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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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1. Introduction

1.1 Hydrogen Economy

Coming into the 21st century, the population growth together with rapid industrialization has led to a surge in the global demand for energy. It has been agreed that the traditional and non-renewable energy sources, such as coal, oil, natural gas, etc., cannot fulfill the need of maintaining the long-term development of modern civilization. At the same time, combustion of the traditional fossil fuels releases substantial amount of carbon dioxide (CO$_2$), in which the rising of its concentration is the ‘Chief Culprit’ resulting in the greenhouse effect[]. Thus, in response to the energy demand of the world and supporting economic development in the future, scientists are going to great lengths to search for and develop new types of renewable technologies to replace fossil fuels by environmentally friendly and inexpensive alternative fuels.

Hydrogen is widely considered as the most promising alternative energy carrier as:

- Its combustion generates only water, which can achieve zero emission of greenhouse gases.
- It has the highest energy storage density (143 MJ/kg) relative to all compounds that are regarded as energy storage materials, and can easily be applied in fuel cells for electricity generation[].

Regarding production of hydrogen, the traditional strategies are well-known. Figure 1 clearly shows the principal production routes, suggesting that 96% is produced from steam reforming of fossil fuels, and 3.9% from electrolysis of water, a procedure which is rather inefficient and that has been much expensive[]. This is obviously not suited for which we achieve the goal of creating a green sustainable society.
In comparison with using fossil fuels for hydrogen production, solar energy is undoubtedly the most attractive source as it is clean, pollution-free and inexhaustible []. In this regard, natural photosynthesis is a central example on utilization of solar energy []; it is a process used by green plants to convert light energy into chemical energy, providing carbohydrates (food), oxygen and fuel for us. Inspired by nature, scientists have spent a large amount of time and efforts on developing the strategies of effective utilization of solar energy. For example, in photoelectrochemical (PEC) water splitting, hydrogen is produced from water using sunlight; where one photosensitized electrode converts light into an electric current, which then drives splitting of water into hydrogen and oxygen []. This, however, is an indirect process that suffers from low efficient energy conversion, because it first produces electricity, which then is used to form hydrogen. Therefore, direct hydrogen production from sunlight might be more advantageous, and mimicking the key steps in natural photosynthesis would be an approach to make humanity’s dream of a clean fuel from sunlight and water come true (More details will be described in section 1.2).

1.2 From Natural to Artificial Photosynthesis

As mentioned in section 1.1, photosynthesis is a well-known example on solar energy conversion. The nature of photosynthesis is the fact that plants or certain bacteria convert CO₂ and H₂O (H₂S and H₂O for bacteria) into organic matter under visible light, with releasing O₂ as only byproduct (H₂ for bacteria) []. The total reaction for oxygen evolution in photosynthesis can be expressed by formula 1 []:

\[6H_2O + 6CO_2 \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2 \] (1)
For green plants, photosynthesis can be divided into two categories: light reactions and dark reactions. The specific processes of light reactions are as follows:

1) Absorption of photons and excited state energy transfer: Chlorophylls are the most important photosynthetic pigments in green plants. They absorb the visible light ranging from 400 nm to 700 nm, and transfer the excited energy to adjacent or heterogeneous pigment molecules in the ground state by means of ‘exciton transfer’ or ‘resonance transfer’ [], and back to ground state;

2) Charge separation: The excited pigment molecules (P_{680}) initiate a redox reaction with electron acceptors presented in the reaction center in photosystem II (PS II), generating charge separation (or electron-hole pairs) [];

3) Water oxidation: In PS II, the oxidative holes are able to activate the oxygen evolving complex (OEC), a cubic Mn_{4}O_{5}Ca cluster, which in turn oxidizes the water into oxygen (O_{2}) and protons;

4) Electron transport: The generated electrons are transferred to photosystem I (PS I) along an electron-transport chain. As a result, it causes the reduction of NADP\(^{+}\) to produce a reducing electron carrier such as NADPH or ATP, as soon as absorbing the second photon in PS I. Such processes can be described by a so-called ‘Z-scheme’ (see Figure 2).

The dark reactions are actually the processes that carry out the fixation of CO\(_{2}\), where NADPH produced by light reactions is used for reducing CO\(_{2}\) to hydrocarbon such as sugar [].

