\text{Ir}]^{+*}$ or the reduced $[\text{Ir}]$, after which it could be protonated by H_2O or methanol. It is hypothesized that the Ni^{I} intermediate could be protonated on Ni (**Int2**) or a phenolic-O (**Int2'**). Both intermediates showed similar stability, although the following reduced Ni^{II} hydride (**Int3**) was marginally more stable than the formally Ni^0 phenol intermediate in **Int3'** (Figure 4.13). Subsequently, another H_3O^+ bound to form an ether stabilized intermediate **Int4**, after which H_2 was produced through a exothermic reaction directly.

Figure 4.13. Proposed reaction pathway for H_2 evolution catalyzed by **2** in the absence of alkali metal cations based on DFT calculations.

In addition, a similar mechanistic pathway for H_2 evolution in the presence of K^+ as a representative example of alkali metal cations was calculated (Figure 4.14). The Ni^{II}

complex in **RC2** with one K^+ cradled by the pendant ether arms and a H_2O molecule could likewise be reduced to a stable Ni^I intermediate in **Int7**. After protonation of the Ni^I complex to form a $Ni^{III}-H$ in **Int8**, the hydride could be subsequently reduced to a Ni^{II} hydride (**Int9**). Upon protonation by another H_3O^+ to produce **Int10**, one proton from H_3O^+ molecule transferred to the K^+ -bound H_2O , which in turn channeled a proton from H_2O to react with the $Ni^{II}-H$ to yield H_2 gas by overcome only $0.02 \text{ kcal mol}^{-1}$ energy barrier and regenerate **2**. In both reaction pathways in Figures 4.13 and 4.14, the first reduction step and the following protonation step are increasingly demanding to access. Accessing **Int2** is likely the rate determining step in the reaction. However, the intermediates with K^+ cation in Figure 4.14 are 6.6 and $2.0 \text{ kcal mol}^{-1}$ lower than the corresponding ones in Figure 4.13. In the following steps, the reaction in the presence of K^+ cations also produces more stable intermediates compared with the reaction in the absence of K^+ cations. **Int11** containing the bound H_2 in Figure 4.14 is the most stable intermediates in both reaction pathways. The calculations suggest that the Ni catalysts together with K^+ cations have lower energy pathways for the catalytic H_2 evolution reaction. It suggests that coordination of Lewis acid cations by the pendant ether arms in close proximity to the catalytic Ni center can potentially enhance the activity for H_2 production.

Figure 4.14. DFT calculated reaction pathway for H_2 evolution catalyzed by **2** in the presence of K^+ .

4.3 Conclusion

In conclusion, we have demonstrated an active salicylaldimine nickel complex for photocatalytic H_2 evolution with $\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})^+$ as a photosensitizer, and TEA as the sacrificial electron donor in methanol/water solution. A high TON (>3800) of light-driven H_2 evolution in the three component system was obtained. The nanosecond time-resolved optical spectroscopy studies suggest that the excited $[\text{Ir}]^{+*}$ can react with both TEA and Ni^{II} . In our three component system, $[\text{Ir}]^{+*}$ is reduced by TEA to form $[\text{Ir}]^+$ first, which then transfers one electron to reduce Ni^{II} to Ni^{I} . The $[\text{Ir}]$ is concomitantly oxidized back to $[\text{Ir}]^+$ with a rate constant of $3.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The DFT calculation studies indicate the Lewis acid cations (K^+) chelated by the ether arms in close proximity to the Ni catalytic center direct protons to the transient metal hydride, resulting in a faster

H₂ production than the system without Lewis acid cations. However, the photocatalytic experiments with added Lewis acid cations are still under investigation. Future work will be focused on the proton reduction experiments with different Lewis acid cations and even using seawater as both the source of protons and Lewis acid cations.

4.4 Experimental Section:

4.4.1 *Materials and Methods*

Chemicals were obtained from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry Co., Ltd. (TCI). Unless otherwise noted, the commercial reagents were used as purchased. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F₂₅₄ silica gel plates. All reactions involving air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under an argon atmosphere. The ¹H and ¹³C NMR measurements were recorded on Bruker AV-400 (400 MHz) or BBFO-400 (400 MHz) NMR spectrometer. The ¹H and ¹³C NMR spectra are reported in parts per million (ppm) downfield referenced to the residual protons of the deuterated solvents. UV-visible absorption measurements were carried out on a Shimadzu UV-3600 spectrophotometer. Elemental analyses were performed with an Elementar vario MICRO cube analyser. High-resolution mass spectra (HR-MS) were obtained with a Q-TOF Premier LC HR mass spectrometer.

4.4.2 *Syntheses*

Compound 2-Hydroxy-3-(2-methoxyethoxy)benzaldehyde (1)

The procedure has been adapted from a published method.^[1] NaH (0.600 g of a 60% dispersion in oil, 15.2 mmol) was suspended in anhydrous DMSO (10 mL) in an oven-dried Schlenk flask equipped with a dropping funnel. The suspension was cooled in

an ice-bath. A solution of 2,3-dihydroxybenzaldehyde (1.00 g, 7.20 mmol) in anhydrous DMSO (10 mL) was added dropwise to the mixture under a flow of Ar over the course of 1 h. Vigorous gas evolution occurred. After complete addition, the dark orange solution was stirred at ambient temperature, and (2-methoxyethoxy)-*p*-toluenesulfonate (1.36 mL, 7.2 mmol) was added in one portion. The solution was then stirred for another 2.5 h. Water (50 mL) was slowly added to quench the reaction, and the solution was extracted with CHCl₃ (3 × 30 mL). The aqueous layer was acidified to pH 2 with 1 M aqueous HCl (15 mL) and the color changed from dark orange to yellow. The aqueous layer was then extracted with CHCl₃ (3 × 30 mL). The organic layer was subsequently rinsed with 1 M HCl (2 × 30 mL), dried with anhydrous Na₂SO₄, and filtered. The solvent was removed *in vacuo* to afford an orange viscous oil. The residue was purified by silica gel column chromatography (hexane:ethyl acetate = 4:1) and **1** (1.19 g, 86.0%) was isolated as a pale green-yellow solid. ¹H NMR (400 Hz, CDCl₃): δ = 3.46 (s, 3 H, -OCH₃), 3.79 (t, *J* = 7.5 Hz, 2 H, CH₂OCH₃), 4.22 (t, *J* = 7.5 Hz, 2 H, OCH₂CH₂O), 6.95 (t, *J* = 7.8 Hz, 1 H), 7.17 – 7.26 (m, 2 H), 9.94 (s, 1 H, CHO), 10.80 (s, 1 H, Ar-OH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 59.7, 69.2, 70.9, 119.4, 121.0, 121.2, 125.3, 147.4, 152.2, 196.2. HR-MS (ESI⁺) calcd for C₁₀H₁₂O₄, [M+H]⁺ *m/z* = 197.0814, found 197.0805.

Ni pyridyl salicylaldimine complex (**2**)

To a solution of **1** (1.00 g, 5.10 mmol) and 2,3-diamino-5-chloropyridine (0.366 g, 2.55 mmol) in ethanol (20 mL) was added Ni(OAc)₂·4H₂O (0.750 g, 2.55 mmol). The mixture was heated under refluxing conditions for 12 h. After cooling to room temperature, the precipitate was collected by filtration, washed with cold ethanol followed by diethyl ether, and dried in vacuum. Complex **2** (1.36 g, 96%) was obtained as an orange powder. Single

crystals were obtained by diffusion of diethyl ether into a methanol and dichloromethane (1:1) solution of **2**. ^1H NMR (400 Hz, CDCl_3): δ = 3.48 (s, 6 H, $-\text{OCH}_3$), 3.83-3.87 (m, 4 H, CH_2OCH_3), 4.13 (t, J = 5.4 Hz, 2 H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.21 (t, J = 5.4 Hz, 2 H, $\text{OCH}_2\text{CH}_2\text{O}$), 6.39 (t, J = 7.8 Hz, 1 H), 6.55 (t, J = 8.0 Hz, 1 H), 6.67 (d, J = 7.6 Hz, 1 H), 6.85 (t, J = 8.4 Hz, 2 H), 6.95 (d, J = 7.2 Hz, 1 H), 7.92 (d, J = 2.0 Hz, 1 H), 8.01 (d, J = 2.0 Hz, 1 H), 8.29 (s, 1 H, $\text{HC}=\text{N}$), 8.76 (s, 1 H, $\text{HC}=\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 59.07, 67.98, 68.06, 70.98, 115.41, 115.55, 117.18, 119.83, 122.86, 125.62, 129.57, 136.40, 144.02, 149.80, 149.88, 151.88, 155.13, 159.07, 159.27. Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_6\text{N}_3\text{NiCl}\cdot\text{H}_2\text{O}$ (%): C 52.35, H 4.54, N 7.33; found C 52.75, H 4.39, N 7.47. HR-MS (ESI^+) calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_6\text{N}_3\text{NiCl}$, $[\text{M}+\text{H}]^+ m/z$ = 556.0785, found 556.0789.

4.4.3 Electrochemical Measurements

Cyclic Voltammetry

The controlled-potential coulometric experiments were performed using a Biologic SP-300 potentiostat. A three-electrode electrochemical cell was used with a glassy carbon working electrode (3 mm in diameter from BAS), a Pt wire counter electrode, and another Pt wire as a pseudoreference electrode. Ferrocene (2 equiv. of catalyst, $E_{\text{Fc}^+/\text{Fc}}^0 = 0.69$ V vs. NHE) was added as the internal standard in anhydrous acetonitrile (ACN). Before each experiment, the working electrode (glassy carbon) was polished using a 0.05 μm alumina suspension on a polishing pad, followed by sonication in deionized (DI) water for 10 min, and dried in air. The saturated Ar solutions were prepared by bubbling Ar through the solvents for 30 min.

Scan Rate Dependence Study

In an electrochemical cell, 1.0 mM of **2** was dissolved in 0.10 M *n*-Bu₄NPF₆ in ACN (5 mL). CV measurements were collected at various scan rates ranging from 50 mV s⁻¹ to 700 mV s⁻¹.

4.4.4 Photocatalytic H₂ evolution experiment

The specific conditions, such as the reagent concentrations and reaction time intervals, have been summarized in Table S1. Typically, [Ir]⁺, **2**, and TEA (0.10 M) in 5.0 mL methanol (MeOH, 5.0% H₂O) were added to a 27 mL Schlenk tube together with a stir bar. The solution was deoxygenated by bubbling with Ar for 20 min after the Schlenk tube was sealed with a septum. The absence of O₂ in the Schlenk tube was verified by gas chromatography (GC, Agilent 7890A gas-chromatograph with a thermal conductivity detector (TCD), a 5 Å molecular sieve column (2 mm × 5 m), and Ar as the carrier gas) before irradiation. The tube was irradiated by visible light supplied by a 300 W xenon lamp with a 420 nm-cutoff UV light filter. After the time intervals shown in Table S1, a gas sample (0.5 mL) was taken from the headspace of the Schlenk tube and analyzed by GC to determine the amount of generated H₂.

4.4.5 Stability study of the photocatalytic system

The stability study of the photocatalytic system was carried out by adding another 2.0 μM of **2** or 0.10 mM [Ir]⁺ dye in the photocatalytic system containing 2.0 μM of **2**, 0.10 mM [Ir]⁺, and 0.10 M TEA in methanol (5 % H₂O) after 7 h visible light irradiation. The H₂ in the headspace was released before the reaction mixture was deoxygenated again by bubbling with Ar for 20 min after the addition of **2** or [Ir]⁺.

4.4.6 TON and TOF calculation

The TON and TOF number of H₂ generated from the photocatalytic experiments were

calculated by the following equations:

$$\text{TON} = n_{\text{hydrogen}}/n_{\text{cat}} \text{ (mol H}_2 \text{ per mol catalyst)}$$

$$\text{TOF} = \text{TON}/(\text{duration of electrolysis}) \text{ (mol H}_2 \text{ per mol catalyst per hour)}$$

The n_{hydrogen} is the number of moles of H_2 generated from the electrolysis, and n_{cat} is the number of moles of catalyst used in the electrolysis experiment.

4.4.7 Transient absorption measurements

The transient absorption and emission measurements were performed using an Edinburgh Instruments model LP920 transient absorption spectrometer equipped with a pulsed Xe probe lamp in conjunction with a Nd:YAG laser (Continuum model Surelite II-10) as the excitation source. The laser pulse width is 5-8 ns and the repetition rate is 10 Hz. During transient absorption measurements, the pulses are synchronized with the LP920 system at a frequency of 1 Hz. The pulse energy used was between 6-20 mJ/pulse.

The data were fit to single exponential or biexponential functions to obtain the time constants for the nanosecond transient optical spectroscopic signals according to the following two equations respectively:

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1}$$

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1} + A_2 e^{-(t-\tau_0)/\tau_2}$$

The parameters y_0 , τ_0 , A_n , and τ_n were determined by a least-squares fitting procedure in Origin. The term y_0 corresponds to the vertical intercept at long lifetimes and indicates whether the signal decays to a ‘permanent’ bleach (negative y_0) or absorption (positive y_0). The variable τ_0 is the delay time of the excitation pulse from the start of the probe measurement during each photoexcitation cycle. A_n is the change in optical density after irradiation for the n th exponential term and τ_n is the corresponding time

constant. The relative contribution of the n th term to the overall transient signal, c_n , was calculated using the following formula:

$$c_n = \frac{A_n}{A_1 + A_2}$$

Stern-Volmer plot for the quenching of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]^{+*}$ by triethylamine

As the concentration of TEA increases, the lifetime τ of the signal owing to $[\text{Ir}]^{+*}$ decreases. The bimolecular quenching rate constant, k_q , is related to the lifetime, τ of $[\text{Ir}]^{+*}$ in the presence of TEA with a concentration of $[Q]$ by the Stern-Volmer equation:

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$

where τ_0 is the lifetime of $[\text{Ir}]^{+*}$ in the absence of TEA

The bimolecular rate constant, k_q , of the of $[\text{Ir}]^{+*}$ by TEA can be obtained by plotting a graph of τ_0/τ against $[Q]$ with a fixed vertical intercept of 1. The gradient ($k_q \tau_0$) was determined to be $2.22 \pm 0.07 \text{ M}^{-1}$ and τ_0 was determined to be $3.92 \pm 0.04 \text{ }\mu\text{s}$. This gives a rate constant, k_q , of $5.66 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Stern-Volmer plot for the quenching of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]^{+*}$ by **2**

As the concentration of **2** increases, the lifetime τ of the signal owing to $[\text{Ir}]^{+*}$ decreases.

The quenching rate constant, k_q , is related to the lifetime, τ , of $[\text{Ir}]^{+*}$ in the presence of **2** with a concentration of $[Q]$ by the Stern-Volmer equation:

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$

where τ_0 is the lifetime of $[\text{Ir}]^{+*}$ in the absence of **2**

The quenching rate constant, k_q , of the of $[\text{Ir}]^{+*}$ by **2** can be obtained by plotting a graph of τ_0/τ against $[Q]$ with a fixed vertical intercept of 1. The gradient ($k_q \tau_0$) was determined to be $2939 \pm 197 \text{ M}^{-1}$ and τ_0 was determined to be $3.92 \pm 0.04 \text{ }\mu\text{s}$. This gives a rate constant, k_q , of $7.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

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Chapter 5. Introduction of Fluorination Reaction

5.1 Fluorination of organic compounds

Fluorinated compounds have been widely used in medicinal chemistry,¹ therapeutic imaging,² agrochemical products,³ and material sciences⁴ due to fluorine's small atomic size and high electronegativity.⁵ So far, approximately 30–40% of agrochemicals and 20% of pharmaceuticals industry sources on the market contain fluorine.⁶ However, there are only a few number of fluorine-containing products are found in Nature.⁷ Fluorinated platform molecules derived from natural products usually possess multiple functional groups that can potentially be transformed into high-value chemical products. As a result, the development of efficient methodologies for the fluorination of organic compounds has gained increasing significance in the fields of organic and medicinal chemistry.

Among the multiple fluorination reactions, monofluorination of organic compounds means to introduce a single C–F bond to the organic molecules. These fluorinations can be classified into three different methods: nucleophilic, electrophilic, and radical fluorination.⁸

Nucleophilic fluorination

In nucleophilic fluorination, the substrate behaves as an electrophile, while the fluoride ion acts as a nucleophile. In a typical nucleophilic substitution reaction, an alkyl chain or aryl ring bearing a suitable leaving group, X, reacts with a fluoride source (F[−]), by substituting the X with F as shown in Scheme 5.1a.⁹ Alkali metal fluorides, HF-based reagents, and tetrabutylammonium fluorides have been chosen as the fluoride source over the years. In earlier research, hypervalent halogen derivatives, such as

bis(pyridine)iodine(I) tetrafluoroborate (IPy₂BF₄)¹⁰ and paratrimethylphenylbromine difluoride¹¹ have been used as the fluoride sources. Recently, some new fluoride sources have been developed for fluorination reactions with higher activity and yield. For example, anhydrous TBAF was developed by DiMaggio and co-workers.¹² An air stable fluorination reagent BrF₃.KHF₂ was prepared by Hara and co-workers.^{3b} Hammond and co-workers described a complex of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone with HF (DMPU/HF) for fluorination reactions too.¹³

Scheme 5.1. Nucleophilic fluorination scheme.⁸

Deoxofluorination presents an alternative route for nucleophilic fluorination of alcohols as shown in Scheme 5.1b. In this reaction, the alcohol functions as nucleophile where it reacts with a deoxofluorinating agent to form an activated alcohol (XO⁻) and a fluoride ion in situ. Subsequently, the fluoride ion then displaces the leaving group (XO⁻) to produce the final fluoride product. Diethylaminosulfur trifluoride (DAST)¹⁴ and bis(2-methoxyethyl)aminosulfur trifluoride (Deoxo-Fluor)¹⁵ are the most commonly used fluoride sources in this type of reactions.

Electrophilic fluorination

In electrophilic fluorination, the substrate behaves as the nucleophile while the electrophile is a reagent that will deliver an equivalent of “F⁺”.¹⁶ As illustrated in Scheme 5.2, a nucleophile can be a carbanion (A), an electron-rich aromatic compound (B), or a substrate bearing a nucleophilic and labile bond (C).

Scheme 5.2. Electrophilic fluorination scheme.⁸

Typical examples of electrophilic fluorine sources (Scheme 5.3) are *N*-fluoropyridinium salts (NFPy),¹⁷ *N*-fluorobenzenesulfonimide (NFSI),¹⁸ 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (Selectfluor®),¹⁹ and its derivative 1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2,2,2]octane bis(tetrafluoroborate) (Accufluor)²⁰.

Scheme 5.3. Commonly used electrophilic fluorine sources.

Radical fluorination

In radical fluorination, the C–F bond is formed when a carbon-based radical reacts with an “atomic fluorine” source as shown in Scheme 5.4.²¹ Formerly, XeF₂, hypofluorite, or difluorine molecules were used as the fluorine source in such reactions. Recently, some electrophilic fluorine source like Selectfluor®²² and *N*-fluorobenzenesulfonimide²³ were

also reported as fluorine atom sources.

Scheme 5.4. Radical fluorination scheme

5.2 Photoredox fluorination reaction

Photochemistry represents an area of valuable and economical chemistry, since visible light is a safe, renewable, and inexpensive source of chemical energy that can facilitate the construction of organic molecules.²⁴ Photoredox fluorination involves a photocatalytic activation of C–H bond to generate a C–F bond in-situ. Ru– and Ir– based complexes are commonly employed as photocatalysts,²⁵ although some organic dyes can also be used as inexpensive alternatives.²⁶ However, the greatest limitation of this approach is the applicability to only substrates bearing suitable electroactive moieties that match the redox potentials (either in the ground or in the excited state) of the photocatalyst used. As a result, new photocatalysts are required that are specific to the photoredox fluorination reactions.

Recently, aromatic ketones were used as photocatalysts in benzylic fluorination of alkylbenzenes by Selectfluor® as the fluorine source. For example, the reaction of ethylbenzene with Selectfluor®, catalyzed by 9-fluorenone under visible-light irradiation, gave a 85% yield product after 6 h (Scheme 5.5a).²⁷ The proposed mechanism is shown in Scheme 5.5b. Generally, visible light activates diarylketones to abstract a benzylic hydrogen atom selectively. Adding a fluorine radical donor yields the benzylic fluoride and regenerates the catalyst.

Scheme 5.5. (a) Visible light fluorination of alkylaromatics and (b) the proposed mechanism.²⁷

Tan's group recently reported that anthraquinone (AQN) as the photocatalyst and Selectfluor® as the fluorine source could be utilized for the photochemical fluorination of sp^3 C–H bonds (Scheme 5.6).²⁸ The proposed mechanism involved an initial energy transfer between the triplet state of anthraquinone (^3AQN) and Selectfluor®, which was also suggested to be a key step of H-abstraction from the substrate. The activated substrate reacted with a fluorine radical and formed the final product. However the proposed mechanism is just based on synthetic selectivity studies and density functional theory (DFT) calculations. The detailed mechanism between AQN and Selectfluor® has

not been worked out yet.