Based on mechanistic understanding of natural photosystem, artificial photosynthesis aims at mimicking the key steps in photosynthesis. There is no need for replicating all processes like in green leaves, but a successful artificial system for water splitting must be made up of three components: (1) Antenna/reaction center complexes (photosensitizers) that are able to harvest
sunlight and generate electrochemical potential; (2) catalysts that oxidize water to produce molecular oxygen; (3) catalysts that reduce protons into hydrogen. The first example for such a system was reported in 1972 by Fujishima et al., where they created a photoelectrochemical cell using a platinum (Pt) as cathode and a TiO$_2$ based as anode to carry on splitting of water under ultraviolet (UV) irradiation [4]. However, as already mentioned before, such a system suffers from a low efficient energy conversion because it undergoes electrical energy conversion step before producing hydrogen. On the other hand, it in general uses the noble metals, Pt and palladium (Pd), or noble metals-based complexes as catalysts for hydrogen production. This is obviously not feasible for future sustainable energy demand, and therefore a new artificial system that contains an earth abundant-element-based molecular catalyst and is able to do direct fuel production will be needed. In 2003, Hammarstrom et al. [5] proposed a model that consists of D-P-A units and catalysts for water splitting as shown in Figure 3, where photoexcited photosensitizer (P*) could deliver an electron to the acceptor (A) and the donor (D) should be able to reduce the oxidized state of photosensitizer P$^+$, generating a charge separated state, D$^+$-P-A$^-$. Then, it oxidizes water into molecular oxygen on the donor side and reduces protons into hydrogen on the acceptor side, with the help of catalysts. Yet, since the entire reaction in this model is quite complex process, only a few examples based on such model have been known to generate molecular hydrogen and oxygen simultaneously so far [5]. A comprehensive helpful approach is to divide this kind of artificial system into two half reactions, i.e. water oxidation reaction and proton (or CO$_2$) reduction reaction. Water oxidation is considered as one of the bottlenecks in the artificial photosystem as it typically involves multiple electron and proton transfers, generating high energetic intermediates. Thus, designing the water oxidation catalyst (WOC) towards high efficiency is crucial to lower reaction barrier. Several groups are focusing on developing molecular catalysts for water oxidation based on transition metals [5], and the best one is to date so-called Ru(bda) complex (TOF > 1000 s$^{-1}$) presented by Sun et al [5].

![Figure 3. An artificial photosystem for water splitting. Adapt from ref.](image_url)
1.2.1 Proton reduction catalysts

The work presented in this thesis only focuses on the proton reduction reaction, and therefore the water oxidation in the half reactions will not be further discussed. Again, the key point of proton reduction in the half reactions is the design of an efficient catalyst. In nature, photosynthesis for hydrogen evolving reaction employs hydrogenase enzymes that are found in certain microorganisms such as algae and cyanobacteria, capable of catalyzing proton reduction or hydrogen oxidation (Formula 2) \[2H^+ + 2e^- \rightarrow H_2\] (2).

\[\text{Hydrogenases}\]

In terms of the constitution of active sites, the hydrogenases can be classified into Fe-only hydrogenase, [Ni-Fe] hydrogenase, and [FeFe] hydrogenase, where [FeFe] hydrogenase is most efficient catalyst for \(\text{H}_2\) production with rate reaching to 9000 turnovers per second at close to thermodynamic potential [1], 10~100 times higher than that of other two hydrogenases.

Considering that a molecular catalyst must be efficient, robust and cheap enough to be cost effective, inspiration for such catalysts has been taken from the active site structure of the [FeFe] hydrogenase for proton reduction reaction. Today, large efforts have been directed toward the synthetic modeling of the active site [1]. The more details about the [FeFe] hydrogenase and its model complexes will be discussed in the following sections.

1.3 [FeFe] hydrogenases

In 1998, Peters and co-workers extracted the [FeFe]-hydrogenase from Clostridium pasteurianum (CpI) [1]. X-ray crystallography studies showed that structure of this enzyme is so-called ‘H-cluster’, which is made up of a binuclear Fe cluster [2Fe2S] connected to a [4Fe4S] cubic cluster through a cysteinate thiol, as shown in Figure 4. The iron connected to [4Fe4S] cubic cluster is named as ‘proximal’, \(\text{Fe}_p\), another one ‘distal’, \(\text{Fe}_d\). In the binuclear Fe cluster, the two Fe atoms are bridged by a dithiolate ligand, –S-CH2-X-CH2-S–, and today, it has been well proven that the atoms in the X position are NH [1]. Moreover, infrared spectroscopic studies reveal that each Fe in the [2Fe2S] unit is coordinated to one CN\(^-\) and one CO, and one more carbonyl dwells in a bridging position between the two irons. The bridging CO group provides the possibility for an excessively negative Fe atom to transfer part of its electron density to a CO group on a less negatively charged Fe atom [1]. Also, these CN\(^-\) and CO ligands play a key role in stabilizing the low oxidation state of
the Fe₂ core. The Fe atoms in the binuclear Fe cluster both exist with an octahedral coordination geometry but with reverse direction, which leads to an open coordination position at distal iron Fe₁.

Figure 4. FeFe-hydrogenase from Clostridium pasteurianum (CpI) and the structure of the active site.

In catalysis of [FeFe]-hydrogenase, two electrons and two protons will be required to produce hydrogen. The mechanism have not been fully realized so far, especially for catalytic intermediates. However, In general, the [2Fe2S] unit is only active site, and the [4Fe4S] cubic cluster could serve as an electron reservoir that affords a pathway for electron transfer from and to the active site during catalysis []. Also, the pendant amine in the azadithiolate ligand acting as proton relay for protonation in the metal center has been frequently proposed [], and subsequent facilitates the hydrogen-bonding formation such as faster intramolecular hydride/proton coupling. In addition, it seemed that involving a PCET reaction in catalysis by FeFe-hydrogenase plays a significant role for lowering overpotential (the extra energy needed to carry on the reaction over the thermodynamic potential) [], because transferring electrons and protons together to the active site is energetically more favorable than stepwise mechanisms.

1.4 Synthetic Molecular Catalysts Inspired by [FeFe]-hydrogenase

Considering the fact that [FeFe]-hydrogenase is not available in large quantities, and limited to the commercialization for hydrogen production. Therefore, mimicking its active site is necessary, and the crystal structure obtained provides a basic for synthetic chemistry. The desirable properties of the synthetic molecular catalysts should resemble those of FeFe-hydrogenase, such as high enough TOF, low overpotential and capable of operating in water at pH 7, etc. Today, large research has been focusing on the structural and functional mimics of the enzyme’s active site to elucidate the structure-function relationship of the enzyme.
1.4.1 Structural mimics

When research interest about mimicking the active site of FeFe-hydrogenase germinated from 1999, synthetic chemists only sought to focus on the [2Fe2S] unit and make the mimics resemble the structure of this enzyme as close as possible. Then, the synthetic pdt-functionalized (pdt = propanedithiolate) complex as biomimetic catalysts for H₂ production, the first structural mimic of the complete [2Fe2S] cluster, has been reported by Darensbourg []. The next generation of mimics carried out along different routes, with the group of Rauchfuss primarily focusing on structural mimics containing the azadithiolate (μ-adt) bridge [], and Lichtenberger et al. as well as other groups focusing on mimics containing aromatic bridges such as the benzenedithiolate (μ-bdt) bridge []. Later on, many research efforts extend to taking care of the ligands substituent based on the three parent complexes (see Figure 5), and there are more than 300 compounds that have been synthesized so far. Experiments in electrochemical and visible-light-driven reduction of protons show that most of them are active [], but unfortunately they all are much less efficient than the enzyme. Thus, mechanistic understanding for catalysts evaluation (heart of the thesis) will be needed.

1.4.2 Functional mimics

Earlier DFT calculations showed that the reaction site for proton reduction catalysis by the FeFe-hydrogenase mainly focused on the open coordination position at distal iron Fe₉. Combining with the crystal structure of FeFe-hydrogenase where a pendant amine is placed in the second coordination sphere brings two protons close enough to react and release as molecular hydrogen, or to help binding H₂ for heterolytic cleavage. The inspired that we could make not only the structural mimics, but also directly mimic the reaction site at open coordination position, i.e. functional mimics of FeFe-hydrogenase.