Scheme 5.6. Fluorination of aromatic ketones.²⁸

5.3 Aims of thesis research

Chemoselective photoredox fluorination is an appealing approach to access fluorinated fine chemicals, but most of the known procedures currently lack time-resolved mechanistic insights. In a collaboration with my colleague, who conducted the nanosecond transient absorption spectroscopic studies, I performed DFT calculations to elucidate the elementary steps after irradiation in a photocatalytic fluorination procedure that was reported by Prof. Choon Hong Tan's group recently.²⁸ My colleague's time-resolved optical spectroscopy suggests that direct reaction only occurs between the photoexcited AQN and Selectfluor®. We observed spectroscopic evidence of a novel transient anthraquinone-Selectfluor® exciplex for the first time. Further mechanistic studies by DFT calculations performed by me suggest that the AQN-Selectfluor® triplet exciplex formed by photoirradiation is responsible for initiating and sustaining the

fluorination reaction.²⁹

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Chapter 6. Mechanistic Understanding of Photoredox Fluorination with Anthraquinone and Selectfluor® Using Time-Resolved Studies

6.1 Introduction

The introduction of fluorine atom(s) into organic molecules *via* various fluorination reactions has advanced in dramatic ways in the recent decades.¹ A number of protocols have been developed for the chemoselective synthesis of fluorinated fine chemicals and drugs.^{1b,2} Most fluorination methods rely on functional group transformation or metal-catalyzed C–H insertion/abstraction.^{2b,2c,3} Recently, photoredox fluorination reaction has emerged as a powerful tool in the synthesis of organofluorides, by harnessing visible light as a sustainable energy source to directly incorporate a fluorine atom onto aromatic compounds under mild conditions.⁴ Selectfluor® is usually employed as the fluorine source for the photocatalytic fluorination of sp^3 C–H bonds^{3b,5} and alkyl radicals generated from decarboxylation reactions.^{4a,4d,6} For example, Chen's group utilized 9-fluorenone as photocatalyst to catalyse benzylic C–H monofluorination with Selectfluor®, they obtain 85% product yields after 6 h of visible-light irradiation.⁷ Ye's group reported a visible-light photoredox catalysis for the decarboxylative fluorination of aliphatic carboxylic acids and Selectfluor® by organic dyes.^{4a} Tan and the co-workers from our university recently employed anthraquinone (AQN) as the photocatalyst and Selectfluor® as the fluorine source to demonstrate the photochemical fluorination of sp^3 C–H bonds (Scheme 6.1). Notably, this system has a preference towards electron rich secondary C–H bonds,⁸ and is consistent with the selectivity of cationic *N*-radicals

reported previously.⁹ The selectivity studies and density functional theory (DFT) calculations suggested that the AQN photosensitizer initiated the photoredox chemistry *via* a reaction between the excited-state AQN¹⁰ and Selectfluor®. A related mechanistic study by Lectka and co-workers supports this hypothesis that cationic *N*-radicals generated from Selectfluor® function as the hydrogen abstractor in a fluorination reaction.¹¹ However, the detailed mechanism between AQN and Selectfluor® has not been studied.

In this work, we use transient absorption spectroscopic studies to demonstrate that AQN only reacts with Selectfluor® to form an AQN-Selectfluor® exciplex, which is supported by our DFT¹² calculations. There is no direct reaction observed between AQN and dimethyl adipate as a representative substrate. The DFT studies also offer insights to the mechanistic pathway for this radical fluorination reaction.

Scheme 6.1. Photoredox fluorination protocol previously reported by Tan and co-workers.¹³

6.2 Results and discussion

6.2.1 Transient absorption property of AQN

Transient absorption measurements of a solution of 165 μM AQN in degassed acetonitrile (ACN), and the same solution of AQN in the presence of Selectfluor®, Selectfluor® II, and 1-fluorotrimethylpyridinium tetrafluoroborate as fluorine sources

were obtained. The transient absorption spectrum in Figure 6.1a (red line) shows that, the absorption of AQN after irradiation with a 355 nm nanosecond pulse is different from the reported spectra. It was previously reported that the triplet $^3\text{AQN}^*$ species displays bands with λ_{max} at 380 and 660 nm.¹⁴ However, according to the transient absorption spectrum that we obtained, it appears to correspond to a superposition of the AQN radical anion ($\bullet\text{AQN}^-$) and the AQN semiquinone radical ($\bullet\text{AQN}^{\text{H}}$).^{14a,15} It could be due to the triplet $^3\text{AQN}^*$ reacting with H atom sources in the solvent to form $\bullet\text{AQN}^{\text{H}}$,¹⁶ or the reaction with ground-state AQN to form the radical cation ($\bullet\text{AQN}^+$) and $\bullet\text{AQN}^-$ at high AQN concentrations.¹⁷

Figure 6.1. (a) Transient absorption spectra of 165 μM AQN (red), in the presence of Selectfluor® (blue), Selectfluor® II (green) or 1-fluorotrimethylpyridinium tetrafluoroborate (grey) obtained 2 μs after pulsed 355 nm irradiation. The black arrow indicates the transient absorption signal assigned to the $\bullet\text{AQN}^{\text{H}}$ radical. (b) Difference spectra obtained by subtracting the transient spectra of AQN from the corresponding normalized transient spectra of AQN (same color scheme as part (a) with the respective fluorinating agents (63 mM), obtained 2 μs after pulsed 355 nm irradiation).

The range of transient absorption measurements were from 365 nm to 805 nm. The temporal profile at 375 nm upon 355 nm pulsed irradiation of AQN only and in the presence of Selectfluor® (Figure 6.2a) can be fit to a bi-exponential decay. The faster component corresponding to a decay lifetime of $16.0 \pm 0.1 \mu\text{s}$ can be attributed to the recovery of AQN from $\bullet\text{AQN}^-$. The slower decay lifetime of $128 \pm 0.6 \mu\text{s}$, can be due to

the recovery of AQN from $\bullet$ AQNH. The related decay lifetimes are all listed in Table 6.1.

Figure 6.2. (a) Transient absorption signal at 375 nm upon 355 nm pulsed irradiation of AQN only (red) and in the presence of Selectfluor® (blue). (b) Transient absorption signal at 375 nm upon 355 nm irradiation of AQN with 94 mM dimethyl adipate in the absence (cyan) and presence of Selectfluor® (orange). The black lines represent the bi-exponential fits for the respective decay signals.

In addition, from the transient absorption spectrum of $\bullet$ AQN⁻ in Figure 1a, we observed that there is a distinctive feature at 545 nm (red square in Figure 6.1a),¹⁵ which has a lifetime of $21.2 \pm 0.1 \mu s$ under our experimental conditions (Figure 6.3a). On the other hand, the transient absorption spectrum of $\bullet$ AQNH displays a broad absorption band centered at 745 nm, which can be fit to a longer-lived decay of $123 \pm 0.8 \mu s$. The results are similar to the decay experiments in Figure 6.2. We also obtained the transient absorption spectra of AQN at different concentrations from 21 μM to 165 μM , but we did not detect the formation of 3 AQN* (Figure 6.3b). The transient absorption spectra that we observed differs from previous reports could be due to the differences in pulse energies used,^{14a} thermal repopulation of the 1 AQN at room temperature,¹⁸ and the high quantum yields of $\bullet$ AQNH formation at low light intensities.¹⁶ Since the purpose of our study is to investigate the mechanism as similar as possible to the photo-fluorination reaction conditions, we did not attempt to access the triplet state under other possible conditions.

Figure 6.3. (a) Transient absorption signal of 165 μM AQN at 545 nm upon 355 nm pulsed irradiation of anthraquinone. The red line is the mono-exponential fit for the decay. (b) Transient absorption spectra of AQN at different concentrations (red: 165 μM , green: 83 μM , blue: 41 μM , black: 21 μM) obtained 2 μs after pulsed 355 nm irradiation. The black arrow indicates the absence of the reported peak at 660 nm expected for $^3\text{AQN}^*$.

Table 6.1. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm, after 355 nm irradiation.

Wavelength	Decay lifetimes ^a (μs)	
	AQN	Selectfluor®
375 nm	16.0 ± 0.1 (60%)	2.04 ± 0.005 (85%)^b
	128 ± 0.6 (40%)	108 ± 0.4 (15%)
455 nm	1.69 ± 0.05 (74%) ^b	3.72 ± 0.01 (86%)^b
	120 ± 1 (26%)	65.9 ± 0.6 (14%)
745nm	10.5 ± 0.1 (62%)	2.39 ± 0.009 (83%) ^b
	123 ± 0.8 (38%)	123 ± 0.8 (17%)

^a Relative contributions of the decay components are presented in parentheses.

^b Lifetimes shorter than 10 μs were fitted from transient absorption data within the first 15 μs .

6.2.2 The effects of Selectfluor®

The time-resolved measurements were carried out on AQN solutions with the addition of 3.8 to 760 equivalents of Selectfluor® (0.63 to 126 mM). The transient *emission* spectrum of AQN only was used as a comparison. From Figure 4, it was observed that the transient *emission* spectra of AQN solution with Selectfluor® are different from AQN itself, which demonstrated a reaction between AQN and Selectfluor®. We used AQN solutions with 380 equivalents of Selectfluor® (63 mM) in most of our experiments in

order to compare with reaction mixtures that were used for the photo-fluorination reaction, which had the same concentrations.⁸ As we showed in Figure 1a, the absorption spectrum of AQN solution with Selectfluor® (blue line) at 2 μ s after 355 nm laser excitation exhibited a different profile from the $\bullet$ AQN⁻ and $\bullet$ AQNH species in red line. The new diagnostic shoulder at $\lambda_{\text{max}} = 455$ nm can be assigned to the absorption of a $\bullet$ AQN-Selectfluor® triplet diradical, which has been corroborated by the results of our new DFT studies (*vide infra*).⁸ Furthermore, the $\bullet$ AQN⁻ species, which has an absorption band at 545 nm was no longer observed in the AQN solution sample with Selectfluor®.

Figure 6.4. Transient *emission* spectra of 165 μ M AQN with different concentrations of Selectfluor® obtained 2 ns after pulsed 355 nm irradiation. The transient *emission* spectrum of 165 μ M AQN only is included for comparison.

At the same time, under the oxidizing conditions of Selectfluor®, the transient absorption signal of $\bullet$ AQNH in the spectrum diminished dramatically. It can be clearly seen from the decay profile at 375 nm. In Figure 6.1a, the blue line of decay profile of AQN solution in the presence of Selectfluor® shows the faster component accounting for 15% of the decay signal, instead of 40% for the signal without Selectfluor® (Table 6.1). Likewise, in

the isolated region at 745 nm, the faster component shows a decreased contribution of 17%, instead of 38% in the sample with the absence of Selectfluor®. However, the band at 455 nm is complicated by the superposition of multiple transient species, but it is still clearly distinct from the data without Selectfluor® (Table 6.1).

Subsequently, we did the concentration-dependence study of Selectfluor® on the lifetimes and absorption spectra of the transient species with the data listed in Table 6.2. When we increased the concentrations of Selectfluor® from 0.63 to 126 mM, the decay lifetimes of the photoexcited transient species did not show any significant change. Even at short time-scales, the decay lifetimes and transient absorption spectra remained similar (Figure 6.5). All these observations demonstrated the formation of a singlet excited state intermediate that decays to a longer-lived triplet AQN-Selectfluor® exciplex within the pulse-width of the UV photoexcitation source.

Table 6.2. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of anthraquinone (AQN) with varying concentrations of Selectfluor®.

Wavelength	Decay lifetimes ^a (μs)			
	126 mM Selectfluor®	63 mM Selectfluor®	6.3 mM Selectfluor®	0.63 mM Selectfluor®
375 nm	3.31 ± 0.01 (84%)^b	2.04 ± 0.005 (85%)^b	5.40 ± 0.03 (85%)^b	5.18 ± 0.03 (82%)^b
	159.4 ± 0.9 (16%)	108 ± 0.4 (15%)	169 ± 1 (15%)	192 ± 1 (18%)
455 nm	5.37 ± 0.07 (75%)^b	3.72 ± 0.01 (86%)^b	7.2 ± 0.1 (86%)^b	5.8 ± 0.1 (80%)^b
	131 ± 1 (25%)	65.9 ± 0.6 (14%)	154 ± 4 (14%)	119 ± 3 (20%)
745nm	3.82 ± 0.02 (82%) ^b	2.39 ± 0.009 (83%) ^b	5.47 ± 0.06 (82%) ^b	5.14 ± 0.6 (80%) ^b
	113 ± 3 (18%)	123 ± 0.8 (17%)	156 ± 2 (18%)	152 ± 2 (20%)

^a Relative contributions of the decay components are presented in parentheses.

^b Lifetimes shorter than 10 μs were fitted from transient absorption decay data within the first 15 μs.

Figure 6.5. (a) Transient absorption spectra of AQN-Selectfluor® exciplex, and (b) transient absorption temporal decay profiles at 455 nm upon 355 nm pulsed irradiation of 165 μ M AQN with different concentrations of Selectfluor® (green: 126 mM, blue: 63 mM, pink: 6.3 mM; gray: 0.63 mM). The black lines represent the mono-exponential fits for the respective decay signals.

In addition, we also conducted the irradiation of AQN solution with other fluorine sources, such as Selectfluor® II and 1-fluoro-2,4,6-trimethylpyridinium BF_4 (F-Py). The resultant transient absorption spectra (green and grey lines in Figure 6.1) were similar to the spectrum when Selectfluor® was used. The time decays observed at 455 nm with these fluorine sources also match the lifetime when Selectfluor® was used (Figure 6.6).

Figure 6.6. Transient absorption signal at 375 nm upon 355 nm pulsed irradiation of AQN in the presence of Selectfluor® II (green) or F-Py (grey). The black lines represent the bi-exponential fits for the respective decay signals.

The use of different fluorine sources (Selectfluor®, Selectfluor® II and F-Py) to react with AQN gave similar transient spectral profiles and lifetimes (Table 6.3) under the same irradiation conditions. Therefore, we believe that the absorption band at 455 nm can be assigned to a •AQN-Selectfluor® triplet diradical. When we compare the transient absorption spectra in Figure 6.1a, the ΔOD of Selectfluor® is higher than Selectfluor® II and F-Py, which indicated that Selectfluor® is the most effective reagent in producing the transient AQN exciplex. However, the absorption of Selectfluor® II is slightly lower than that of F-Py. It could be due to the lower solubility of Selectfluor® II in ACN resulting in a lower concentration of Selectfluor® II during the experiments. On the other hand, we noticed that the trend of ΔOD is correlated with the thermodynamic driving force for fluorine transfer to AQN; when we compare the reduction potentials of the fluorine sources, it also decreases in a similar fashion (Selectfluor®: -0.04 V; Selectfluor® II: -0.09 V and F-Py: -0.73 V vs SCE).¹⁹ Based on these studies, we were able to extract the difference spectra between AQN *with* the fluorine source, and the spectrum of AQN *without* fluorine source (Figure 6.1b). The difference spectra in Figure 6.1b exhibit a significant band of $\lambda_{\max}$ around 425 nm, which is supported by our DFT calculations (*vide infra*).

Table 6.3. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of AQN with either 63 mM Selectfluor® II or F-Py.

Wavelength	Decay lifetimes ^a (μ s)	
	Selectfluor® II	1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (F-Py)
375 nm	3.65 ± 0.01 (72%) ^b	2.31 ± 0.01 (65%) ^b
	128 ± 0.5 (28%)	157 ± 0.7 (35%)
455 nm	4.67 ± 0.07 (74%) ^b	3.47 ± 0.05 (76%) ^b
	86 ± 2 (26%)	140 ± 2 (24%)
745nm	3.50 ± 0.03 (85%) ^b	2.56 ± 0.03 (70%) ^b
	111 ± 2 (15%)	139 ± 2 (30%)

^a Relative contributions of the decay components are presented in parentheses.

^b Lifetimes shorter than 10 μ s were fitted from transient absorption decay data within the first 15 μ s.

6.2.3 The influence study of substrates

To study the effect of reaction substrates in the photo-fluorination reaction, we conducted the transient absorption study of AQN with substrates in degassed ACN solution. Here, we use dimethyl adipate as an example. Compared to the AQN spectrum, the spectrum of AQN with dimethyl adipate in Figure 6.7a (cyan line) remains largely unchanged. When Selectfluor® was added to the AQN solution containing dimethyl adipate, the transient absorption spectrum of the three-component sample also coincided with those containing only AQN and Selectfluor® (Figure 6.7b). The excited state decay lifetime of the AQN solution with dimethyl adipate at 375 nm is also similar to that in the absence of Selectfluor® (Table 6.4). As a result, we confirm that the substrates, such as dimethyl adipate, do not directly react with the photoexcited AQN, since there are no dramatic changes in the time-resolved spectroscopic studies. On the contrary, the data indicates that the photoexcited AQN reacts with Selectfluor® to form an AQN-Selectfluor® exciplex, which is being observed here for the first time experimentally. Since the cationic *N*-radicals and substrate radicals do not possess spectral signatures in the wavelength range of our experiments, we are able to spectrally detect the AQN-Selectfluor® exciplex. The remarkable selectivity for the fluorination reactions in our previous report⁸ can be attributed to the controlled abstraction of secondary H atoms from sites furthest from electron-withdrawing groups.

Figure 6.7. (a) Transient absorption spectra of 165 μM AQN only (red), and in the presence of 94 mM dimethyl adipate (cyan), 2 μs after pulsed 355 nm irradiation. (b) Transient absorption spectra of 165 μM AQN in the presence of 63 mM Selectfluor®, in the absence (blue), and in the presence of 94 mM dimethyl adipate (orange), 2 μs after pulsed 355 nm irradiation.

Table 6.4. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of 165 μM AQN and 94 mM dimethyl adipate with and without 63 mM Selectfluor®.

Wavelength	Decay lifetimes ^a (μs)	
	94 mM dimethyl adipate	94 mM dimethyl adipate and 63 mM Selectfluor®
375 nm	17.2 ± 0.1 (65%)	1.97 ± 0.005 (86%) ^b
	141 ± 0.6 (35%)	117 ± 0.5 (14%)
455 nm	2.42 ± 0.02 (74%) ^b	3.53 ± 0.02 (87%)^b
	119.7 ± 0.9 (26%)	216 ± 3 (13%)
745nm	22.9 ± 0.3 (63%)	2.76 ± 0.01 (88%) ^b
	208 ± 2 (37%)	170 ± 2 (12%)

^a Relative contributions of the decay components are presented in parentheses.

^b Lifetimes shorter than 10 μs were fitted from transient absorption decay data within the first 15 μs .

6.2.4 The quenching study of the AQN-Selectfluor® exciplex

Since we proposed that the photoexcited AQN can react with Selectfluor® to form an AQN-Selectfluor® exciplex, we were interested in studying the quenching rate of the AQN-Selectfluor® exciplex. We proceeded to measure the lifetimes and absorption spectra of the AQN exciplex with different dimethyl adipate concentrations. From Figure

6.8, we observed that there was a decrease in both the intensity and lifetime of the transient signal of exciplex at 455 nm as the concentration of dimethyl adipate increases from 1.5 to 12 equivalents. It demonstrated that the AQN-Selectfluor® exciplex was quenched in the presence of dimethyl adipate. A Stern-Volmer plot (Figure 6.9) was obtained from the decay lifetimes of transient signal at 455 nm arising from the exciplex in the presence of varying amounts of dimethyl adipate. A quenching rate constant k_q of $1.5 \pm 0.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ was obtained. In the absence of dimethyl adipate, the exciplex prefers to decay back to form AQN and Selectfluor®. On the other hand, in the presence of dimethyl adipate, the exciplex is expected to initiate a chain reaction with the substrate to give HF and alkyl radicals, the latter of which can then react with more Selectfluor® or the transient exciplex to give the fluorinated product.

We also determined the quantum yield of the fluorination reaction by using a ferrioxalate actinometer.²⁰ However, a low quantum yield of only 0.13 was obtained. This suggests a possibility of a closed catalytic loop or inefficient chain processes.²¹ In another case, it may also form *N*-(chloromethylated)-1,4-diazabicyclo[2.2.2]octane as a side product which complicates the reaction.²² Attempts carried out to trap the cationic *N*-radical and alkyl radical intermediates with TEMPO and nitrosobenzene were unsuccessful. A probable reason is that the radical traps quench the reaction between AQN and Selectfluor®.

Figure 6.8. Transient absorption signal of AQN-Selectfluor® exciplex at 455 nm upon 355 nm pulsed irradiation of 165 μM AQN with 63 mM Selectfluor® with varying concentrations of dimethyl adipate (blue: 0 mM; orange: 94 mM; red: 376 mM; green: 752 mM).

Figure 6.9. Stern-Volmer plot for the quenching of the transient absorption signal of AQN-Selectfluor® exciplex at 455 nm by varying concentrations of dimethyl adipate.

6.2.5 Proposed mechanism of the photofluorination reaction

UV-vis spectroscopy was utilized to study the steady-state absorption behaviors before

and after laser flash photolysis (Figure 6.10). The results observed agreed with the mechanism proposed in Figure 6.11. The UV-vis spectra in Figure 6.10a show that in the absence of Selectfluor®, there was a characteristic absorption at $\lambda_{\text{max}} = 380$ nm in both AQN solution with or without substrates. The vibronic structure of that absorption can be attributed to the formation of 9,10-dihydroxyanthracene (DHA, black arrow, Figure 6.10a) during the photolysis. After AQN was irradiated, the excited triplet state $^3\text{AQN}^*$ reacts with H atom sources in the solvent to form $\bullet\text{AQN}^{\text{H}}$, or reacts with ground-state AQN to form $\bullet\text{AQN}^-$. Both $\bullet\text{AQN}^{\text{H}}$ and $\bullet\text{AQN}^-$ radicals can form DHA in a series of disproportionation and acid-base reactions.^{10,14a}

Figure 6.10. (a) UV-vis spectra of AQN after transient absorption measurements without (red) and with dimethyl adipate (cyan). The black arrow indicates the appearance of 9,10-dihydroxyanthracene after transient absorption measurements. The UV-vis spectrum of AQN only before photolysis (purple) is included for comparison. (b) UV-vis spectra of AQN after transient absorption measurements in the presence of Selectfluor® (blue), Selectfluor® II (grey), F-py (green) and both Selectfluor® and dimethyl adipate (orange).

On the other hand, the UV-vis spectra after photolysis of AQN with different fluorine sources resulted in gradual photobleaching, but there was no characteristic absorption of DHA observed. It could be because the oxidizing environments in the presence of the cationic fluorinating agents preclude the formation of DHA. NMR spectroscopy and mass spectrometry were employed to probe the identity of the photobleached products.

AQN remained unchanged after the irradiation, while Selectfluor® was found to have degraded and gave *N*-(chloromethylated)-1,4-diazabicyclo[2.2.2]octane cation as the byproduct. The formation of the byproduct could be due to H abstraction by the cationic *N*-radicals from impurities in ACN solution. A fluoride-containing byproduct was also found in ^{19}F NMR spectrum with a chemical shift at 183.8 ppm. The chemical shift indicates the existence of HF in the ACN solution.²³ However, since borosilicate glass NMR tubes was used for NMR characterization, HF will probably etch the glass, so we postulate that this signal originated from a solvated F^- , a result of AQN-Selectfluor® exciplex photodegradation in the absence of substrate.

Figure 6.11. (a) Proposed reaction pathways for AQN after 355 nm photoexcitation in ACN in the absence of a substrate. (b) The TD-DFT calculated UV-vis absorption spectra. The black vertical lines represent the oscillator strengths from TD-DFT results and the observed transient absorption spectrum for the AQN-Selectfluor® exciplex from Fig 1b is in dark grey.

A proposed mechanism of the photofluorination reaction is shown in Scheme 6.2. The reactants AQN and Selectfluor® would be activated after irradiation to generate an AQN-Selectfluor® exciplex. When an alkyl substrate is present, the AQN-Selectfluor® exciplex reacts with the alkyl substrate in solution to give cationic *N*-radicals and alkyl radicals. The cationic *N*-radicals are expected to initiate a chain reaction with the another equivalent substrate to form more alkyl radicals, which can in turn react with Selectfluor® or the AQN-Selectfluor® exciplex to yield the fluorinated product. DFT calculations were utilized to further investigate the proposed mechanism.

Scheme 6.2. Proposed mechanism of the photofluorination reaction.

6.2.6 TD-DFT calculation of the exciplex

The identity of the newly observed AQN-Selectfluor® exciplex was confirmed through time-dependent DFT (TD-DFT) calculations by using the WB97XD functional developed by Head-Gordon et al. and the 6-311G+(2d) basis set. All the calculations were performed with the Gaussian 09 software. As we can see from Figure 6.11b, the calculated absorption spectrum of the AQN-Selectfluor® exciplex (blank line) exhibits an absorption band centered around 433 nm. These calculated UV-vis bands of the

exciplex are similar to the dark grey transient spectra that we have observed (Figure 6.1b).

6.2.7 DFT calculations on the exciplex

The reaction mechanism of AQN in the presence of Selectfluor® and pentane as a representative sp^3 hybridized substrate was further investigated with DFT calculations by using the WB97XD functional and the 6-311G+(2d) basis set. The WB97XD functional is known to be a good choice to study the reaction mechanisms of small organic compounds, including excited state reactions. The calculations with other functionals were also attempted. However, the results suggested that they were not suitable for handling the open-shell systems involved in this project. The calculations were carried out under non-solvent conditions, since the electronic energy change was the main part of energy landscape in this photofluorination reaction. Some DFT calculations in the presence of solvents were also carried out, but the results showed that they were not significant compared to the electronic energy change. All the calculations were performed with the Gaussian 09 software.

As shown in Figure 6.12a, AQN and Selectfluor® (S_0) can interact to form a van der Waal's complex **RC1**, which can be photoexcited to a short-lived S_1 state after irradiation with an energy gap of about $68.3 \text{ kcal mol}^{-1}$. This energy gap corresponds to a photon of $\sim 419 \text{ nm}$, which concurs with the fact that common, low-powered household lamps and our 355 nm nanosecond pulses have the requisite energy to trigger this photoexcitation. Rapid intersystem crossing will occur in an exothermic, non-radiative relaxation from the S_1 to the T_1 state, after which a spontaneous intramolecular reorganization process will occur to give the AQN-Selectfluor® exciplex (**Int1**). No transition state was detected by

DFT calculations.

The geometry of AQN-Selectfluor® exciplex exhibits a dramatically lengthened N-F bond with a distance of 2.0 Å, instead of the 1.3 Å originally found in Selectfluor®. The average C-F bond distance in AQN-Selectfluor® exciplex is 2.9 Å. This suggests that the AQN-Selectfluor® exciplex possesses a highly activated transferable fluorine with the fluorine atom stabilized by one of the aromatic rings of AQN. The spin density of AQN-Selectfluor® exciplex is predominantly delocalized over AQN and F (61%), with only small contributions from Selectfluor® (Figure 6.12c). Since the optical absorption bands are largely dictated by the AQN-F interactions (Selectfluor® is aliphatic and colorless), the transient absorption spectra will be independent of the electrophilic fluorinating agent employed.

A pentane molecule was used as the model alkyl substrate in the calculation. When pentane was added close to **Int1**, a van der Waal's complex (**Int2**) formed at -9.9 kcal mol⁻¹ first (Figure 6.12b). The reactive AQN-Selectfluor® exciplex in **Int2** was found to be able to abstract a hydrogen atom from pentane and initiate the radical fluorination process when the distance of fluorine atom and hydrogen atom (bold in Figure 6.12b) was shortened. The weakest *sp*³ hybridized secondary carbon in **TS1** would react to yield a secondary pentane radical, a Selectfluor® *N*-radical, HF, and AQN with a thermally accessible activation barrier of only 9.9 kcal mol⁻¹.

Figure 6.12. Proposed reaction pathway from DFT calculations for the initiation of the radical fluorination process by (a) formation of the AQN-Selectfluor® exciplex in **Int1**, and (b) generation of the secondary pentane and Selectfluor® N-radicals from the exciplex. (c) Depiction of the spin density for the triplet AQN-Selectfluor® exciplex. Note the significant spin density on the fluorine atom of the elongated N-F bond bridging Selectfluor® and AQN.

Both the Selectfluor® N-radical and secondary pentane radical formed from the dissociation of **Int3** were expected to have reaction activity in the solution. When Selectfluor® N-radical and another pentane came close, a stable van der Waal's complex (**Int4**) formed (Figure 6.13a). The active Selectfluor® N-radical in **Int4** can abstract a hydrogen atom from pentane to generate a Selectfluor® N-H molecule and a pentane radical and readily overcome the thermally accessible activation barrier of only 2.0 kcal mol⁻¹ via **TS2**.

The active pentane radical was proposed to abstract a fluorine atom from both Selectfluor® and AQN-Selectfluor® exciplex to produce the final fluorinated product. It was clarified in the following calculation. As shown in Figure 6.13b, the secondary pentane radical could react in a facile fashion with Selectfluor® to surmount a thermally accessible activation barrier of only 7.6 kcal mol⁻¹ between **Int6** and **Int7** via **TS3** in the highly exothermic fluorine atom transfer process.

Concurrently, the pentane radical can also react with the AQN-Selectfluor® exciplex through a barrierless fluorine atom transfer process due to the extremely exothermic nature of this step (Figure 6.13c). The radical intermediates in both processes can then propagate the chain reaction. Both reaction pathways are thermodynamically and kinetically feasible under ambient conditions. However, since the quantum yield that measured is only 0.13, the chain propagation is likely to be inefficient. It indicates that

the AQN-Selectfluor® exciplex route is necessary for sustaining this radical fluorination process.

Figure 6.13. Proposed reaction pathway from DFT calculations for the propagation of the radical fluorination process through (a) hydrogen atom abstraction by the Selectfluor® *N*-radical from pentane to give a secondary radical, (b) fluorine atom transfer from Selectfluor® to the pentane radical to yield 3-fluoropentane and the Selectfluor® *N*-radical, and (c) fluorine atom transfer from **Int1** to the pentane radical to yield 3-fluoropentane, AQN, and the Selectfluor® *N*-radical.

6.3 Conclusion

In summary, both nanosecond transient absorption spectroscopy and DFT calculations have been used to study the detailed mechanism of a photoredox fluorination protocol reported previously. In light of the time-resolved optical spectroscopic study, we have observed a transient AQN-Selectfluor® exciplex formed only between the photoexcited AQN and Selectfluor® reaction for the first time. Moreover, no direct reaction was detected between AQN and the substrate. The formation of the AQN-Selectfluor® exciplex was confirmed by both TD-DFT and DFT calculations. The DFT calculations suggested that the AQN-Selectfluor® exciplex reacted with the substrate to form a secondary aliphatic and a Selectfluor® *N*-radical, both of which have thermally accessible activation barriers for exothermic F and H atom transfer processes, respectively. However, the sub-unity quantum yield of 0.13 indicates that chain reaction will be terminated during the catalytic process. Thus the formation AQN-Selectfluor® exciplex is the critical step to sustain the photodriven radical fluorination reaction.

6.4 Experimental Section

6.4.1. General information

All chemicals were obtained from Sigma-Aldrich and used as received without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories

and were used as received. Anhydrous ACN was collected from an Inert PureSolv MD5 solvent purification system prior to being degassed on a Schlenk line using several freeze-pump-thaw cycles. All solutions were prepared in a glovebox and transferred into a modified Schlenk apparatus fused with a quartz fluorimeter cuvette (Starna, 10 mm pathlength) before transient absorption and emission measurements were performed. UV-visible spectroscopic measurements were performed using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer and steady-state photoluminescence measurements were conducted using a Varian Cary Eclipse fluorescence spectrophotometer. The ^1H and ^{19}F NMR spectra were recorded at room temperature on a Bruker AVANCE 400 MHz spectrometer. The ^1H NMR chemical shifts (δ reported in ppm) were referenced to the residual solvent signal(s) while the ^{19}F NMR chemical shifts were referenced internally to α,α,α -trifluorotoluene (-63.72 ppm vs CFCl_3). Solutions of anthraquinone (AQN) were prepared by diluting a 1.65 mM stock solution of AQN (10.3 mg, 0.0495 mmol in 30.0 ml of degassed ACN).

6.4.2. Transient absorption measurements

The transient absorption and emission measurements were performed using an Edinburgh Instruments model LP920 transient absorption spectrometer equipped with a pulsed Xe probe lamp in conjunction with a Nd:YAG laser (Continuum model Surelite II-10) as the excitation source. The laser pulse width is 5-8 ns and the repetition rate is 10 Hz. During transient absorption measurements, the pulses are synchronized with the LP920 system at a frequency of 1 Hz. The pulse energy used was between 6-20 mJ/pulse. The data were fit to single exponential or biexponential functions to obtain the time constants for the transient signals according to the following two equations respectively:

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1}$$

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1} + A_2 e^{-(t-\tau_0)/\tau_2}$$

The parameters: y_0 , τ_0 , A_n , and τ_n were determined by a least-squares fitting procedure in Origin. The term y_0 corresponds to the vertical intercept at long lifetimes and indicates whether the signal decays to a ‘permanent’ bleach (negative y_0) or absorption (positive y_0). The variable τ_0 is the delay time of the excitation pulse from the start of the probe measurement during each photoexcitation cycle. A_n is the change in optical density after irradiation for the n th exponential term and τ_n is the corresponding time constant. The relative contribution of the n th term to the overall transient signal, c_n , was calculated using the following formula:

$$c_n = \frac{A_n}{A_1 + A_2}$$

6.4.3. Stern-Volmer plot for the quenching of $\bullet$ AQN-F radicals by dimethyl adipate

As the concentration of dimethyl adipate increases, the lifetime τ of the signal owing to AQN-Selecfleur® exciplex decreases. The quenching rate constant, k_q , is related to the lifetime, τ , of the AQN-Selecfleur® exciplex in the presence of dimethyl adipate with a concentration of $[Q]$ by the Stern-Volmer equation:

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$

where τ_0 is the lifetime of AQN-Selecfleur® exciplex in the absence of dimethyl adipate. The quenching rate constant, k_q , of the AQN-Selecfleur® exciplex by dimethyl adipate can be obtained by plotting a graph of τ_0/τ against $[Q]$ with a fixed vertical intercept of 1. The gradient ($k_q \tau_0$) was determined to be $0.54 \pm 0.05 \text{ M}^{-1}$ and τ_0 was determined to be $3.72 \pm 0.01 \text{ } \mu\text{s}$. This gives a rate constant, k_q , of $1.5 \pm 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

6.4.4. Quantum yield measurements

Potassium ferrioxalate ($\text{K}_3[\text{Fe}(\text{OX})_3] \cdot 3\text{H}_2\text{O}$, OX = oxalate) is a standard chemical actinometer for the determination of quantum yields for photochemical reactions under visible light in an aqueous medium.²⁴ Since the photoredox fluorination is performed in ACN, it is necessary to use a chemical actinometer that functions in ACN. Previously, our group has synthesized $(n\text{-Bu}_4\text{N})_3[\text{Fe}(\text{OX})_3]$ for this purpose and found that its quantum yield is 0.966 at 334 nm under AM1.5 irradiation.^{20b} Similarly, we have adopted this value and the same AM1.5 irradiation source to determine the quantum yield of the photoredox fluorination under AM1.5 irradiation.

The quantum yield of a photoreaction can be calculated using the equation

$$\Phi_2 = (f_1 \bullet \Phi_1 \bullet r_2) / (f_2 \bullet r_1),$$

where Φ_1 = a known quantum yield of a reference photoreaction,

r_1 = rate of reference photoreaction,

f_1 = fraction of light absorbed by the photoactive species in the reference photoreaction,

r_2 = rate of the photoreaction investigated,

f_2 = fraction of light absorbed by the photoactive species in the photoreaction investigated,

Φ_2 = quantum yield of the photoreaction investigated.

A 0.60 mL solution of 118 μM AQN with 44 mM Selectfluor[®] and 66 mM dimethyl adipate (0.0396 mmol) was irradiated in a J-Young NMR tube for 1 hour under AM1.5 solar irradiation. After 1 hour, an internal standard (1, 1, 2, 2-tetrachloroethane) was added before the NMR spectrum of the reaction mixture was collected. The amount of product obtained was determined to be 0.0107 mmol. The rate, r_2 was determined to be

$2.97 \times 10^{-6} \text{ mmol s}^{-1}$. The absorbance of this sample was found to be 0.48 at 334 nm, and the fraction of light absorbed at 334 nm, f_2 was determined to be 0.67 ($f_2 = 1 - 10^{-0.48} = 0.67$). The previously obtained values for the *n*-butylammonium ferrioxalate actinometer in ACN was $\Phi_1 = 0.966$ at 334 nm, $f_1 = 0.99$ at 334 nm, and $r_1 = 3.23 \times 10^{-5} \text{ mmol s}^{-1}$ under the same AM1.5 solar irradiation.^{20b}

Hence, the quantum yield for the photoredox fluorination can be determined:

$$\Phi_2 = (f_1 \bullet \Phi_1 \bullet r_2) / (f_2 \bullet r_1)$$

$$= \frac{0.99 \times 0.966 \times 2.97 \times 10^{-6} \text{ mmol s}^{-1}}{0.67 \times 3.23 \times 10^{-5} \text{ mmol s}^{-1}} = 0.13$$

6.4.5. DFT and TD-DFT calculations

All calculations in this work were performed using the Gaussian 09 D01 package.¹⁴ The WB97XD DFT functional¹⁷ was used in DFT and TD-DFT calculations together with the 6-311+G(2d) basis set. Preliminary calculations with other functionals suggested that they were not suitable for handling the open-shell systems involved in our study. Ultrafine grids were adopted for the numerical integration and default convergence criteria and integration grids were utilized for the numerical integration in both DFT and TD-DFT calculations.

6.5 References

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Appendix

Chapter 3

X-ray crystal structure data of complexes **6c** and **6c+KPF₆**.

Table A.3.1. Crystal data and structure refinement for **6c** grown from dichloromethane and methanol by diffusion with diethyl ether

Chemical formula	C ₂₆ H ₂₆ N ₂ NiO ₆	
Formula weight	521.20	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 × 0.200 × 0.260 mm	
Crystal habit	red plate	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 11.4913(4) Å	α = 90°
	b = 18.0722(7) Å	β = 90°
	c = 22.1742(11) Å	γ = 90°
Volume	4605.0(3) Å ³	
Z	8	
Density (calculated)	1.504 g/cm ³	
Absorption coefficient	0.889 mm ⁻¹	
F(000)	2176	
Theta range for data collection	2.25 to 28.28°	
Index ranges	-15 ≤ h ≤ 14, -23 ≤ k ≤ 24, -15 ≤ l ≤ 29	
Reflections collected	25084	
Independent reflections	5710 [R(int) = 0.0780]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9650 and 0.8020	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(F _o ² - F _c ²) ²	
Data / restraints / parameters	5710 / 0 / 318	
Goodness-of-fit on F²	1.065	
Δ/σ_{max}	0.001	
Final R indices	3631 data; I > 2σ(I)	R1 = 0.0444, wR2 = 0.1095
	all data	R1 = 0.0947, wR2 = 0.1583
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0772P) ²], where P=(F _o ² +2F _c ²)/3	
Largest diff. peak and hole	0.710 and -0.813 eÅ ⁻³	
R.M.S. deviation from mean	0.265 eÅ ⁻³	

Table Table A.3.2. Select bond lengths (Å) for **6c**

Ni1-O2	1.842(2)	Ni1-O1	1.846(2)
Ni1-N1	1.856(3)	Ni1-N2	1.864(3)
C7-N1	1.303(4)	C17-N2	1.304(4)

Table A.3.3. Select bond angles (°) for **6c**

O2-Ni1-O1	84.15(10)	O2-Ni1-N1	176.99(11)
O1-Ni1-N1	95.09(11)	O2-Ni1-N2	94.56(11)
O1-Ni1-N2	178.65(11)	N1-Ni1-N2	86.22(12)
C7-N1-Ni1	125.9(2)	C1-N1-Ni1	113.5(2)
C6-N2-Ni1	113.0(2)	C17-N2-Ni1	126.5(2)
C23-O2-Ni1	127.8(2)	C13-O1-Ni1	127.9(2)