Significant progress has been achieved by incorporating the pendant amine into the second coordination sphere of a mononuclear nickel complex,
[Ni(P^{R_2N^{R'}_2})_2] (see Figure 6b), to mimicking the function of the proton shuttle in the active site of FeFe-hydrogenase. Indeed, such catalyst shows impressive enhancements in rate for H2 production [], which in turn provide insight into the function of the enzyme. Later on, such functional approach is extended to introduce additional enzyme-like functionality such as peptides into the outer coordination sphere to create the proton channels and pursue more efficient and faster catalysis [].

In addition, mimicking the electron distribution and coordination mode of the distal iron Fe₃ in FeFe-hydrogenase has been presented by Artero and Peters et al. This family of systems include molecular Co- and Mo-based complexes, which also show remarkable efficiency for H2 evolution (Figure 6c-d).

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1.5 Proton Reduction Mechanisms

For molecular catalysts (e.g. diiron, nickel and cobalt catalysts) as mentioned above, the mechanism of the catalysis of proton reduction at metallic centers has been investigated experimentally and theoretically [ref.]. Most of these studies have been done in organic solvent due to the fact that these synthetic molecular complexes are not soluble in water. Whereas these studies could
afford valuable view for the future design of a robust and efficient catalyst that would ultimately be used for water splitting. A schematic cubic for mechanism of proton reduction at metallic center LM\textsuperscript{n+} (L = entire ligand set) is shown in Figure 7, which summarizes the catalytic cycle for H\textsubscript{2} production. While the facial simplicity of \(2e^- + 2H^+ \rightleftharpoons H_2\) reaction, the coupling of two electrons and two protons at the metallic center LM\textsuperscript{n+} would follow a number of different pathways. It depends on many things such as catalyst itself and reaction conditions including solvent, strength of acid added, temperature, ability of reducing agent and concentrations. A common route is that reduction of LM\textsuperscript{n+} followed by protonation forms the key intermediate hydride, [LM-H]\textsuperscript{n+}. [LM-H]\textsuperscript{n+} can react in different ways: 1) it could involve the protonation of hydride to form dihydrogen bond, accompanied by release of H\textsubscript{2} and regeneration of the starting material (pathway I) ; 2) further reduction of hydride [LM-H]\textsuperscript{n+} results in a stronger base, which directly undergoes electrophilic attack from external proton to eliminate H\textsubscript{2} (pathway II). When the catalyst LM\textsuperscript{n+} contains a basic ligand site, a ligand protonation can occur before or after protonation of metal center,
2. Fundamentals and Methods

2.1 Studied Systems

2.1.1 Photochemical Reduction Systems

Photosensitizer

As mentioned in the introduction, a photocatalytic system for hydrogen formation is typically made up of a catalyst, an electron donor, and possibly photosensitizer, as well as an acid to afford the proton source. Such systems are used in chapter 3 of this thesis, and Papers I, II, III to obtain the one-electron reduced intermediates of biomimetic catalysts, and subsequent their reactivity towards protons. The catalysts investigated in the thesis are listed in Figure 9 in the following section, which are the structural mimics of active site of FeFe-hydrogenase.

The photosensitizer is particularly important in photocatalytic systems, because the catalysts presented in this thesis are not intrinsically photoactive, mainly the reduced states and protonated states relevant to catalysis (see below). The photosensitizer used in this thesis is Ru(bpy)_3(PF_6)_2 (bpy = 2, 2'-bipyridine), or its derivatives to tune the redox properties. [Ru(bpy)_3]^{2+} is a quite photostable compound, and shows an absorption maximum of 459 nm in acetonitrile that corresponds to a metal-to-ligand charge transfer (MLCT), with extinction coefficient of about 14700 M^{-1}cm^{-1} (see Figure 8) [ref.]. Upon excitation with visible light [Ru(bpy)_3]^{2+} can be initially excited to a singlet MLCT state, which then rapidly converts into its lowest triplet MLCT state via intersystem crossing. The nature of the MLCT excitation is to show a metal-centered oxidation process and six distinct ligand-centered reduction processes. Thus, [Ru(bpy)_3]^{2+}, in its ^3MLCT excited-state, is both a good oxidant and a good reductant. In addition, the ^3MLCT state has a lifetime of about 1µs in oxygen-free acetonitrile, which is long-lived enough for which electron transfer reactions occur in homogenous solution if the donor-acceptor pair has a high cage yield, or gives a high yield of charge separation. When exciting the [Ru(bpy)_3]^{2+} sample, the generating transient concentration is limited to the optical path length. It typically generates excited concentration of about 2 µM in UV-Vis (1 cm optical path length) and 20 µM in IR (1 mm) experiments; details about experimental setup will be discussed in section 2.3.
Figure 8. Schematic representation of simplified photophysical and electrochemical properties of \([\text{Ru(bpy)}_3]^{2+}\) in oxygen-free acetonitrile. The potential values are referred to Fc\(^+/\text{Fc}\).