Table A.3.4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for **6c**

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Ni1	0.16758(4)	0.05382(2)	0.62575(2)	0.01336(14)
C1	0.9806(3)	0.97119(18)	0.66465(15)	0.0156(7)
C2	0.8926(3)	0.91916(19)	0.66966(17)	0.0221(8)
C3	0.8233(3)	0.9190(2)	0.72062(17)	0.0233(8)
C4	0.8426(3)	0.96934(19)	0.76675(16)	0.0206(8)
C5	0.9317(3)	0.02050(18)	0.76258(15)	0.0172(7)
C6	0.0006(3)	0.02172(17)	0.71120(15)	0.0148(7)
C7	0.0451(3)	0.93955(18)	0.56636(15)	0.0172(7)
C8	0.1167(3)	0.94245(18)	0.51438(15)	0.0173(7)
C9	0.0900(3)	0.89376(19)	0.46557(15)	0.0200(7)
C10	0.1570(3)	0.8939(2)	0.41478(16)	0.0237(8)
C11	0.2536(3)	0.94126(19)	0.41043(15)	0.0215(8)
C12	0.2808(3)	0.98946(18)	0.45659(15)	0.0179(7)
C13	0.2122(3)	0.99238(17)	0.51011(14)	0.0147(7)
C14	0.4572(3)	0.0278(2)	0.40926(16)	0.0237(8)
C15	0.5510(3)	0.0843(2)	0.41636(16)	0.0235(8)
C16	0.6060(4)	0.2013(2)	0.37841(18)	0.0342(10)
C17	0.1263(3)	0.11977(17)	0.74004(15)	0.0162(7)
C18	0.2234(3)	0.16833(17)	0.73532(15)	0.0156(7)
C19	0.2493(3)	0.21472(18)	0.78543(15)	0.0170(7)
C20	0.3482(3)	0.25722(19)	0.78583(16)	0.0198(8)
C21	0.4233(3)	0.25493(18)	0.73579(16)	0.0195(8)
C22	0.4005(3)	0.21070(17)	0.68691(15)	0.0158(7)
C23	0.2981(3)	0.16617(17)	0.68482(15)	0.0148(7)
C24	0.4497(3)	0.2200(2)	0.58172(15)	0.0218(8)

	x/a	y/b	z/c	U(eq)
C25	0.5582(3)	0.22590(19)	0.54423(16)	0.0207(8)
C26	0.7273(3)	0.2974(2)	0.52936(19)	0.0295(9)
N1	0.0577(2)	0.97979(15)	0.61468(12)	0.0152(6)
N2	0.0956(2)	0.07089(14)	0.69982(12)	0.0138(6)
O1	0.24062(19)	0.03903(12)	0.55259(10)	0.0172(5)
O2	0.28237(19)	0.12349(12)	0.63753(10)	0.0167(5)
O3	0.3731(2)	0.03715(13)	0.45640(11)	0.0209(5)
O4	0.5119(2)	0.15407(14)	0.39447(12)	0.0276(6)
O5	0.48491(19)	0.20397(13)	0.64308(10)	0.0194(5)
O6	0.6238(2)	0.28821(13)	0.56381(12)	0.0241(6)

Table A.3.5. Anisotropic atomic displacement parameters (Å²) for **6c**

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ni1	0.0151(2)	0.0139(2)	0.0111(2)	-0.00002(17)	0.00143(17)	0.00094(17)
C1	0.0178(17)	0.0139(15)	0.0150(16)	0.0017(13)	0.0018(14)	0.0032(13)
C2	0.0250(19)	0.0193(17)	0.0221(18)	-0.0025(15)	0.0029(16)	-0.0028(15)
C3	0.0220(19)	0.0199(17)	0.028(2)	0.0037(16)	0.0021(16)	-0.0020(15)
C4	0.0237(18)	0.0178(17)	0.0204(18)	0.0017(14)	0.0068(16)	0.0023(15)
C5	0.0198(17)	0.0144(16)	0.0173(17)	-0.0010(14)	0.0022(15)	0.0029(14)
C6	0.0142(16)	0.0136(15)	0.0167(16)	0.0029(13)	-0.0009(14)	0.0027(13)
C7	0.0191(17)	0.0137(16)	0.0188(17)	0.0022(14)	-0.0010(14)	0.0011(13)
C8	0.0208(17)	0.0163(17)	0.0148(16)	0.0010(14)	-0.0014(15)	0.0053(14)
C9	0.0242(19)	0.0183(17)	0.0173(16)	-0.0026(14)	-0.0016(15)	0.0029(15)
C10	0.033(2)	0.0223(19)	0.0155(16)	-0.0035(15)	-0.0029(16)	0.0053(16)
C11	0.0290(19)	0.0236(19)	0.0118(16)	-0.0003(14)	0.0032(15)	0.0090(16)
C12	0.0204(18)	0.0166(17)	0.0166(17)	0.0029(14)	0.0011(15)	0.0057(14)
C13	0.0205(17)	0.0132(16)	0.0104(15)	0.0003(13)	-0.0018(14)	0.0066(14)
C14	0.027(2)	0.029(2)	0.0156(17)	0.0020(15)	0.0083(16)	0.0085(17)
C15	0.0221(18)	0.031(2)	0.0171(17)	0.0061(16)	0.0028(15)	0.0092(16)
C16	0.034(2)	0.041(2)	0.028(2)	0.0027(19)	0.0030(19)	-0.0139(19)
C17	0.0172(16)	0.0170(17)	0.0144(16)	0.0023(14)	0.0008(14)	0.0055(13)
C18	0.0148(16)	0.0143(16)	0.0178(17)	0.0017(13)	-0.0019(14)	0.0038(13)
C19	0.0176(16)	0.0182(17)	0.0153(16)	0.0011(13)	0.0017(14)	0.0049(14)
C20	0.0218(18)	0.0179(17)	0.0198(17)	-0.0032(14)	-0.0048(15)	0.0050(14)
C21	0.0184(18)	0.0185(17)	0.0215(18)	0.0009(14)	-0.0009(16)	0.0020(14)
C22	0.0172(17)	0.0161(16)	0.0141(16)	0.0007(13)	-0.0003(14)	0.0043(13)
C23	0.0157(16)	0.0139(16)	0.0146(16)	0.0026(13)	-0.0016(14)	0.0018(13)
C24	0.0195(17)	0.028(2)	0.0177(17)	0.0044(15)	-0.0012(15)	-0.0017(15)
C25	0.0204(17)	0.0210(18)	0.0207(18)	0.0002(15)	0.0022(15)	-0.0049(15)
C26	0.0205(19)	0.028(2)	0.040(2)	-0.0011(18)	0.0113(17)	-0.0062(16)

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N1	0.0191(14)	0.0132(13)	0.0134(14)	0.0016(11)	0.0007(12)	0.0011(12)
N2	0.0151(14)	0.0139(13)	0.0123(13)	0.0012(11)	-0.0015(11)	0.0023(11)
O1	0.0195(12)	0.0174(12)	0.0147(11)	-0.0017(9)	0.0023(10)	0.0010(10)
O2	0.0183(12)	0.0184(12)	0.0133(12)	-0.0020(10)	0.0025(10)	-0.0017(10)
O3	0.0219(12)	0.0237(13)	0.0171(12)	-0.0008(10)	0.0080(11)	0.0024(10)
O4	0.0204(13)	0.0284(14)	0.0339(15)	0.0117(12)	0.0003(12)	-0.0023(11)
O5	0.0134(11)	0.0297(14)	0.0153(11)	0.0019(10)	-0.0023(10)	-0.0002(10)
O6	0.0232(13)	0.0190(13)	0.0301(14)	-0.0053(11)	0.0094(12)	-0.0060(10)

Table A.3.6. Crystal data and structure refinement for **6c**+KPF₆ grown from dichloromethane and acetone by diffusion with diethyl ether

Chemical formula	C ₂₆ H ₂₆ F ₆ KN ₂ NiO ₆ P		
Formula weight	705.27 g/mol		
Temperature	103(2) K		
Wavelength	0.71073 Å		
Crystal size	0.120 × 0.140 × 0.420 mm		
Crystal habit	red needle		
Crystal system	monoclinic		
Space group	P 1 21/n 1		
Unit cell dimensions	a = 9.4723(5) Å	α = 90°	
	b = 18.6903(10) Å	β = 96.0152(16)°	
	c = 15.7123(9) Å	γ = 90°	
Volume	2766.4(3) Å ³		
Z	4		
Density (calculated)	1.693 g/cm ³		
Absorption coefficient	0.996 mm ⁻¹		
F(000)	1440		
Theta range for data collection	2.18 to 31.05°		
Index ranges	-13<=h<=13, -27<=k<=27, -22<=l<=22		
Reflections collected	58973		
Independent reflections	8845 [R(int) = 0.0744]		
Coverage of independent reflections	99.8%		
Absorption correction	Multi-Scan		
Max. and min. transmission	0.8900 and 0.6800		
Structure solution technique	direct methods		
Structure solution program	XT, VERSION 2014/4		
Refinement method	Full-matrix least-squares on F ²		
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)		
Function minimized	Σ w(F _o ² - F _c ²) ²		
Data / restraints / parameters	8845 / 820 / 519		
Goodness-of-fit on F ²	1.033		

$\Delta/\sigma_{\text{max}}$	0.001	
Final R indices	6390 data; $I > 2\sigma(I)$	R1 = 0.0411, wR2 = 0.0725
	all data	R1 = 0.0732, wR2 = 0.0842
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2 + 2.0817P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.509 and -0.618 eÅ ⁻³	
R.M.S. deviation from mean	0.085 eÅ ⁻³	

Table A.3.7. Select bond lengths (Å) for **6c** + KPF₆

Ni1-O1	1.8566(13)	Ni1-O4	1.8551(13)
N1-Ni1	1.8618(16)	N2-Ni1	1.8562(15)
K1-O1	2.7268(14)	K1-O2	2.8217(14)
K1-O3	2.7973(15)	K1-O4	2.6968(13)
K1-O5	2.7215(14)	K1-O6	2.928(13)
K1-F1	2.862(4)	K1-F2	2.926(5)
K1-F3	3.364(4)		

Table A.3.8. Select bond angles (°) for **6c** + KPF₆

N2-Ni1-N1	85.68(7)	N2-Ni1-O4	94.76(6)
O4-Ni1-O1	84.75(6)	O1-Ni1-N1	94.82(6)
C17-N2-Ni1	126.05(13)	C7-N1-Ni1	126.23(14)
C9-O1-Ni1	127.06(12)	C19-O4-Ni1	127.44(12)
Ni1-O1-K1	107.40(6)	Ni1-O4-K1	108.63(6)
O1-K1-O2	56.44(4)	O3-K1-O2	60.00(4)
O3-K1-O6	59.43(4)	O5-K1-O6	56.67(4)
O4-K1-O5	58.37(4)	O4-K1-O1	54.93(4)

Table A.3.9. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for **6c** + KPF₆

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.3537(2)	0.58270(10)	0.62780(12)	0.0183(4)
C2	0.4038(2)	0.62157(11)	0.70042(13)	0.0248(5)
C3	0.3415(2)	0.61110(12)	0.77512(13)	0.0274(5)
C4	0.2311(2)	0.56302(12)	0.77790(13)	0.0268(5)
C5	0.1826(2)	0.52294(12)	0.70689(13)	0.0234(4)
C6	0.2468(2)	0.53218(11)	0.63131(12)	0.0184(4)
C7	0.1191(2)	0.44320(10)	0.54795(13)	0.0185(4)
C8	0.0798(2)	0.40055(10)	0.47454(13)	0.0178(4)
C9	0.1434(2)	0.40978(10)	0.39826(12)	0.0164(4)
C10	0.1020(2)	0.36128(10)	0.32945(13)	0.0185(4)

	x/a	y/b	z/c	U(eq)
C11	0.9993(2)	0.31025(11)	0.33730(14)	0.0228(4)
C12	0.9342(2)	0.30338(11)	0.41327(14)	0.0252(5)
C13	0.9749(2)	0.34697(11)	0.48104(14)	0.0218(4)
C14	0.1359(2)	0.32337(11)	0.18744(13)	0.0235(4)
C15	0.2416(2)	0.33584(11)	0.12392(14)	0.0275(5)
C16	0.1314(3)	0.42774(15)	0.03524(16)	0.0391(6)
C17	0.4925(2)	0.63905(10)	0.53104(12)	0.0177(4)
C18	0.5497(2)	0.65106(10)	0.45319(12)	0.0168(4)
C19	0.51035(19)	0.60814(10)	0.38001(12)	0.0152(4)
C20	0.5789(2)	0.62362(10)	0.30505(12)	0.0156(4)
C21	0.6807(2)	0.67595(10)	0.30564(13)	0.0185(4)
C22	0.7180(2)	0.71768(11)	0.37877(13)	0.0219(4)
C23	0.6528(2)	0.70611(10)	0.45059(13)	0.0207(4)
C24	0.5990(2)	0.59690(11)	0.15855(12)	0.0204(4)
C25	0.5303(2)	0.54925(11)	0.08878(13)	0.0223(4)
C26	0.3532(3)	0.62804(13)	0.02640(14)	0.0316(5)
P1	0.0726(4)	0.66850(17)	0.2065(2)	0.0194(6)
F1	0.2204(4)	0.6536(2)	0.2601(2)	0.0332(8)
F2	0.1076(6)	0.6145(2)	0.1344(3)	0.0395(11)
F3	0.9997(4)	0.60663(17)	0.2562(2)	0.0494(8)
F4	0.0310(6)	0.7226(3)	0.2801(4)	0.0343(11)
F5	0.9207(5)	0.6878(3)	0.1538(4)	0.0340(12)
F6	0.1402(3)	0.73424(19)	0.1597(2)	0.0358(8)
P1A	0.0726(10)	0.6638(4)	0.2068(7)	0.034(2)
F1A	0.2464(9)	0.6580(7)	0.2263(9)	0.031(2)
F2A	0.0884(14)	0.5926(5)	0.1446(8)	0.031(2)
F3A	0.0688(8)	0.6033(4)	0.2816(5)	0.0400(17)
F4A	0.0679(14)	0.7269(8)	0.2703(10)	0.037(3)
F5A	0.9111(8)	0.6565(5)	0.1822(6)	0.042(2)
F6A	0.0957(9)	0.7121(5)	0.1289(5)	0.044(2)
P1B	0.0703(13)	0.6647(5)	0.1929(7)	0.029(2)
F1B	0.2335(15)	0.6463(12)	0.2243(16)	0.029(3)
F2B	0.1053(10)	0.6608(7)	0.0952(6)	0.030(2)
F3B	0.0334(12)	0.5806(5)	0.1870(8)	0.037(2)
F4B	0.0302(12)	0.6691(8)	0.2883(6)	0.045(3)
F5B	0.9082(18)	0.6813(17)	0.1602(18)	0.027(4)
F6B	0.1069(13)	0.7473(5)	0.1965(9)	0.036(3)
K1	0.28744(5)	0.50736(2)	0.22828(3)	0.02135(10)
N1	0.21346(16)	0.49411(8)	0.55323(10)	0.0159(3)
N2	0.40097(17)	0.58948(8)	0.54555(10)	0.0156(3)
Ni1	0.31782(3)	0.52464(2)	0.46598(2)	0.01406(6)
O1	0.23774(14)	0.45913(7)	0.38620(8)	0.0170(3)

	x/a	y/b	z/c	U(eq)
O2	0.17003(15)	0.37191(7)	0.25742(9)	0.0213(3)
O3	0.24773(16)	0.40776(8)	0.09503(9)	0.0260(3)
O4	0.41854(14)	0.55574(7)	0.37787(8)	0.0157(3)
O5	0.53583(14)	0.58138(7)	0.23561(8)	0.0184(3)
O6	0.38225(15)	0.56182(7)	0.06875(9)	0.0219(3)

Table A.3.10. Anisotropic atomic displacement parameters ($\text{\AA}^2$) for **6c** + KPF_6
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.0229(10)	0.0168(9)	0.0149(9)	-0.0014(7)	0.0009(8)	0.0059(8)
C2	0.0357(12)	0.0205(10)	0.0175(10)	-0.0011(8)	-0.0006(9)	0.0036(9)
C3	0.0398(13)	0.0255(11)	0.0164(10)	-0.0057(8)	-0.0001(9)	0.0098(10)
C4	0.0342(12)	0.0325(12)	0.0144(10)	-0.0007(9)	0.0058(9)	0.0126(10)
C5	0.0250(10)	0.0270(11)	0.0187(10)	0.0016(9)	0.0043(8)	0.0078(9)
C6	0.0219(9)	0.0189(10)	0.0138(9)	-0.0006(7)	-0.0006(7)	0.0087(8)
C7	0.0187(9)	0.0184(9)	0.0186(10)	0.0046(8)	0.0028(8)	0.0053(8)
C8	0.0164(9)	0.0154(9)	0.0212(10)	0.0033(8)	0.0002(8)	0.0040(7)
C9	0.0171(9)	0.0128(9)	0.0185(9)	0.0018(7)	-0.0022(7)	0.0026(7)
C10	0.0197(9)	0.0141(9)	0.0210(10)	0.0005(8)	-0.0016(8)	0.0027(7)
C11	0.0234(10)	0.0148(9)	0.0289(11)	-0.0013(8)	-0.0029(9)	-0.0017(8)
C12	0.0199(10)	0.0181(10)	0.0373(13)	0.0025(9)	0.0021(9)	-0.0028(8)
C13	0.0198(10)	0.0196(10)	0.0264(11)	0.0033(8)	0.0050(8)	0.0023(8)
C14	0.0300(11)	0.0185(10)	0.0209(10)	-0.0052(8)	-0.0021(9)	-0.0029(8)
C15	0.0334(12)	0.0218(11)	0.0265(11)	-0.0076(9)	-0.0008(9)	0.0006(9)
C16	0.0364(13)	0.0506(16)	0.0282(13)	0.0092(12)	-0.0069(11)	-0.0004(12)
C17	0.0205(9)	0.0140(9)	0.0175(9)	-0.0039(7)	-0.0027(7)	0.0025(7)
C18	0.0183(9)	0.0141(9)	0.0172(9)	-0.0015(7)	-0.0026(7)	0.0016(7)
C19	0.0145(8)	0.0132(9)	0.0169(9)	0.0000(7)	-0.0019(7)	0.0040(7)
C20	0.0195(9)	0.0132(9)	0.0137(9)	0.0002(7)	-0.0009(7)	0.0043(7)
C21	0.0207(9)	0.0159(9)	0.0185(10)	0.0029(8)	0.0000(8)	0.0011(8)
C22	0.0229(10)	0.0178(10)	0.0241(11)	0.0009(8)	-0.0019(8)	-0.0034(8)
C23	0.0239(10)	0.0162(9)	0.0207(10)	-0.0039(8)	-0.0033(8)	-0.0012(8)
C24	0.0243(10)	0.0216(10)	0.0157(10)	0.0010(8)	0.0040(8)	0.0000(8)
C25	0.0277(11)	0.0221(10)	0.0173(10)	-0.0014(8)	0.0026(8)	0.0038(8)
C26	0.0396(13)	0.0316(12)	0.0230(11)	0.0083(10)	0.0005(10)	0.0080(10)
P1	0.0181(11)	0.0228(9)	0.0174(11)	0.0045(8)	0.0018(9)	-0.0047(8)
F1	0.0351(16)	0.0248(14)	0.0359(18)	0.0021(15)	-0.0141(13)	0.0080(12)
F2	0.0317(19)	0.053(3)	0.034(2)	-0.014(2)	0.0039(13)	0.0084(19)
F3	0.056(2)	0.0346(15)	0.060(2)	0.0136(14)	0.0152(16)	-0.0191(15)
F4	0.041(3)	0.0330(18)	0.0295(16)	-0.0079(13)	0.0057(16)	-0.0024(17)
F5	0.0184(15)	0.042(2)	0.040(3)	-0.0070(18)	-0.0025(16)	0.0029(15)

F6	0.0275(16)	0.0398(18)	0.041(2)	0.0246(15)	0.0101(13)	-0.0005(12)
P1A	0.031(3)	0.039(3)	0.033(4)	0.000(3)	0.006(3)	-0.010(2)
F1A	0.024(3)	0.027(4)	0.042(5)	0.004(4)	-0.002(3)	-0.002(3)
F2A	0.026(4)	0.043(4)	0.023(3)	-0.001(3)	-0.001(3)	0.001(3)
F3A	0.047(4)	0.041(3)	0.034(3)	0.010(3)	0.015(3)	-0.011(3)
F4A	0.030(5)	0.034(4)	0.049(5)	-0.004(3)	0.005(4)	-0.006(3)
F5A	0.021(3)	0.059(5)	0.047(5)	-0.011(4)	0.010(3)	-0.003(3)
F6A	0.049(5)	0.042(4)	0.042(4)	0.024(3)	0.013(3)	0.016(3)
P1B	0.018(3)	0.035(4)	0.036(4)	0.002(3)	0.009(3)	-0.005(3)
F1B	0.023(4)	0.026(6)	0.039(6)	0.005(5)	0.002(4)	-0.001(4)
F2B	0.022(4)	0.040(6)	0.030(4)	0.002(4)	0.014(3)	-0.007(4)
F3B	0.033(4)	0.035(4)	0.045(5)	0.010(3)	0.006(4)	-0.013(3)
F4B	0.039(5)	0.069(7)	0.028(4)	0.000(4)	0.009(4)	-0.002(5)
F5B	0.017(5)	0.046(8)	0.021(7)	0.006(6)	0.012(4)	-0.007(4)
F6B	0.027(5)	0.029(4)	0.050(7)	0.002(4)	-0.004(5)	0.005(4)
K1	0.0284(2)	0.0206(2)	0.0143(2)	-0.00123(16)	-0.00108(17)	-0.00566(18)
N1	0.0177(8)	0.0151(8)	0.0144(8)	-0.0001(6)	-0.0011(6)	0.0052(6)
N2	0.0198(8)	0.0144(8)	0.0123(8)	-0.0021(6)	-0.0001(6)	0.0044(6)
Ni1	0.01713(11)	0.01296(11)	0.01158(11)	-0.00116(9)	-0.00087(9)	0.00098(10)
O1	0.0219(7)	0.0140(6)	0.0147(7)	0.0001(5)	0.0003(5)	-0.0031(5)
O2	0.0281(8)	0.0182(7)	0.0171(7)	-0.0030(6)	0.0001(6)	-0.0050(6)
O3	0.0310(8)	0.0267(8)	0.0193(7)	-0.0016(6)	-0.0030(6)	-0.0019(7)
O4	0.0198(7)	0.0141(6)	0.0127(6)	-0.0012(5)	-0.0011(5)	-0.0009(5)
O5	0.0233(7)	0.0191(7)	0.0130(7)	-0.0017(5)	0.0023(5)	-0.0011(6)
O6	0.0256(7)	0.0210(7)	0.0185(7)	0.0007(6)	-0.0001(6)	0.0031(6)

Chapter 4

Geometry-optimized XYZ coordinates data of all reactants, intermediates and transition states in DFT calculation.