**Photoinduced Reduction Reactions of Biomimetic Catalysts**

Figure 8 also summarizes the electrochemical properties of \([\text{Ru(bpy)}_3]^{2+}\) upon excitation. It was however apparent that photoexcited \([\text{Ru(bpy)}_3]^{2+}\) (\(E^0 = -1.17\) V) can directly not deliver an electron to the catalysts presented in this thesis (Complex 1-5), where reduction potentials of these catalysts are not less than 1.2 V versus Fc\(^+/\text{Fc}\) in acetonitrile and are summarized in Figure 9. Thus, photoexcited \([\text{Ru(bpy)}_3]^{2+}\) must be reductively quenched by an electron donor (D) to form \([\text{Ru(bpy)}_3]^+\), which has stronger reducing ability, with reduction potential of -1.7 versus versus Fc\(^+/\text{Fc}\) in acetonitrile. The electron donor employed in this thesis is tetrathiafuvalene (TTF). An important advantage choosing TTF as electron donor is that it is relatively stable in the presence of acid (pK\(_a\) > 8 in acetonitrile), unlike other electron donors such as a series of amine-based derivatives, where they are easily protonated to form DH\(^+\) that does not have the electron-donating ability at all. TTF also has a high cage yield and quenches the excited sensitizer \([\text{Ru(bpy)}_3]^{2+}\) in a diffusion-controlled reaction when a large excess of TTF is used, yielding oxidized TTF\(^+\) and reduced \([\text{Ru(bpy)}_3]^+\) (Figure 9, reaction 3). The absorption spectrum of oxidized TTF\(^+\) and reduced \([\text{Ru(bpy)}_3]^+\) has been reported in the literature [ref.], or can be found in paper I. TTF is a thermodynamically reversible electron donor, giving rise to a charge recombination between TTF\(^+\) and \([\text{Ru(bpy)}_3]^+\), with a rate constant of \(6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) (reaction 4). From kinetics measurement, the recombination reaction gives a half-life of about 80 \(\mu\)s under our experimental conditions (see paper I, II for details). Thus, when adding a large excess of catalyst to the solution, the reduced \([\text{Ru(bpy)}_3]^+\) will first
react with catalyst in pseudo first-order reaction (reaction 5), and oxidation of the catalyst by weak oxidant TTF$^+$ is thermodynamically disfavored. The reduced catalyst recombines with TTF$^+$ in a diffusion-controlled reaction (reaction 6). Protonation reaction of the reduced catalyst (reaction 7) is about 2-3 orders of magnitude in slower than diffusion-limited reaction but can compete with TTF$^+$/Cat$^-$ recombination when in the presence of a large excess of acids. These transient species, i.e. reduced catalyst and reduced protonated catalyst, can be monitored and characterized by transient absorption spectroscopy; more details will be discussed in chapter 3.

![Reaction Scheme](image)

**Figure 9.** Reaction scheme for the photo-induced reduction of biomimetic catalysts. The potential values are referred to Fc$^+$/Fc in acetonitrile.

### 2.1.3 Chemical Reduction Systems
In photoinduced reduction of biomimetic catalysts as described above, the photogenerated reducing equivalent (about 2 μM) reacts with large excess of catalyst to reach pseudo first order reaction, which favorably competes with charge recombination of TTF\(^+\) with [Ru(bpy)\(_3\)]\(^+\). This leads to the fact that only one-electron reduced product can be obtained, even if further reduction of one-electron reduced intermediate is thermodynamically favorable. Chemical reduction could by contrast achieve the goal of multi-electron reduction of a catalyst, if thermodynamically allows. The reductant employed in the chemical reduction experiments of biomimetic catalysts is cobaltocene (CoCp, E\(^0\) = -1.33 V vs Fc\(^+\)/Fc). The reactivity of CoCp with a catalyst is addressed by stopped-flow IR spectroscopy, where the precursors of the chemical reaction are rapidly mixed; More details will be discussed in the following sections, or seen in the Paper II, III.