Table A.4.1. Geometry-optimized XYZ coordinates of Ni complex in **RC1**.

<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;"> <p>Ni complex in RC1</p> </div> <div> </div> </div>			
	X	Y	Z
Ni	1.9257	0.9726	13.8755
C	-0.2229	-0.5207	14.7381
C	-1.2342	-1.461	14.8492
H	-1.379	-2.0964	14.1582
C	-2.0305	-1.4638	15.9792
C	-1.8087	-0.5541	17.0021
H	-2.3638	-0.5657	17.7726
C	0.0069	0.3925	15.7703
C	0.5183	-1.0925	12.5586
H	-0.2011	-1.7132	12.5506
C	1.341	-1.0401	11.406
C	1.0342	-1.92	10.3236
H	0.2919	-2.5084	10.3886
C	1.8041	-1.9175	9.1974
H	1.5881	-2.4976	8.475
C	2.9142	-1.0616	9.101
H	3.4566	-1.0825	8.322
C	3.2268	-0.1905	10.1245
C	2.4385	-0.1377	11.3113
C	5.2538	0.5024	9.075
H	4.816	0.6072	8.1934
H	5.6434	-0.4066	9.1202
C	6.3317	1.5235	9.2324
H	6.5776	1.603	10.1868
H	7.1349	1.2398	8.73
C	6.9637	3.6379	8.3909
H	7.6015	3.6849	9.1336
H	6.6213	4.5343	8.1956
H	7.4142	3.2801	7.5969
C	1.4514	2.1645	16.4098
H	0.9193	2.2283	17.1939
C	2.5672	3.0421	16.3051
C	2.8648	3.8805	17.4163

H	2.2707	3.909	18.1585
C	4.0013	4.6485	17.4252
H	4.2024	5.2012	18.1718
C	4.8643	4.6071	16.3156
H	5.648	5.1452	16.3158
C	4.6023	3.8078	15.2317
C	3.4256	3.0031	15.1853
C	5.1676	3.9759	12.8992
H	4.6609	4.8271	12.8677
H	4.5862	3.253	12.5528
C	6.4144	4.0825	12.0679
H	6.9545	3.2584	12.1648
H	6.1743	4.1855	11.1137
C	8.3576	5.3747	11.7381
H	8.838	4.5217	11.6925
H	8.9264	6.0488	12.1625
H	8.1255	5.6674	10.8321
N	0.663	-0.3652	13.63
N	1.0986	1.2811	15.5179
O	2.765	0.7054	12.2532
O	3.2448	2.2317	14.1367
O	4.2874	0.6714	10.1203
O	5.8824	2.7844	8.7471
O	5.5722	3.6862	14.2598
O	7.1683	5.2086	12.502
N	-0.7849	0.3705	16.9096
Cl	-3.33919	-2.63194	16.12198

Table A.4.2. Geometry-optimized XYZ coordinates of Ni complex in **RC2**.

Ni complex in RC2

	X	Y	Z
C	2.3163	10.8908	9.8099
C	2.6712	11.6173	10.9446
H	3.3911	12.2365	10.9162
C	1.9581	11.4217	12.1118
C	0.908	10.523	12.1553
H	0.4145	10.419	12.9604
C	1.2988	9.9466	9.8648
C	0.2257	8.2836	8.5621
H	-0.2965	8.108	9.336
C	-0.0258	7.4864	7.4151

C	0.7028	7.6588	6.223
C	0.4235	6.7525	5.148
C	-0.5624	5.7986	5.2706
H	-0.7445	5.2182	4.5409
C	-1.3034	5.6702	6.4577
H	-1.9919	5.0189	6.5223
C	-1.0295	6.4849	7.5166
H	-1.5129	6.3824	8.3279
C	0.9788	6.0439	2.9289
H	0.0989	6.2117	2.5072
H	0.9995	5.1081	3.2514
C	2.0847	6.2769	1.9363
H	2.9441	6.013	2.3509
H	1.9371	5.6898	1.153
C	1.1865	7.9946	0.5507
H	1.1865	7.3631	-0.1987
H	1.3705	8.8975	0.2171
H	0.3103	7.9808	0.9895
C	3.7905	11.9441	8.298
H	4.0065	12.5204	9.0216
C	4.4603	12.1685	7.0815
C	4.2084	11.3663	5.938
C	4.9813	11.6556	4.7667
C	5.9446	12.6336	4.7758
H	6.463	12.785	3.9943
C	6.1772	13.4136	5.9186
H	6.8451	14.0891	5.9081
C	5.4411	13.1974	7.0409
H	5.5838	13.7401	7.8074
C	5.4126	11.1562	2.4775
H	6.3784	10.9858	2.6121
H	5.294	12.1072	2.2293
C	4.8766	10.2657	1.3872
H	5.4184	10.4008	0.5697
H	4.9827	9.3215	1.6655
C	3.3025	11.7383	0.4125
H	3.3641	12.4699	1.0617
H	2.4147	11.7437	-0.0024
H	3.987	11.8565	-0.2788
K	2.3469	9.4826	3.5671
N	1.1111	9.235	8.6446
N	2.8998	11.0175	8.5247
Ni	2.2433	9.8058	7.2813
O	1.616	8.5812	6.0346
O	1.1868	6.9511	4.0224
O	2.1901	7.6211	1.4849
O	3.3424	10.387	5.9045
O	4.6876	10.8662	3.6816
O	3.5076	10.5006	1.0742
N	0.5656	9.7739	11.0458
Cl	2.39104	12.32575	13.55847

O	0.25384	11.08859	3.04173
H	-0.06511	11.18227	2.14112
H	-0.17417	11.56804	3.75484

Table A.4.3. Geometry-optimized XYZ coordinates of Ni complex in **Int1**.

Ni complex in Int1

	X	Y	Z
Ni	0.95336	0.13311	-0.17253
C	3.62775	-0.34356	0.11067
C	4.90501	-0.88478	0.24527
H	5.08434	-1.96006	0.31575
C	5.98158	-0.00428	0.28653
C	5.7647	1.37374	0.19587
H	6.61654	2.06313	0.22972
C	3.51485	1.05824	0.02443
C	2.33364	-2.32922	0.13201
H	3.2675	-2.89484	0.26853
C	1.15522	-3.10616	0.06427
C	1.27383	-4.52274	0.17021
H	2.26938	-4.9546	0.3132
C	0.16535	-5.31912	0.08926
H	0.24738	-6.4059	0.16651
C	-1.11012	-4.73178	-0.10095
H	-1.98078	-5.38797	-0.16525
C	-1.26744	-3.36452	-0.2004
C	-0.12229	-2.48787	-0.12215
C	-3.58499	-3.53574	-0.62278
H	-3.77877	-4.20952	0.23511
H	-3.42072	-4.16933	-1.5163
C	-4.79454	-2.67462	-0.83717
H	-4.57481	-1.88216	-1.58496
H	-5.58941	-3.3161	-1.27203
C	-6.52835	-1.62687	0.30578
H	-6.63469	-0.83292	-0.46129
H	-6.79384	-1.20131	1.28495
H	-7.25525	-2.42763	0.0629
C	1.94809	2.80393	-0.17697
H	2.81682	3.47805	-0.12797
C	0.66409	3.38436	-0.29422
C	0.54733	4.80074	-0.34285
H	1.46192	5.40031	-0.29217
C	-0.6833	5.39969	-0.44847

H	-0.77639	6.48766	-0.48516
C	-1.8423	4.59248	-0.49146
H	-2.83856	5.04084	-0.55534
C	-1.77055	3.21607	-0.45482
C	-0.49994	2.55411	-0.37709
C	-3.16047	1.50212	0.44276
H	-2.77312	1.84801	1.42106
H	-2.65306	0.55462	0.19521
C	-4.63731	1.28096	0.5391
H	-5.03991	1.03216	-0.46917
H	-4.81922	0.39133	1.1796
C	-6.64469	2.27068	1.1676
H	-7.12165	2.07388	0.18532
H	-7.06678	3.19984	1.57707
H	-6.91843	1.43504	1.84422
N	2.40782	-1.02558	0.0445
N	2.19736	1.52086	-0.10965
O	-0.30738	-1.22807	-0.22883
O	-0.47893	1.27366	-0.39211
O	-2.45033	-2.73711	-0.38278
O	-5.22297	-2.12101	0.37518
O	-2.91247	2.49034	-0.5483
O	-5.26336	2.41917	1.05578
N	4.54708	1.88241	0.06723
Cl	7.59907	-0.6085	0.44757

Table A.4.4. Geometry-optimized XYZ coordinates of Ni complex in **Int2**.

Ni complex in Int2

	X	Y	Z
Ni	0.94146	0.13361	-0.14724
C	3.63093	-0.28964	0.12038
C	4.90819	-0.8069	0.262
H	5.106	-1.87224	0.31881
C	5.95702	0.088	0.33237
C	5.72294	1.4528	0.26227
H	6.55185	2.15549	0.31782
C	3.49089	1.10017	0.05992
C	2.38639	-2.29618	0.04255
H	3.32829	-2.84179	0.13453

C	1.23091	-3.09361	-0.05236
C	1.39231	-4.50173	-0.03461
H	2.39668	-4.90883	0.05613
C	0.31358	-5.32153	-0.13473
H	0.43012	-6.40064	-0.12702
C	-0.97646	-4.76798	-0.2499
H	-1.82224	-5.44249	-0.33049
C	-1.17498	-3.41065	-0.26038
C	-0.06096	-2.51149	-0.16991
C	-3.50532	-3.64194	-0.55473
H	-3.60316	-4.35431	0.27665
H	-3.38847	-4.21738	-1.48417
C	-4.74641	-2.81183	-0.63875
H	-4.61653	-1.98781	-1.35996
H	-5.55809	-3.45399	-1.01815
C	-6.37879	-1.78011	0.65332
H	-6.49943	-0.9656	-0.07607
H	-6.56793	-1.38805	1.65417
H	-7.12705	-2.55358	0.42812
C	1.89771	2.81076	-0.15415
H	2.74488	3.49902	-0.10448
C	0.61101	3.36548	-0.28845
C	0.48845	4.7718	-0.36692
H	1.39405	5.37242	-0.3167
C	-0.73295	5.36262	-0.50533
H	-0.82732	6.44194	-0.56792
C	-1.88028	4.55456	-0.55251
H	-2.86724	5.00076	-0.65127
C	-1.80357	3.18895	-0.47786
C	-0.54309	2.53285	-0.36053
C	-3.25953	1.60765	0.51403
H	-2.96693	2.09992	1.45253
H	-2.70804	0.66332	0.43715
C	-4.7277	1.33732	0.51397
H	-5.03837	0.95571	-0.47484
H	-4.94072	0.54427	1.25006
C	-6.82322	2.28488	0.83955
H	-7.18288	1.94554	-0.14308
H	-7.31575	3.22615	1.08794
H	-7.10471	1.52923	1.58793
N	2.4249	-0.9955	0.02622
N	2.16543	1.53921	-0.08042
O	-0.292	-1.25131	-0.20535
O	-0.5213	1.24936	-0.33805
O	-2.38223	-2.80676	-0.35967
O	-5.0798	-2.3091	0.62981
O	-2.94939	2.45856	-0.58536
O	-5.43928	2.50549	0.82974

N	4.50133	1.94634	0.12769
Cl	7.58765	-0.49023	0.51155
H	0.81344	0.17943	1.29637

Table A.4.4. Geometry-optimized XYZ coordinates of Ni complex in **Int2'**.

<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center; margin-right: 20px;"> Ni complex in Int2' </div> </div>			
	X	Y	Z
Ni	0.94146	0.13361	-0.14724
C	3.63093	-0.28964	0.12038
C	4.90819	-0.8069	0.262
H	5.106	-1.87224	0.31881
C	5.95702	0.088	0.33237
C	5.72294	1.4528	0.26227
H	6.55185	2.15549	0.31782
C	3.49089	1.10017	0.05992
C	2.38639	-2.29618	0.04255
H	3.32829	-2.84179	0.13453
C	1.23091	-3.09361	-0.05236
C	1.39231	-4.50173	-0.03461
H	2.39668	-4.90883	0.05613
C	0.31358	-5.32153	-0.13473
H	0.43012	-6.40064	-0.12702
C	-0.97646	-4.76798	-0.2499
H	-1.82224	-5.44249	-0.33049
C	-1.17498	-3.41065	-0.26038
C	-0.06096	-2.51149	-0.16991
C	-3.50532	-3.64194	-0.55473
H	-3.60316	-4.35431	0.27665
H	-3.38847	-4.21738	-1.48417
C	-4.74641	-2.81183	-0.63875
H	-4.61653	-1.98781	-1.35996
H	-5.55809	-3.45399	-1.01815
C	-6.37879	-1.78011	0.65332
H	-6.49943	-0.9656	-0.07607
H	-6.56793	-1.38805	1.65417
H	-7.12705	-2.55358	0.42812
C	1.89771	2.81076	-0.15415
H	2.74488	3.49902	-0.10448
C	0.61101	3.36548	-0.28845
C	0.48845	4.7718	-0.36692
H	1.39405	5.37242	-0.3167
C	-0.73295	5.36262	-0.50533

H	-0.82732	6.44194	-0.56792
C	-1.88028	4.55456	-0.55251
H	-2.86724	5.00076	-0.65127
C	-1.80357	3.18895	-0.47786
C	-0.54309	2.53285	-0.36053
C	-3.25953	1.60765	0.51403
H	-2.96693	2.09992	1.45253
H	-2.70804	0.66332	0.43715
C	-4.7277	1.33732	0.51397
H	-5.03837	0.95571	-0.47484
H	-4.94072	0.54427	1.25006
C	-6.82322	2.28488	0.83955
H	-7.18288	1.94554	-0.14308
H	-7.31575	3.22615	1.08794
H	-7.10471	1.52923	1.58793
N	2.4249	-0.9955	0.02622
N	2.16543	1.53921	-0.08042
O	-0.292	-1.25131	-0.20535
O	-0.5213	1.24936	-0.33805
O	-2.38223	-2.80676	-0.35967
O	-5.0798	-2.3091	0.62981
O	-2.94939	2.45856	-0.58536
O	-5.43928	2.50549	0.82974
N	4.50133	1.94634	0.12769
Cl	7.58765	-0.49023	0.51155
H	-0.60285	1.28023	0.61798

Table A.4.5. Geometry-optimized XYZ coordinates of Ni complex in **Int3**.

Ni complex in Int3

	X	Y	Z
Ni	-0.88469	-0.14112	-0.24337
C	-3.63542	0.37953	0.03123
C	-4.91297	0.92898	0.1587
H	-5.07795	2.00911	0.17543
C	-5.9984	0.06797	0.2567
C	-5.79397	-1.31495	0.23372
H	-6.65129	-1.99449	0.31193
C	-3.53242	-1.03784	0.01013
C	-2.34357	2.37981	0.04065
H	-3.26106	2.97021	0.20809
C	-1.14566	3.14237	-0.00845

C	-1.27453	4.55268	0.15694
H	-2.27749	4.96941	0.29513
C	-0.17623	5.36798	0.14048
H	-0.27907	6.44926	0.25983
C	1.11302	4.80806	-0.02895
H	1.97656	5.47675	-0.03408
C	1.2877	3.44752	-0.17479
C	0.15252	2.55076	-0.19403
C	3.62348	3.65028	-0.47197
H	3.75047	4.30913	0.40965
H	3.51681	4.29968	-1.36295
C	4.85226	2.8008	-0.61166
H	4.68895	2.00972	-1.37536
H	5.67065	3.44936	-0.9885
C	6.5042	1.74078	0.63598
H	6.64742	0.93665	-0.11496
H	6.70961	1.32602	1.63401
H	7.24977	2.53345	0.42472
C	-2.00776	-2.83935	-0.07314
H	-2.87492	-3.50613	0.06998
C	-0.72938	-3.44998	-0.16082
C	-0.66359	-4.86402	-0.02019
H	-1.60002	-5.41256	0.12645
C	0.53721	-5.52844	-0.06066
H	0.58035	-6.61489	0.04715
C	1.72946	-4.78861	-0.22163
H	2.70416	-5.28627	-0.23327
C	1.71375	-3.41855	-0.36805
C	0.47474	-2.68975	-0.38078
C	3.19444	-1.70565	0.34602
H	2.96622	-2.02691	1.38186
H	2.59533	-0.80533	0.12953
C	4.65164	-1.38458	0.23203
H	4.90157	-1.16436	-0.83057
H	4.84983	-0.45121	0.80237
C	6.78949	-2.21376	0.63298
H	7.11911	-2.02238	-0.409
H	7.32192	-3.1004	1.00664
H	7.09486	-1.34072	1.24506
N	-2.43864	1.08341	-0.07793
N	-2.24368	-1.55484	-0.12954
O	0.37245	1.30817	-0.39119
O	0.51032	-1.43123	-0.60161
O	2.48348	2.83697	-0.32767
O	5.20087	2.24357	0.62455
O	2.88542	-2.75817	-0.55712
O	5.4184	-2.45148	0.71088
N	-4.58408	-1.83842	0.11533
Cl	-7.60906	0.69598	0.40269
H	-0.75912	-0.19922	1.1691

Table A.4.5. Geometry-optimized XYZ coordinates of Ni complex in **Int3'**.**Ni complex in Int3'**

	X	Y	Z
Ni	-0.8803	-0.05128	-0.04702
C	-3.62838	-0.43189	-0.0527
C	-5.02004	-0.33006	-0.11657
H	-5.52213	0.63833	-0.18523
C	-5.77443	-1.49775	-0.09575
C	-5.1391	-2.73761	-0.01607
H	-5.73322	-3.65928	-0.00096
C	-3.07454	-1.74107	0.01984
C	-3.04868	1.87366	-0.0424
H	-4.11615	2.15907	0.00716
C	-2.13753	2.97016	-0.06963
C	-2.71288	4.27541	-0.04034
H	-3.80507	4.35478	-0.00117
C	-1.93738	5.40306	-0.06059
H	-2.39037	6.39761	-0.03714
C	-0.52667	5.27908	-0.11328
H	0.08248	6.18632	-0.13015
C	0.07277	4.03847	-0.14325
C	-0.7027	2.81256	-0.1164
C	2.26252	4.94768	-0.227
H	2.13065	5.56281	0.68626
H	2.04182	5.59514	-1.09883
C	3.68087	4.46598	-0.30964
H	3.78522	3.77487	-1.17437
H	4.34571	5.33359	-0.51
C	5.33163	3.31772	0.85554
H	5.46579	2.56881	0.0486
H	5.53612	2.82996	1.81959
H	6.08654	4.11498	0.6991
C	-1.09472	-2.96996	0.22157
H	-1.73197	-3.86424	0.32073
C	0.32983	-3.20365	0.28834
C	0.75856	-4.53746	0.48749
H	-0.00479	-5.31798	0.55959

C	2.0982	-4.85985	0.58818
H	2.40379	-5.89869	0.73472
C	3.07569	-3.86132	0.49229
H	4.1391	-4.10599	0.52755
C	2.68652	-2.5425	0.30173
C	1.32257	-2.20828	0.19962
C	4.80955	-1.47933	0.7695
H	4.85985	-2.22315	1.58389
H	4.96149	-0.48351	1.21403
C	5.88198	-1.72746	-0.25235
H	5.75372	-1.01639	-1.0971
H	6.86776	-1.50142	0.20852
C	6.78004	-3.32918	-1.68719
H	6.64283	-2.69258	-2.58343
H	6.67155	-4.38113	-1.98567
H	7.81209	-3.17268	-1.31553
N	-2.71548	0.6128	-0.06488
N	-1.66612	-1.81373	0.06657
O	-0.07571	1.70373	-0.13318
O	1.01873	-0.90589	0.01178
O	1.4093	3.83304	-0.20048
O	4.03335	3.82713	0.88159
O	3.51037	-1.4707	0.19319
O	5.82789	-3.04822	-0.70314
N	-3.81672	-2.83571	0.03826
Cl	-7.50839	-1.42328	-0.17443
H	1.84283	-0.3825	0.02819

Table A.4.6. Geometry-optimized XYZ coordinates of Ni complex in **Int4**.

Ni complex in Int4

	X	Y	Z
Ni	-1.47974	0.18724	0.55184
C	-4.17709	0.49228	0.07989
C	-5.46798	0.97342	-0.05144
H	-5.67481	2.01306	-0.28634
C	-6.51235	0.08885	0.1387
C	-6.25492	-1.23444	0.44748
H	-7.07677	-1.93329	0.59434
C	-4.00271	-0.86596	0.41268
C	-2.95402	2.45055	-0.43955
H	-3.87863	2.95071	-0.74883
C	-1.78318	3.24882	-0.48546

C	-1.91167	4.56469	-0.99258
H	-2.88922	4.88763	-1.34543
C	-0.84439	5.40777	-1.04077
H	-0.94578	6.41499	-1.43323
C	0.40805	4.96995	-0.57139
H	1.25016	5.65328	-0.61474
C	0.57093	3.70582	-0.06468
C	-0.52723	2.7812	-0.00259
C	2.87104	4.0522	0.38089
H	2.69121	4.95334	0.98547
H	3.09341	4.37241	-0.64727
C	4.04155	3.29583	0.92367
H	4.14592	2.33584	0.39211
H	4.96034	3.87607	0.73574
C	4.91955	2.31404	2.83578
H	4.97636	1.32293	2.36282
H	4.73249	2.18524	3.90264
H	5.88948	2.81523	2.70276
C	-2.42893	-2.56479	0.704
H	-3.28609	-3.17635	1.00638
C	-1.2005	-3.2362	0.57146
C	-1.07682	-4.47027	1.26014
H	-1.94038	-4.8333	1.81665
C	0.09309	-5.16843	1.28095
H	0.18321	-6.09848	1.83394
C	1.20673	-4.64556	0.588
H	2.16384	-5.16381	0.61447
C	1.11793	-3.50446	-0.15145
C	-0.1281	-2.77391	-0.30162
C	2.65212	-1.75889	-0.48835
H	2.87895	-1.72739	0.58888
H	1.87401	-1.01399	-0.6969
C	3.87845	-1.44257	-1.28045
H	3.68545	-1.60898	-2.35387
H	4.12274	-0.37488	-1.15522
C	6.11853	-1.97723	-1.58843
H	5.97419	-2.18561	-2.65865
H	6.91365	-2.62105	-1.20915
H	6.43159	-0.92778	-1.48338
N	-2.99092	1.21433	-0.05745
N	-2.67156	-1.28854	0.51375
O	-0.29634	1.61705	0.48783
O	-0.27309	-1.88002	-1.1743
O	1.74043	3.20969	0.40467
O	3.87219	3.0762	2.29885
O	2.1951	-3.05727	-0.83648
O	4.95516	-2.24029	-0.85392
N	-5.01937	-1.69941	0.57298
Cl	-8.16311	0.63334	-0.00916
H	-0.43399	-0.6038	1.2674
O	2.20202	1.77852	1.35653

H	1.39779	2.26477	1.16067
H	3.05813	2.18144	1.19423
H	2.15015	0.88934	1.71468

Table A.4.7. Geometry-optimized XYZ coordinates of Ni complex in **Int5**.

<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;"> <p>Ni complex in Int5</p> </div> <div> </div> </div>			
	X	Y	Z
C	2.3163	10.8908	9.8099
C	2.6712	11.6173	10.9446
H	3.3911	12.2365	10.9162
C	1.9581	11.4217	12.1118
C	0.908	10.523	12.1553
H	0.4145	10.419	12.9604
C	1.2988	9.9466	9.8648
C	0.2257	8.2836	8.5621
H	-0.2965	8.108	9.336
C	-0.0258	7.4864	7.4151
C	0.7028	7.6588	6.223
C	0.4235	6.7525	5.148
C	-0.5624	5.7986	5.2706
H	-0.7445	5.2182	4.5409
C	-1.3034	5.6702	6.4577
H	-1.9919	5.0189	6.5223
C	-1.0295	6.4849	7.5166
H	-1.5129	6.3824	8.3279
C	0.9788	6.0439	2.9289
H	0.0989	6.2117	2.5072
H	0.9995	5.1081	3.2514
C	2.0847	6.2769	1.9363
H	2.9441	6.013	2.3509
H	1.9371	5.6898	1.153
C	1.1865	7.9946	0.5507
H	1.1865	7.3631	-0.1987
H	1.3705	8.8975	0.2171
H	0.3103	7.9808	0.9895
C	3.7905	11.9441	8.298
H	4.0065	12.5204	9.0216
C	4.4603	12.1685	7.0815
C	4.2084	11.3663	5.938

C	4.9813	11.6556	4.7667
C	5.9446	12.6336	4.7758
H	6.463	12.785	3.9943
C	6.1772	13.4136	5.9186
H	6.8451	14.0891	5.9081
C	5.4411	13.1974	7.0409
H	5.5838	13.7401	7.8074
C	5.4126	11.1562	2.4775
H	6.3784	10.9858	2.6121
H	5.294	12.1072	2.2293
C	4.8766	10.2657	1.3872
H	5.4184	10.4008	0.5697
H	4.9827	9.3215	1.6655
C	3.3025	11.7383	0.4125
H	3.3641	12.4699	1.0617
H	2.4147	11.7437	-0.0024
H	3.987	11.8565	-0.2788
K	2.3469	9.4826	3.5671
N	1.1111	9.235	8.6446
N	2.8998	11.0175	8.5247
Ni	2.2433	9.8058	7.2813
O	1.616	8.5812	6.0346
O	1.1868	6.9511	4.0224
O	2.1901	7.6211	1.4849
O	3.3424	10.387	5.9045
O	4.6876	10.8662	3.6816
O	3.5076	10.5006	1.0742
N	0.5656	9.7739	11.0458
Cl	2.39104	12.32575	13.55847
O	0.25384	11.08859	3.04173
H	-0.06511	11.18227	2.14112
H	-0.17417	11.56804	3.75484

Table A.4.8. Geometry-optimized XYZ coordinates of Ni complex in **Int6**.

Ni complex in Int6

	X	Y	Z
C	-3.82283	-0.26163	0.00659
C	-5.11784	-0.76723	0.10525
H	-5.33988	-1.83584	0.05374
C	-6.15493	0.14307	0.28133
C	-5.88136	1.51271	0.35697
H	-6.70223	2.22642	0.49379

C	-3.65213	1.12985	0.10246
C	-2.02355	2.81696	0.13773
H	-2.8654	3.49838	0.33203
C	-0.73041	3.37987	0.03335
C	0.39886	2.56341	-0.27623
C	1.65494	3.24354	-0.45527
C	1.75492	4.60566	-0.24703
H	2.71944	5.10487	-0.36183
C	0.62792	5.38525	0.09617
H	0.74484	6.46078	0.2467
C	-0.5954	4.78351	0.21946
H	-1.48975	5.36469	0.46391
C	3.98517	3.00912	-0.86914
H	4.2603	3.37123	0.14194
H	4.02243	3.87673	-1.55477
C	4.94932	1.96403	-1.37029
H	4.61198	1.61388	-2.36078
H	5.94317	2.43547	-1.50462
C	5.83211	1.00002	0.60172
H	6.88095	1.22956	0.33302
H	5.79913	0.05439	1.16194
H	5.45783	1.8077	1.25873
C	-2.62421	-2.27226	-0.30915
H	-3.59031	-2.7977	-0.31584
C	-1.48235	-3.09841	-0.43439
C	-0.16735	-2.54379	-0.41245
C	0.92448	-3.47996	-0.43847
C	0.69412	-4.83759	-0.52903
H	1.53688	-5.53152	-0.55983
C	-0.61826	-5.35924	-0.58477
H	-0.76458	-6.43912	-0.6577
C	-1.68555	-4.50376	-0.53198
H	-2.71204	-4.88241	-0.55251
C	3.26782	-3.76591	-0.12733
H	3.44079	-4.44925	-0.97982
H	3.07138	-4.39677	0.76169
C	4.49153	-2.90299	0.06451
H	5.35402	-3.56477	0.28108
H	4.7182	-2.36313	-0.87149
C	4.20064	-2.42177	2.36556
H	3.21549	-2.89872	2.52639
H	4.28591	-1.57234	3.05827
H	4.99138	-3.15751	2.60546
K	2.56521	-0.22583	-0.13349
N	-2.31689	1.55194	0.00773
N	-2.62941	-0.97474	-0.16671
Ni	-1.12016	0.14209	-0.23094
O	0.35727	1.28114	-0.4035
O	2.68786	2.45193	-0.83302
O	5.03865	0.83205	-0.54566
O	0.08844	-1.2827	-0.36149

O	2.15955	-2.92207	-0.36201
O	4.34395	-1.92472	1.0604
N	-4.64605	1.98431	0.26895
Cl	-7.7911	-0.40975	0.41566
O	2.77117	1.1927	2.11925
H	3.47285	1.25631	2.7783
H	2.22893	1.97457	2.28361
H	-0.95266	0.07721	1.20789

Table A.4.9. Geometry-optimized XYZ coordinates of Ni complex in Int7.

Ni complex in Int7

	X	Y	Z
C	3.83452	0.23404	-0.04301
C	5.14833	0.70006	0.03426
H	5.39125	1.76115	-0.06282
C	6.1664	-0.22274	0.23457
C	5.85937	-1.58203	0.35612
H	6.6631	-2.31191	0.51162
C	3.62662	-1.16274	0.08732
C	1.99038	-2.85705	0.154
H	2.81859	-3.54804	0.38257
C	0.68852	-3.41451	0.06336
C	-0.4568	-2.64142	-0.32458
C	-1.71489	-3.3424	-0.40739
C	-1.80926	-4.67846	-0.07679
H	-2.77339	-5.19001	-0.1267
C	-0.66757	-5.41603	0.31404
H	-0.77265	-6.47508	0.56081
C	0.55334	-4.79897	0.37001
H	1.44937	-5.35623	0.66096
C	-4.05901	-3.10048	-0.74322
H	-4.28293	-3.37579	0.3072
H	-4.15892	-4.01582	-1.35707
C	-5.01794	-2.05834	-1.2605
H	-4.70994	-1.76815	-2.27964
H	-6.02888	-2.50509	-1.3349
C	-5.84436	-0.96827	0.66307
H	-6.90114	-1.16729	0.40109
H	-5.77949	0.0002	1.17701
H	-5.5075	-1.76203	1.35673
C	2.68813	2.30599	-0.2417
H	3.64584	2.84653	-0.14941

C	1.53717	3.14011	-0.33612
C	0.20109	2.62609	-0.40903
C	-0.8645	3.5934	-0.38376
C	-0.6059	4.94838	-0.35145
H	-1.4322	5.66306	-0.35595
C	0.72004	5.43261	-0.31145
H	0.89913	6.50985	-0.28524
C	1.76365	4.54501	-0.2947
H	2.79713	4.90214	-0.24417
C	-3.21679	3.89099	-0.15679
H	-3.36831	4.61079	-0.98353
H	-3.04285	4.48467	0.76207
C	-4.44225	3.01978	-0.02092
H	-5.31307	3.67296	0.18981
H	-4.64188	2.5006	-0.9743
C	-4.17308	2.48429	2.2688
H	-3.16379	2.8953	2.46022
H	-4.33008	1.63402	2.94782
H	-4.92125	3.26535	2.50314
K	-2.56627	0.22273	-0.34386
N	2.30215	-1.5999	-0.01372
N	2.68841	1.00504	-0.22642
Ni	1.04703	-0.13655	-0.27467
O	-0.43126	-1.3896	-0.60405
O	-2.75104	-2.5784	-0.82669
O	-5.04317	-0.88619	-0.48638
O	-0.11507	1.38053	-0.50232
O	-2.10763	3.05511	-0.40171
O	-4.31693	2.01726	0.9534
N	4.61424	-2.02417	0.28429
Cl	7.81698	0.29537	0.33819
O	-2.72788	-1.0269	1.99688
H	-3.43171	-1.09559	2.65293
H	-2.1808	-1.80449	2.16681
H	0.90883	-0.10612	1.14072

Table A.4.10. Geometry-optimized XYZ coordinates of Ni complex in **Int8**.

Ni complex in Int8

	X	Y	Z
C	3.84382	0.59997	0.04649
C	5.08401	1.22486	-0.05311
H	5.18577	2.28793	-0.28414

C	6.22245	0.45225	0.15862
C	6.09698	-0.90649	0.45669
H	6.99607	-1.51087	0.62664
C	3.81971	-0.78078	0.35515
C	2.38194	-2.64374	0.37514
H	3.29429	-3.24201	0.54037
C	1.17625	-3.35504	0.14992
C	0.05506	-2.76199	-0.5546
C	-1.14005	-3.59072	-0.62535
C	-1.15902	-4.88922	-0.17459
H	-2.06732	-5.49199	-0.26444
C	0.0004	-5.47629	0.40058
H	-0.03106	-6.51857	0.72767
C	1.13534	-4.72443	0.54668
H	2.03111	-5.1553	1.00817
C	-3.48949	-3.5107	-1.02666
H	-3.64161	-3.8372	0.02202
H	-3.61069	-4.4085	-1.66355
C	-4.50965	-2.4738	-1.42688
H	-4.3172	-2.15572	-2.46613
H	-5.51987	-2.92622	-1.4047
C	-5.12632	-1.43562	0.60587
H	-6.20331	-1.64267	0.46014
H	-5.02273	-0.48163	1.14381
H	-4.70872	-2.24087	1.23936
C	2.40746	2.43173	-0.42806
H	3.2858	3.06439	-0.63575
C	1.14041	3.07996	-0.54216
C	-0.08152	2.42301	-0.19577
C	-1.29485	3.15803	-0.4329
C	-1.26912	4.44907	-0.92351
H	-2.20173	4.98925	-1.09978
C	-0.04699	5.09398	-1.20793
H	-0.05332	6.11993	-1.58296
C	1.13113	4.41687	-1.02119
H	2.08973	4.89213	-1.25323
C	-3.67355	3.09443	-0.4521
H	-3.74911	3.32985	-1.53123
H	-3.76138	4.04887	0.10218
C	-4.78168	2.15978	-0.05541
H	-5.74351	2.53709	-0.44613
H	-4.62005	1.15851	-0.49583
C	-5.65258	2.95421	2.01476
H	-5.27309	3.97891	1.85658
H	-5.62141	2.7306	3.08897
H	-6.69891	2.90433	1.6679
K	-2.04302	-0.1103	-1.43378
N	2.53768	-1.34122	0.39264
N	2.58116	1.18285	-0.11666
Ni	1.20779	-0.01293	0.46467
O	0.06702	-1.62473	-1.08609

O	-2.20909	-2.94577	-1.17307
O	-4.46124	-1.31587	-0.62518
O	-0.1771	1.2308	0.29012
O	-2.4415	2.46802	-0.16433
O	-4.8634	1.99022	1.34787
N	4.91405	-1.50126	0.54184
Cl	7.80006	1.16699	0.04835
O	-1.88819	-0.86519	1.33568
H	-2.09371	-1.73053	1.7219
H	-0.66749	-0.81086	1.32285
H	0.42187	-0.87423	1.46169
O	-2.77694	0.95779	2.61429
H	-2.32648	0.02027	1.99015
H	-3.52309	1.40662	2.1244
H	-3.12315	0.68639	3.47714

Table A.4.12. Geometry-optimized XYZ coordinates of Ni complex in TS1.

Ni complex in TS1

	X	Y	Z
C	-3.82849	-0.61105	0.04785
C	-5.06452	-1.24527	-0.04198
H	-5.16242	-2.30895	-0.27104
C	-6.20597	-0.47932	0.17744
C	-6.08702	0.88071	0.47388
H	-6.9885	1.47945	0.65018
C	-3.8118	0.76775	0.35446
C	-2.38159	2.63801	0.37885
H	-3.29728	3.2274	0.55421
C	-1.18242	3.35806	0.15357
C	-0.05679	2.76331	-0.53872
C	1.12254	3.60734	-0.64975
C	1.12775	4.91385	-0.22136
H	2.0268	5.52682	-0.33214
C	-0.03178	5.49593	0.35765
H	-0.00923	6.54378	0.66688
C	-1.15598	4.73403	0.52856
H	-2.05344	5.16189	0.98895
C	3.47689	3.52679	-1.02419
H	3.60699	3.85684	0.0264
H	3.61938	4.41985	-1.66289
C	4.49802	2.48038	-1.39632

H	4.33026	2.16282	-2.44006
H	5.51132	2.92351	-1.34828
C	5.06251	1.43204	0.64896
H	6.14665	1.61229	0.52206
H	4.92523	0.48259	1.18799
H	4.65283	2.25087	1.2701
C	-2.38633	-2.43065	-0.44884
H	-3.26775	-3.05582	-0.66251
C	-1.12453	-3.08303	-0.5686
C	0.09507	-2.42591	-0.22145
C	1.31065	-3.15913	-0.4488
C	1.2845	-4.45045	-0.93946
H	2.21765	-4.99127	-1.11068
C	0.06358	-5.0949	-1.23112
H	0.07252	-6.12044	-1.60708
C	-1.11596	-4.41945	-1.04956
H	-2.07372	-4.89426	-1.28502
C	3.68937	-3.09843	-0.44871
H	3.77235	-3.33529	-1.527
H	3.76898	-4.05248	0.10741
C	4.79857	-2.16713	-0.043
H	5.75874	-2.54719	-0.43785
H	4.63956	-1.165	-0.4833
C	5.6491	-2.97161	2.02476
H	5.2609	-3.99368	1.86559
H	5.61208	-2.74974	3.09966
H	6.70039	-2.93778	1.68815
K	2.06998	0.12113	-1.41166
N	-2.53211	1.33479	0.3812
N	-2.5611	-1.1844	-0.12361
Ni	-1.19095	0.01649	0.41966
O	-0.05437	1.60336	-1.02401
O	2.19537	2.96867	-1.19542
O	4.41736	1.32402	-0.59441
O	0.18307	-1.23042	0.25865
O	2.45425	-2.4705	-0.17351
O	4.87793	-1.99925	1.35635
N	-4.90732	1.48287	0.54989
Cl	-7.77877	-1.20397	0.07964
O	1.80369	0.93658	1.3207
H	2.03192	1.7839	1.7342
H	0.62684	0.85045	1.33018
H	-0.45367	0.875	1.53486
O	2.74801	-0.95334	2.69369
H	2.19231	0.17565	1.91076
H	3.45369	-1.4183	2.18689
H	3.16378	-0.69571	3.52709

Table A.4.13. Geometry-optimized XYZ coordinates of **P1**.

P1

	X	Y	Z
Ni	-0.65131	0.15365	-0.06435
C	-3.40425	-0.03192	-0.01412
C	-4.78093	0.16763	-0.0514
H	-5.222	1.14705	-0.25244
C	-5.61026	-0.9275	0.17066
C	-5.04458	-2.17903	0.41622
H	-5.69581	-3.04457	0.59169
C	-2.91732	-1.34115	0.22116
C	-2.675	2.21256	-0.17689
H	-3.72248	2.54353	-0.09099
C	-1.70712	3.26319	-0.23308
C	-2.12697	4.61216	-0.10864
H	-3.1985	4.8217	-0.02808
C	-1.20777	5.63657	-0.06868
H	-1.53613	6.67286	0.04067
C	0.17176	5.35134	-0.15738
H	0.9006	6.16573	-0.11133
C	0.60511	4.04866	-0.3032
C	-0.32503	2.96997	-0.33982
C	2.8872	4.34478	0.33648
H	2.53054	4.50481	1.37234
H	3.11036	5.33447	-0.10399
C	4.1466	3.52824	0.33486
H	4.48561	3.34706	-0.70577
H	4.94131	4.10318	0.84669
C	5.14921	1.61239	1.26218
H	5.75103	1.4905	0.34185
H	4.89148	0.61802	1.65381
H	5.75716	2.1532	2.00883
C	-1.04725	-2.70232	0.46562
H	-1.76356	-3.36138	0.98433
C	0.20161	-3.28513	0.20604
C	0.45005	-4.52871	0.87978
H	-0.31299	-4.89099	1.57841
C	1.59179	-5.24831	0.67957
H	1.76637	-6.19114	1.20443
C	2.5667	-4.74637	-0.22918
H	3.50484	-5.2868	-0.39896
C	2.36891	-3.5884	-0.92842
C	1.14021	-2.79659	-0.81093
C	3.93351	-1.93147	-1.61639

H	3.21846	-1.11852	-1.82223
H	4.75025	-1.87363	-2.35331
C	4.51029	-1.77057	-0.23187
H	5.01755	-2.71399	0.05691
H	5.28777	-0.97851	-0.24404
C	3.63992	-2.04974	1.95168
H	3.61025	-3.15541	1.87598
H	2.79836	-1.72186	2.58082
H	4.58482	-1.76247	2.45512
N	-2.40871	0.93883	-0.16759
N	-1.53198	-1.50301	0.15897
O	0.1537	1.77437	-0.46299
O	0.92968	-1.82982	-1.56101
O	1.90378	3.65749	-0.40696
O	3.94412	2.29629	0.99918
O	3.32599	-3.1966	-1.8195
O	3.50131	-1.44743	0.69774
N	-3.73316	-2.37033	0.42571
Cl	-7.33805	-0.74868	0.12959
H	0.69562	-0.39518	0.42982
O	2.38311	0.7595	-0.5164
H	1.68917	1.4701	-0.71232
H	2.94673	1.18773	0.18714
H	1.51732	-0.00819	0.01142

Table A.4.14. Geometry-optimized XYZ coordinates of **P2**.

P2

	X	Y	Z
C	3.74861	0.15307	-0.44486
C	5.08811	0.52694	-0.52878
H	5.39168	1.55905	-0.72079
C	6.05682	-0.45768	-0.35901
C	5.67093	-1.77804	-0.12234
H	6.43609	-2.55323	0.0088
C	3.45485	-1.21239	-0.19595
C	1.71858	-2.78665	-0.14601
H	2.52094	-3.52135	0.04143
C	0.41759	-3.31018	-0.34618
C	-0.61588	-2.5923	-1.07746
C	-1.9268	-3.24388	-1.08316
C	-2.12926	-4.4974	-0.55811
H	-3.11839	-4.96274	-0.60185
C	-1.05642	-5.22007	0.03415

H	-1.23468	-6.22691	0.42058
C	0.17938	-4.63885	0.12097
H	1.0096	-5.17401	0.59635
C	-4.23416	-2.88395	-1.55282
H	-4.48178	-3.11734	-0.49705
H	-4.41769	-3.80352	-2.14292
C	-5.09583	-1.7614	-2.07291
H	-4.75359	-1.48927	-3.0857
H	-6.14398	-2.10941	-2.15732
C	-5.86534	-0.6135	-0.16158
H	-6.92997	-0.60223	-0.465
H	-5.64381	0.28417	0.4335
H	-5.70257	-1.4999	0.48077
C	2.70634	2.26214	-0.77549
H	3.69318	2.73861	-0.90415
C	1.58255	3.14008	-0.85917
C	0.25082	2.68476	-0.60759
C	-0.81006	3.63136	-0.81763
C	-0.55016	4.94837	-1.13257
H	-1.3773	5.65206	-1.2629
C	0.77904	5.39595	-1.30874
H	0.96803	6.44391	-1.55417
C	1.81595	4.50361	-1.1862
H	2.85	4.8279	-1.34542
C	-3.12322	3.94179	-0.31415
H	-3.40459	4.64165	-1.12421
H	-2.82593	4.55764	0.55823
C	-4.31466	3.06562	-0.0002
H	-5.12503	3.71052	0.39764
H	-4.69015	2.59781	-0.92737
C	-3.57644	2.38777	2.14952
H	-2.55567	2.81488	2.12153
H	-3.54916	1.4851	2.77659
H	-4.25395	3.1275	2.6178
K	-2.34896	0.19951	-0.59746
N	2.09063	-1.52656	-0.16343
N	2.62998	0.97997	-0.57157
Ni	1.03137	0.02434	-0.05673
O	-0.45405	-1.50634	-1.67371
O	-2.89319	-2.47666	-1.65257
O	-5.01591	-0.60264	-1.2796
O	-0.07575	1.50746	-0.20625
O	-2.05564	3.10418	-0.68483
O	-4.03011	2.00771	0.87782
N	4.39541	-2.13505	-0.05434
Cl	7.74481	-0.05551	-0.44392
O	-2.85605	-1.54638	1.41199
H	-3.59136	-1.91369	1.91708
H	-2.26926	-2.30349	1.26746
H	-0.01816	-0.67624	0.75226
O	0.28105	-0.75457	4.23857

H	1.23702	-0.84241	4.23857
H	-0.12087	0.11725	4.23857
H	-0.27301	-1.53855	4.23857

Table A.4.14. Geometry-optimized XYZ coordinates of TEA.

TEA

	X	Y	Z
C	5.07074	5.413	5.91917
H	5.54356	5.9588	5.12959
H	5.30032	5.87267	6.85774
C	6.96394	4.06002	6.1197
H	7.19278	4.51888	7.05884
H	7.32066	3.05123	6.1193
C	4.73501	2.90156	5.74545
H	3.89463	3.14259	5.12856
H	5.31104	2.13042	5.27808
C	4.23987	2.41158	7.1189
H	3.6641	3.18283	7.5864
H	3.63124	1.54119	6.98888
H	5.08025	2.17026	7.73569
C	7.64595	4.84611	4.98457
H	7.64374	5.88945	5.22189
H	8.65491	4.50791	4.87268
H	7.11305	4.68714	4.07043
C	3.54574	5.41754	5.70476
H	3.06491	4.97803	6.5536
H	3.20555	6.42481	5.58399
H	3.3072	4.85294	4.8277
N	5.54808	4.06502	5.91917

Table A.4.14. Geometry-optimized XYZ coordinates of TEA-N radical cation.

TEA-N radical cation

	X	Y	Z
C	0.24337	1.1216	-0.46282
H	-0.62749	1.78785	-0.59072
H	0.51016	0.79151	-1.49711
C	-1.36335	-0.6491	-0.15826
H	-1.25963	-0.89324	-1.24326
H	-1.46574	-1.6215	0.3565
C	0.89147	-0.92493	0.70824

H	1.65138	-0.38593	1.302
H	0.46499	-1.67536	1.39857
C	1.56941	-1.63298	-0.45551
H	2.06977	-0.92153	-1.13442
H	2.33784	-2.33286	-0.09077
H	0.85148	-2.21756	-1.05513
C	-2.63341	0.15164	0.05375
H	-2.64005	1.09271	-0.51932
H	-3.51518	-0.42529	-0.26652
H	-2.75566	0.406	1.11911
C	1.38445	1.9253	0.12332
H	2.33944	1.37543	0.10958
H	1.53712	2.85317	-0.44869
H	1.16822	2.19988	1.16927
N	-0.17404	0.00252	0.36266

Table A.4.14. Geometry-optimized XYZ coordinates of deprotonated **TEA-N** radical cation.

TEA-N radical cation lose one proton.

	X	Y	Z
C	0.24337	1.1216	-0.46282
H	0.51016	0.79151	-1.49711
C	-1.36335	-0.6491	-0.15826
H	-1.25963	-0.89324	-1.24326
H	-1.46574	-1.6215	0.3565
C	0.89147	-0.92493	0.70824
H	1.65138	-0.38593	1.302
H	0.46499	-1.67536	1.39857
C	1.56941	-1.63298	-0.45551
H	2.06977	-0.92153	-1.13442
H	2.33784	-2.33286	-0.09077
H	0.85148	-2.21756	-1.05513
C	-2.63341	0.15164	0.05375
H	-2.64005	1.09271	-0.51932
H	-3.51518	-0.42529	-0.26652
H	-2.75566	0.406	1.11911
C	1.38445	1.9253	0.12332
H	2.33944	1.37543	0.10958
H	1.53712	2.85317	-0.44869
H	1.16822	2.19988	1.16927
N	-0.17404	0.00252	0.36266

Table A.4.14. Geometry-optimized XYZ coordinates of Et₂N=CHCH₃ cation.

Et₂N=CHCH₃ cation

	X	Y	Z
C	0.24337	1.1216	-0.46282
H	0.51016	0.79151	-1.49711
C	-1.36335	-0.6491	-0.15826
H	-1.25963	-0.89324	-1.24326
H	-1.46574	-1.6215	0.3565
C	0.89147	-0.92493	0.70824
H	1.65138	-0.38593	1.302
H	0.46499	-1.67536	1.39857
C	1.56941	-1.63298	-0.45551
H	2.06977	-0.92153	-1.13442
H	2.33784	-2.33286	-0.09077
H	0.85148	-2.21756	-1.05513
C	-2.63341	0.15164	0.05375
H	-2.64005	1.09271	-0.51932
H	-3.51518	-0.42529	-0.26652
H	-2.75566	0.406	1.11911
C	1.38445	1.9253	0.12332
H	2.33944	1.37543	0.10958
H	1.53712	2.85317	-0.44869
H	1.16822	2.19988	1.16927
N	-0.17404	0.00252	0.36266

Table A.4.14. Geometry-optimized XYZ coordinates of acetaldehyde.**Acetaldehyde**

	X	Y	Z
C	5.07074	5.413	5.91917
H	5.30032	5.87267	6.85774
C	3.54574	5.41754	5.70476
H	3.06491	4.97803	6.5536
H	3.20555	6.42481	5.58399
H	3.3072	4.85294	4.8277
O	5.70264	6.14244	4.86394

Table A.4.14. Geometry-optimized XYZ coordinates of diethylamine.

Diethylamine

	X	Y	Z
C	5.07074	5.413	5.91917
H	5.30032	5.87267	6.85774
C	3.54574	5.41754	5.70476
H	3.06491	4.97803	6.5536
H	3.20555	6.42481	5.58399
H	3.3072	4.85294	4.8277
C	7.12271	6.04682	5.00226
H	7.59487	6.50191	4.15677
H	7.40709	5.01681	5.05803
C	7.56319	6.7713	6.28784
H	7.45768	6.11114	7.12327
H	8.5866	7.06985	6.19619
H	6.95134	7.63629	6.43727
N	5.70264	6.14244	4.86394
H	5.2253	6.6421	4.1411
H	5.42791	4.40438	5.91917

Table A.4.14. Geometry-optimized XYZ coordinates of H₂.

H₂

	X	Y	Z
H	5.54808	4.06502	5.91917
H	4.94808	4.06502	5.91917

Table A.4.14. Geometry-optimized XYZ coordinates of H₂O.

H₂O

	X	Y	Z
O	5.54808	4.06502	5.91917
H	6.50808	4.06502	5.91917
H	5.22763	4.96996	5.91917

Table A.4.14. Geometry-optimized XYZ coordinates of H₃O⁺.

H₃O⁺

	X	Y	Z
O	5.54808	4.06502	5.91917
H	6.50405	3.97718	5.91917
H	5.14617	4.93684	5.91917
H	4.99402	3.28105	5.91917

Chapter 6

1. Geometry-optimized XYZ coordinates data of all reactants, intermediates and transition states.
2. Oscillator strengths for the TD-DFT-calculated absorption spectra of the AQN-Selectfluor® exciplex.

Table A.6.1. Geometry-optimized XYZ coordinates of AQN (singlet ground state).

AQN (singlet ground state)

	X	Y	Z
C	-3.67995	0.69539	0.00013
C	-2.48349	1.39043	0.00005
C	-1.27744	0.6983	-0.00003
C	-1.2774	-0.69832	-0.00006
C	-2.48348	-1.3904	-0.00008
C	-3.67994	-0.69536	0.00006
C	0	1.47179	-0.00008
C	0	-1.47182	-0.00006
C	1.2774	-0.69832	-0.00009
C	1.27744	0.69831	0
C	2.48349	1.39043	0.00012
H	2.45924	2.47442	0.00016
C	3.67995	0.69539	0.00018
C	3.67994	-0.69536	0.00002
C	2.48348	-1.3904	-0.00015
H	-4.6199	1.2372	0.00033
H	-2.45924	2.47441	0.00004
H	-2.45927	-2.47439	-0.00016
H	-4.61988	-1.2372	0.00016
H	4.6199	1.23721	0.00042
H	4.61988	-1.2372	0.00006
H	2.45927	-2.47439	-0.00027
O	0	-2.68357	0.00011
O	0	2.68353	-0.00021

Table A.6.2. Geometry-optimized XYZ coordinates of Selectfluor®.

Selectfluor®

	X	Y	Z
F	-3.18047	-0.54851	-0.00214
C	-1.25832	-0.6585	1.29408

C	-1.19384	-0.89899	-1.15149
C	-1.7514	1.27291	-0.14213
C	0.26716	-0.50129	1.16467
H	-1.55362	-1.69537	1.44921
H	-1.69707	-0.04613	2.08097
C	0.21681	-0.30069	-1.28163
H	-1.80265	-0.71824	-2.03638
H	-1.19649	-1.96619	-0.93336
H	-2.09377	1.52782	-1.14424
H	-2.42662	1.72066	0.58579
C	-0.2814	1.64431	0.1198
H	0.76325	-1.45231	0.98378
H	0.69121	-0.06421	2.06815
H	0.27994	0.42982	-2.08822
H	0.95301	-1.08118	-1.4651
H	0.06299	2.38102	-0.60522
H	-0.1347	2.05256	1.11954
N	-1.85564	-0.21087	-0.00076
N	0.57549	0.40823	0.00026
C	2.03475	0.83945	-0.00068
H	2.19196	1.44022	-0.89496
H	2.19233	1.44211	0.8924
Cl	3.12664	-0.51758	-0.00032

Table A.6.3. Geometry-optimized XYZ coordinates of Selectfluor® •N-radical.

Selectfluor® •N-radical

	X	Y	Z
C	-4.11277	7.61995	1.31211
C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152
H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254

N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389
Cl	-3.71053	6.43153	-3.0592

Table A.6.4. Geometry-optimized XYZ coordinates of Selectfluor®-H.

Selectfluor®-H

	X	Y	Z
C	-4.11277	7.61995	1.31211
C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152
H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254
N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389
Cl	-3.71053	6.43153	-3.0592
H	-4.62898	6.34432	2.80952

Table A.6.5. Geometry-optimized XYZ coordinates of pentane.

pentane

	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871
C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
H	1.4597	-0.17147	0.5611
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873

Table A.6.6. Geometry-optimized XYZ coordinates of 3-pentane radical.

3-pentane radical

	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871
C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873

Table A.6.7. Geometry-optimized XYZ coordinates of 3-fluoropentane.

3-fluoropentane

	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871
C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873
F	1.37937	-0.28191	0.7497

Table A.6.8. Geometry-optimized XYZ coordinates of **RC1**.

<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 20px;">RC1</div> </div>			
	X	Y	Z
C	-1.40306	3.8216	-0.92742
C	-1.24168	2.55351	-1.46299
C	-1.80594	1.45669	-0.82286
C	-2.53078	1.63949	0.36438
C	-2.66354	2.9094	0.91063
C	-2.10738	3.99832	0.25822
C	-1.60077	0.10398	-1.383
C	-3.14564	0.48784	1.05465
C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82794	-2.04126	-1.73798
H	-2.32947	-2.1599	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.4066	-2.38864
H	-3.21587	3.03568	1.83406

H	-2.23379	4.99277	0.66857
H	-3.93369	-3.88921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
O	-0.71203	-0.16774	-2.15882
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847
C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02014
C	3.13575	-1.32074	-0.5765
H	1.04148	-1.48549	-1.1863
H	1.48822	-2.61275	0.101
C	2.9991	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.3828
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211
H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.4584	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339
C	5.16558	-0.29341	0.45865
H	5.4696	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229

Table A.6.9. Geometry-optimized XYZ coordinates of S_1 .

<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 20px;">S_1</div> </div>			
	X	Y	Z
C	2.63299	3.39975	-1.15251
C	1.79869	2.40402	-1.63233
C	1.83499	1.13524	-1.05824
C	2.6992	0.87602	0.01488
C	3.51062	1.88834	0.50669
C	3.48424	3.14261	-0.08429
C	0.93759	0.07652	-1.55479
C	2.7297	-0.46866	0.65547

C	2.05495	-1.58605	-0.07094
C	1.21582	-1.3221	-1.15956
C	0.60466	-2.37579	-1.83761
H	-0.00007	-2.16812	-2.71336
C	0.82769	-3.68036	-1.42904
C	1.64276	-3.93811	-0.33194
C	2.25157	-2.89516	0.34874
H	2.63126	4.37753	-1.61873
H	1.14524	2.58878	-2.47675
H	4.16816	1.67783	1.34144
H	4.13793	3.92391	0.28424
H	0.3845	-4.50281	-1.97778
H	1.81954	-4.96034	-0.01969
H	2.89863	-3.08294	1.19719
O	3.25502	-0.64863	1.72894
O	-0.06152	0.34817	-2.21803
F	-3.84406	0.47601	-2.12658
C	-2.45226	-0.87617	-0.8572
C	-2.35607	1.58289	-0.73485
C	-4.31519	0.37873	0.1342
C	-1.94306	-1.04708	0.58386
H	-1.64018	-0.76049	-1.57726
H	-3.1202	-1.68056	-1.15616
C	-1.55351	1.37974	0.56085
H	-3.00178	2.4582	-0.71205
H	-1.69254	1.61345	-1.59899
H	-4.97359	1.22257	-0.05982
H	-4.87517	-0.5453	0.00847
C	-3.62358	0.48574	1.50424
H	-0.88032	-1.28444	0.58207
H	-2.47788	-1.82903	1.12077
H	-1.58218	2.27124	1.18446
H	-0.51445	1.14023	0.35102
H	-3.746	1.47521	1.94092
H	-4.02802	-0.24947	2.19706
N	-3.24215	0.39119	-0.8979
N	-2.14544	0.23782	1.34791
C	-1.54472	0.14894	2.73996
H	-1.81073	1.0646	3.26347
H	-1.99471	-0.71207	3.22897
Cl	0.19363	-0.03387	2.71993

Table A.6.10. Geometry-optimized XYZ coordinates of **T₁**.

T₁

	X	Y	Z
C	0.25484	2.72823	0.3213
C	-0.4498	3.90625	0.35762
C	0.19714	5.14737	0.35525
C	1.61095	5.15117	0.3096
C	2.32432	3.94069	0.27426
C	1.65261	2.74654	0.28089
C	-0.56141	6.38066	0.39869
C	2.2972	6.40077	0.3006
C	1.5944	7.64085	0.32883
C	0.18071	7.6246	0.37504
C	-0.48238	8.85698	0.39794
H	-1.56854	8.85894	0.42698
C	0.20602	10.04484	0.37946
C	1.60384	10.04609	0.33754
C	2.29141	8.86127	0.31197
H	-0.2695	1.77728	0.32287
H	-1.53599	3.89002	0.3847
H	3.41049	3.95966	0.24097
H	2.20707	1.81362	0.25319
H	-0.33112	10.98848	0.39657
H	2.14575	10.98667	0.324
H	3.37772	8.85733	0.27784
O	3.58732	6.40965	0.26482
O	-1.82185	6.37185	0.45859
F	-4.59866	6.33729	3.17515
C	-4.11277	7.61995	1.31211
C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152
H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254
N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389

Cl	-3.71053	6.43153	-3.0592
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Table A.6.11. Geometry-optimized XYZ coordinates of AQN-Selectfluor® exciplex (Int1).

AQN-Selectfluor® exciplex (Int1).

	X	Y	Z
C	1.53217	3.69301	1.10184
C	1.26936	2.38615	1.48684
C	1.83729	1.33337	0.78548
C	2.68227	1.60165	0.30109
C	2.91918	2.91074	0.70165
C	2.34891	3.955	0.00773
C	1.53327	0.06597	-1.1899
C	3.32046	0.49017	1.028
C	3.41805	0.82886	0.31829
C	2.56389	1.08768	-0.7996
C	2.75839	2.21745	1.54037
H	2.15484	-2.4011	2.42069
C	-3.7413	-3.1373	1.13411
C	4.54335	-2.9143	0.01449
C	4.36318	1.78409	0.75684
H	1.10611	4.51551	1.66384
H	0.64031	2.175	2.34349
H	3.56537	3.10076	1.55033
H	2.55398	4.9783	0.28181
H	3.88206	4.04964	1.70324
H	-5.3012	-3.6398	0.28273
H	4.95694	-1.5681	1.63626
O	3.75101	0.55393	2.15282
O	0.64094	0.35303	1.95646
F	0.68326	0.58963	0.77053
C	1.7452	1.56116	0.19612
C	1.62786	0.83064	0.05917
C	1.76587	0.58308	2.00479
C	3.26052	1.35968	0.43247
H	1.19154	1.54202	1.13221
H	1.53203	2.49555	0.31811
C	3.1555	1.01487	0.2099
H	1.08179	1.611	0.58452
H	1.31195	0.82988	0.98162
H	1.45669	0.29709	2.56353
H	1.30997	1.45573	2.46566
C	3.30544	0.72109	1.93901
H	3.47593	0.98648	1.42986

H	3.82908	-2.2748	0.27675
H	3.4172	1.69539	1.0191
H	3.61636	1.37124	0.70749
H	3.80334	0.07391	2.65868
H	3.6373	1.74467	2.1053
N	1.30041	-0.4599	0.63791
N	3.76498	0.32576	0.55125
C	5.26871	0.25716	0.56802
H	5.5559	0.53431	1.25565
H	5.63922	1.21656	0.92043
Cl	5.96126	0.07955	1.01021

Table A.6.12. Geometry-optimized XYZ coordinates of **Int2**.

Int2

	X	Y	Z
C	-1.40306	3.8216	-0.92742
C	-1.24168	2.55351	-1.46299
C	-1.80594	1.45669	-0.82286
C	-2.53078	1.63949	0.36438
C	-2.66354	2.9094	0.91063
C	-2.10738	3.99832	0.25822
C	-1.60077	0.10398	-1.383
C	-3.14564	0.48784	1.05465
C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82794	-2.04126	-1.73798
H	-2.32947	-2.1599	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.4066	-2.38864
H	-3.21587	3.03568	1.83406
H	-2.23379	4.99277	0.66857
H	-3.93369	-3.88921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
O	-0.71203	-0.16774	-2.15882
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847
C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02014

C	3.13575	-1.32074	-0.5765
H	1.04148	-1.48549	-1.1863
H	1.48822	-2.61275	0.101
C	2.9991	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.3828
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211
H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.4584	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339
C	5.16558	-0.29341	0.45865
H	5.4696	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229
C	-0.55197	-3.85574	1.54605
C	-0.55197	-3.85574	3.08605
H	-1.48832	-4.23115	3.44272
H	-0.40891	-2.85713	3.44272
C	-0.75787	-5.29299	1.03272
H	0.03542	-5.91619	1.38938
C	-0.75788	-5.29299	-0.50728
H	-0.84753	-6.2978	-0.86395
H	-1.58325	-4.71294	-0.86395
H	0.15714	-4.86822	-0.86395
C	0.58977	-4.75268	3.59938
H	0.86086	-4.45296	4.59013
H	0.26462	-5.77201	3.61152
H	1.43713	-4.65627	2.95317
H	-1.69422	-5.6684	1.38938
H	0.38438	-3.48033	1.18938
H	-1.34526	-3.23254	1.18938

Table A.6.13. Geometry-optimized XYZ coordinates of **Int3**.

Int3
	X	Y	Z

C	-1.45777	-5.02294	0.22667
C	-1.13383	-3.89643	0.96528
C	-1.65302	-2.6592	0.60118
C	-2.49367	-2.55625	-0.51918
C	-2.79112	-3.68582	-1.26887
C	-2.28142	-4.91727	-0.88824
C	-1.28724	-1.46407	1.38327
C	-3.05138	-1.25129	-0.93271
C	-2.96729	-0.12167	0.06013
C	-2.18111	-0.26995	1.25098
C	-2.26666	0.6675	2.24044
H	-1.70281	0.54876	3.15733
C	-3.09015	1.78538	2.04314
C	-3.81455	1.97071	0.83474
C	-3.7308	1.04291	-0.16105
H	-1.07353	-5.99116	0.52377
H	-0.4963	-3.96919	1.83824
H	-3.4304	-3.592	-2.13833
H	-2.53397	-5.80271	-1.45876
H	-3.1673	2.53455	2.82294
H	-4.44305	2.84595	0.72493
H	-4.27578	1.13865	-1.09165
O	-3.57579	-1.04099	-1.9963
O	-0.32193	-1.41079	2.11568
F	-0.74175	-0.06567	-0.93101
C	1.66413	0.66139	0.64655
C	1.72272	-1.4115	-0.58059
C	1.7515	0.68915	-1.75866
C	3.18867	0.47258	0.82465
H	1.11918	0.2234	1.48039
H	1.39009	1.70923	0.55751
C	3.25828	-1.40923	-0.76001
H	1.22995	-1.93769	-1.39469
H	1.42312	-1.86728	0.36087
H	1.51252	0.09861	-2.63965
H	1.2232	1.63664	-1.83021
C	3.2733	0.90151	-1.59087
H	3.42752	-0.27455	1.57654
H	3.6905	1.40164	1.08929
H	3.56086	-1.66221	-1.77528
H	3.75149	-2.08837	-0.06976
H	3.82133	0.6619	-2.50027
H	3.52019	1.9199	-1.29466
N	1.29793	-0.02326	-0.58057
N	3.76627	-0.01146	-0.48735
C	5.27006	0.03621	-0.48879
H	5.61336	-0.37452	-1.43491
H	5.56771	1.07798	-0.39912
Cl	5.9902	-0.87987	0.82533
C	-0.64302	3.35499	-0.34882
C	-1.52301	3.73385	-1.53742

H	-2.575	3.67872	-1.23462
H	-1.40373	2.97823	-2.32031
C	-0.86191	4.18633	0.909
H	-0.66047	5.24014	0.70526
C	-0.00623	3.73122	2.08217
H	-0.20467	4.31236	2.9832
H	-0.17874	2.67659	2.32429
H	1.059	3.8484	1.86101
C	-1.23858	5.1144	-2.11339
H	-1.85063	5.30566	-2.99483
H	-1.44776	5.91042	-1.39751
H	-0.1922	5.21036	-2.41493
H	-1.92358	4.14842	1.18451
H	0.41247	3.4567	-0.64734
H	-1.61552	0.0389	-0.93101

Table A.6.14. Geometry-optimized XYZ coordinates of **Int4**.

Int4

	X	Y	Z
C	1.25575	0.99436	-1.87949
C	1.33144	-1.47062	-1.92466
C	-0.82372	-0.31293	-1.6809
C	1.17441	0.97395	-3.40719
H	2.29932	0.98284	-1.5524
H	0.70952	1.81689	-1.41252
C	1.08014	-1.49265	-3.43312
H	0.91903	-2.33589	-1.40216
H	2.39826	-1.34485	-1.715
H	-1.20079	-1.26094	-1.29156
H	-1.29403	0.50463	-1.13082
C	-0.9775	-0.17424	-3.19938
H	2.18238	0.87459	-3.81891
H	0.67799	1.86228	-3.80493
H	0.44584	-2.32752	-3.74269
H	2.03797	-1.52914	-3.95747
H	-1.58773	-0.98237	-3.6098
H	-1.43968	0.77711	-3.47415
N	0.63466	-0.26839	-1.37649
N	0.376	-0.22588	-3.854
C	0.16069	-0.20468	-5.35817
H	-0.41661	-1.09693	-5.611
H	-0.41481	0.69563	-5.5855
Cl	1.65799	-0.19406	-6.2508

C	5.08225	-0.62435	-3.4896
H	5.43892	-0.11995	-2.61594
C	5.59559	0.10161	-4.747
H	6.66559	0.10329	-4.74602
H	5.24052	-0.40392	-5.62065
C	5.59557	-2.07628	-3.4896
H	6.66557	-2.07629	-3.48997
H	5.23859	-2.58079	-4.36306
C	5.08267	-2.80208	-2.23192
H	5.43741	-3.81156	-2.23308
H	5.44155	-2.29892	-1.35846
H	4.01267	-2.80004	-2.23037
C	5.07998	1.55273	-4.74841
H	5.50034	2.08141	-3.91853
H	5.3683	2.0328	-5.66016
H	4.01304	1.55221	-4.66751
H	4.01225	-0.62433	-3.4896

Table A.6.15. Geometry-optimized XYZ coordinates of **Int5**.

Int5

	X	Y	Z
C	-0.77903	1.21477	-0.4512
C	-2.28647	1.21178	-0.23443
H	-0.3125	2.08244	0.08125
H	-0.54424	1.32327	-1.54074
H	-2.58756	2.0785	0.40756
H	-2.81918	1.31777	-1.21371
C	-0.4862	-0.21567	1.5609
H	-0.03649	-1.16258	1.95476
H	-0.01555	0.63595	2.11517
C	-1.99353	-0.21757	1.77843
H	-2.31112	-1.16494	2.28401
H	-2.29045	0.63373	2.44261
C	-2.31372	-1.26444	-0.45365
H	-2.63397	-2.22372	0.02723
H	-2.84756	-1.18575	-1.43488
C	-0.80646	-1.26139	-0.67166
H	-0.35937	-2.21947	-0.30259
H	-0.57285	-1.1803	-1.76383
N	-0.17704	-0.08653	0.07189
N	-2.71143	-0.091	0.43754
C	-4.16637	-0.0936	0.64742
H	-4.45715	-1.0093	1.11842
H	-4.438	0.73107	1.27275

Cl	-4.98326	0.05302	-0.90461
C	3.35637	-0.08023	-0.43792
H	3.56573	0.01033	-1.48332
C	3.95399	-1.39645	0.09315
H	3.73954	-1.48983	1.13727
H	3.52388	-2.22195	-0.43453
C	5.47928	-1.39014	-0.11908
H	5.89441	-2.30497	0.24922
H	5.69373	-1.29598	-1.16313
H	5.90948	-0.56508	0.40923
C	3.98163	1.10835	0.31569
H	3.94857	0.92032	1.36852
H	4.99878	1.23106	0.00706
C	3.19055	2.39092	-0.00181
H	2.74772	2.30583	-0.97215
H	2.42209	2.52642	0.73031
H	3.85221	3.23163	0.01581
H	2.29734	-0.08212	-0.28512

Table A.6.16. Geometry-optimized XYZ coordinates of **Int7**.

<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 20px;">Int7</div> </div>			
	X	Y	Z
C	1.25575	0.99436	-1.87949
C	1.33144	-1.47062	-1.92466
C	-0.82372	-0.31293	-1.6809
C	1.17441	0.97395	-3.40719
H	2.29932	0.98284	-1.5524
H	0.70952	1.81689	-1.41252
C	1.08014	-1.49265	-3.43312
H	0.91903	-2.33589	-1.40216
H	2.39826	-1.34485	-1.715
H	-1.20079	-1.26094	-1.29156
H	-1.29403	0.50463	-1.13082
C	-0.9775	-0.17424	-3.19938
H	2.18238	0.87459	-3.81891
H	0.67799	1.86228	-3.80493
H	0.44584	-2.32752	-3.74269
H	2.03797	-1.52914	-3.95747
H	-1.58773	-0.98237	-3.6098
H	-1.43968	0.77711	-3.47415
N	0.63466	-0.26839	-1.37649
N	0.376	-0.22588	-3.854
C	0.16069	-0.20468	-5.35817

H	-0.41661	-1.09693	-5.611
H	-0.41481	0.69563	-5.5855
Cl	1.65799	-0.19406	-6.2508
C	3.76209	-0.48522	-2.66367
H	4.11876	0.01918	-1.79002
C	4.27543	0.24074	-3.92107
H	5.34543	0.24242	-3.9201
H	3.92036	-0.26479	-4.79472
C	4.2754	-1.93715	-2.66367
H	5.3454	-1.93717	-2.66405
H	3.91842	-2.44166	-3.53713
C	3.76251	-2.66295	-1.40599
H	4.11725	-3.67243	-1.40716
H	4.12139	-2.15979	-0.53253
H	2.69251	-2.66092	-1.40445
C	3.75982	1.69185	-3.92248
H	4.18018	2.22053	-3.09261
H	4.04814	2.17193	-4.83424
H	2.69288	1.69134	-3.84158
F	0.76986	-0.2883	-0.01645

Table A.6.17. Geometry-optimized XYZ coordinates of **TS1**.

TS1

	X	Y	Z
C	-0.7567	4.50922	-0.14605
C	-0.46727	3.51545	0.77432
C	0.52493	2.58203	0.49499
C	1.23066	2.65423	-0.71373
C	0.91245	3.63391	-1.64587
C	-0.07648	4.56113	-1.3582
C	0.79106	1.49054	1.4586
C	2.33548	1.7103	-1.00041
C	2.90777	0.96932	0.17527
C	2.1424	0.84666	1.38311
C	2.67216	0.20054	2.47126
H	2.09426	0.10626	3.38193
C	3.96857	-0.30362	2.38583
C	4.73802	-0.16109	1.19449
C	4.20126	0.45572	0.09477
H	-1.50768	5.25564	0.08351
H	-0.99129	3.46537	1.72182
H	1.46029	3.67335	-2.57975

H	-0.30585	5.3419	-2.07328
H	4.41391	-0.79726	3.24196
H	5.7492	-0.54941	1.17281
H	4.75497	0.56563	-0.82882
O	2.81538	1.5459	-2.09305
O	-0.01317	1.13598	2.29116
F	0.62981	-0.55897	-0.36972
C	-1.74671	-1.301	0.82084
C	-2.14183	0.73504	-0.38253
C	-1.71511	-1.30424	-1.5782
C	-3.2847	-1.41679	0.92576
H	-1.33524	-0.78623	1.68701
H	-1.26802	-2.27461	0.74252
C	-3.63871	0.44766	-0.64136
H	-1.73002	1.38051	-1.15667
H	-1.99065	1.21586	0.58092
H	-1.55177	-0.66993	-2.44698
H	-1.02195	-2.13978	-1.63607
C	-3.17668	-1.80119	-1.49553
H	-3.70092	-0.74772	1.67396
H	-3.61142	-2.43041	1.15181
H	-3.9344	0.65708	-1.66864
H	-4.28467	1.00912	0.02842
H	-3.71645	-1.64602	-2.42806
H	-3.24341	-2.85465	-1.22804
N	-1.444	-0.53818	-0.377
N	-3.88438	-1.02383	-0.40706
C	-5.34885	-1.35616	-0.48213
H	-5.72035	-1.00328	-1.44082
H	-5.44704	-2.43665	-0.41358
Cl	-6.29214	-0.61452	0.80122
C	2.32083	-2.38158	-0.6748
C	3.46066	-2.25803	-1.66943
H	4.35103	-1.86937	-1.16634
H	3.20054	-1.52675	-2.44009
C	2.67824	-2.92972	0.68123
H	3.23666	-3.86773	0.5688
C	1.49181	-3.12569	1.60876
H	1.79718	-3.51084	2.5822
H	0.96225	-2.18262	1.76934
H	0.78225	-3.84269	1.187
C	3.81156	-3.58654	-2.33799
H	4.63558	-3.46088	-3.04043
H	4.11305	-4.34081	-1.60875
H	2.96199	-3.98578	-2.89578
H	3.41506	-2.26198	1.16562
H	1.50378	-2.97631	-1.11081
H	1.74716	-1.38646	-0.53335

Table A.6.18. Geometry-optimized XYZ coordinates of **TS2**.

TS2

	X	Y	Z
C	0.02549	-1.4198	0.42843
C	-0.01042	0.13113	-1.44069
C	-1.13602	-2.01279	-1.61491
C	-1.15576	-0.56671	0.99905
H	0.98247	-1.04001	0.78779
H	-0.06981	-2.47447	0.67584
C	-1.42065	0.71082	-1.08681
H	0.1665	0.17562	-2.51445
H	0.79262	0.64436	-0.9168
H	-1.16898	-1.80822	-2.68237
H	-0.97789	-3.0774	-1.44896
C	-2.42778	-1.52136	-0.87804
H	-0.80389	0.37146	1.41916
H	-1.69741	-1.11973	1.76413
H	-2.05244	0.80959	-1.9678
H	-1.32374	1.67964	-0.60314
H	-3.2232	-1.32274	-1.59381
H	-2.77689	-2.25119	-0.15004
N	-0.08624	-1.23874	-0.99642
N	-2.1037	-0.24429	-0.13574
C	-3.4107	0.34005	0.38128
H	-4.01502	0.59784	-0.48549
H	-3.89972	-0.4333	0.96948
Cl	-3.16534	1.76293	1.36894
C	3.20101	0.29069	0.19544
H	2.85047	-0.47969	-0.51389
C	4.04741	-0.37854	1.27061
H	4.93679	-0.81069	0.80505
H	4.41242	0.3828	1.96446
C	3.9154	1.38804	-0.5827
H	4.80748	0.96677	-1.05306
H	4.27555	2.1463	0.11701
C	3.04336	2.04383	-1.64262
H	3.58198	2.82273	-2.18124
H	2.70785	1.31813	-2.39206
H	2.16345	2.52554	-1.19831
C	3.30161	-1.45709	2.04151
H	2.96261	-2.26345	1.38108
H	3.93259	-1.92057	2.79918
H	2.4342	-1.04521	2.57251
H	2.3046	0.72764	0.67557

Table A.6.19. Geometry-optimized XYZ coordinates of **TS3**.

<div> <div>TS3</div> </div>				
	X	Y	Z	
C	-0.22021	1.04897	1.02801	
C	0.07326	-0.78983	-0.56444	
C	-0.4918	-1.27094	1.77458	
C	-1.62951	1.13967	0.41893	
H	0.49447	1.68968	0.51244	
H	-0.19166	1.27166	2.09279	
C	-1.43178	-0.97885	-0.80469	
H	0.63605	-1.71234	-0.69691	
H	0.52159	-0.01693	-1.18602	
H	-0.20696	-2.28965	1.51961	
H	-0.1647	-1.05453	2.78945	
C	-1.99214	-0.98785	1.57903	
H	-1.61994	1.59529	-0.56765	
H	-2.29382	1.71932	1.05713	
H	-1.7278	-2.02614	-0.7654	
H	-1.72449	-0.57162	-1.76945	
H	-2.55739	-1.91746	1.54855	
H	-2.39677	-0.36384	2.37418	
N	0.23752	-0.35804	0.8536	
N	-2.1956	-0.25345	0.27543	
C	-3.68513	-0.22669	-0.02498	
H	-4.00209	-1.2563	-0.17588	
H	-4.18138	0.20113	0.84351	
Cl	-4.06614	0.71854	-1.44615	
C	3.74831	0.2976	-0.37985	
H	4.45131	0.15523	0.43612	
C	3.19339	1.65696	-0.60481	
H	3.73195	2.14884	-1.42859	
H	2.16312	1.57695	-1.00635	
C	3.65678	-0.75677	-1.42272	
H	4.45138	-0.60111	-2.16799	
H	2.73075	-0.63194	-2.00508	
C	3.76741	-2.18182	-0.88958	
H	3.72219	-2.91398	-1.69598	
H	4.71252	-2.33192	-0.36652	
H	2.97274	-2.41629	-0.17269	
C	3.22349	2.56481	0.6184	
H	4.24949	2.74305	0.94109	
H	2.77994	3.53961	0.41042	
H	2.70432	2.12136	1.47435	
F	1.58929	-0.40939	1.14653	

Table A.6.20. Oscillator strengths for the TD-DFT-calculated absorption spectra of the AQN-Selectfluor® exciplex.

Wavelength (nm)	Oscillator strength
492.61	0.0282
479.36	0.0078
432.67	0.083
422.59	0.0075
416.22	0.0012
413.25	0.0062
396.37	0.0031
382.93	0.0246
379.75	0.0032
361.27	0.0037
342.08	0.0022
332.59	0.0013
320.65	0.0017
311.51	0.0026
299.58	0.0362
298.82	0.021
296.1	0.0493
292.86	0.0049
286.12	0.056
282.8	0.0014
280.67	0.0855
276.46	0.04
273.18	0.0585
267.92	0.1016
263.53	0.0125
261.21	0.0223
257.32	0.0382
255.53	0.0011
253.47	0.0033
243.9	0.0654
239.97	0.0582
234.89	0.0451
233.71	0.0048
232.07	0.005

229.97	0.0197
227.77	0.1167
225.07	0.009
221.76	0.0172
221.27	0.0064
220.08	0.1802
217.22	0.0076
214.87	0.0093
214.6	0.0694
212.97	0.0117
212.18	0.0311
211.14	0.003
208.61	0.0652
207.58	0.0126
206.88	0.0204
205.3	6.00E-04
204.75	3.00E-04
203.69	0.0025
203.06	0.0109

List of Publications

1. Enhancing Electrocatalytic Hydrogen Evolution by Nickel Salicylaldimine Complexes with Alkali Metal Cations in Aqueous Media, Shao, H.; Muduli, S. K.; Tran, P. D.; Soo, H. S. *Chem. Commun.* **2016**, 52, 2948-2951.
2. Mechanistic Understanding of Photoredox Fluorination with Anthraquinone and Selectfluor® Using Time-Resolved Studies, Kee, J. W.; Shao, H.; Kee, C. W.; Lu, Y.; Soo, H. S.; Tan, C. H. *Catal. Sci. Technol.* **2016**, Submitted.
3. Visible Light-Driven Hydrogen Evolution Catalyzed by Nickel Salicylaldimine Complex, Shao, H.; Ho, X.; Ng, Y. Y.; Lu, Y.; Soo, H. S. **2016**, Submitted.