2.2 Techniques

For above systems, electron transfer and proton transfer reactions could result in changes in the electronic configuration, and structural geometry of catalysts. This in general leads to spectral differences in the absorption measurements. In this thesis, most relevant to the studies of above systems is absorption changes in the UV-Vis and mid-IR region. These concepts and techniques, including stopped-flow rapid mixing, steady state and transient absorption spectroscopy, will be described in the following sections. In addition, electrochemistry is also a powerful tool to investigate redox catalysts. This is because the power of electrochemistry can provide the thermodynamic and kinetic parameter relevant for above systems involving redox processes of chemical species. It is a straightforward way to estimate and control the driving force of a chemical reaction. The corresponding techniques, i.e. cyclic voltammetry and bulk electrolysis, will be briefly explained below.

2.2.1 Steady State Absorption Spectroscopy

Spectroscopy presented in this thesis is a tool that is used to describe the interaction between light with material. Components of molecular systems mentioned in section 2.1 have well-defined energy levels, and therefore point to different absorption properties, which take a possibility to identify and distinguish molecular species. The absorption spectrum of a sample is commonly recorded using a steady state spectrophotometer, where a typical setup is presented in Figure 10a. It describes that a lamp passes through a monochromator, which then allows one to do measurements at single wavelength. The light is split into two beams: one passes through the cuvette containing samples to measure the intensity of light after being absorbed by molecules, defined as \(I;\)
the other beam is directed into a reference (in general only solvent) to record the intensity of light that is not absorbed by sample, defined as $I_0$. The collected spectrum shows the fraction of incident light absorbed by the sample over a range of frequencies. The absorption extent by the samples is reported as absorbance (Abs) or optical density (OD), which can be described by the Beer-Lambert law (equation 2.1),

$$A(\lambda) = OD(\lambda) = -\log_{10} \frac{I(\lambda)}{I_0(\lambda)} = \varepsilon_{\lambda} \cdot c \cdot l \quad (2.1)$$

where $\varepsilon_{\lambda}$ is extinction coefficient of a molecule and the wavelength dependent, $c$ stands for the concentration of sample, and $l$ represents the path length. The shape of the spectrum can also give insights about the properties of electronic transition. For example, absorption spectrum of $[\text{Ru(bpy)}_3]^2+$ presented in this thesis features $\pi \rightarrow \pi^*$ transition of ligands around 360 nm and MLCT absorption around 450 nm.

FT-IR (Fourier Transform Infrared) Spectroscopy is to study the interaction between infrared light with matter, and to probe vibrational transitions of a molecule. Figure 10b presents a common setup for FTIR spectrometer, which is composed of an IR lamp, interferometer, sample compartment, detector, processor, and a computer. The IR light passes the sample through the interferometer and reaches the detector. Then the signal is processed and converted to an interferogram. Finally, the interferogram is transferred to a computer in which Fourier transform is carried out. This results in a frequency domain trace, commonly intensity vs. wavenumber (cm$^{-1}$). The basic measurement obtained in the IR spectroscopy is an IR spectrum, which provides more insights about the structure of a molecule; more details will be continuously discussed in the following sections (transient IR absorption spectroscopy).
Figure 10. Schematic representations of the working principles of a steady-state UV-Vis absorption (a) and (b) FTIR spectroscopy.

2.2.2 Nanosecond Transient Absorption Spectroscopy

**UV-Vis Spectroscopy.** As discussed before, most of studies in this thesis are based on the fact that the light absorbed by the sample should be able to trigger a chemical reaction, followed by absorption changes of the sample. This is not the case for steady state techniques, since the signal obtained in the steady-states measurements is averaged over the time scale of second, which is much longer than the rate of a chemical reaction. This results in the consequence that absorption is actually detected as the system is already in a steady-state. To investigate the reaction dynamics or mechanism for molecular systems as presented in the section 2.1.1, nanosecond (ns) transient absorption spectroscopy, or called laser flash photolysis in this thesis, was used. Specifically, a nanosecond laser (pump light) is used to excite the sample, and a probe light is then to measure the transmission of the sample. There is a time interval between pump and probe light. By varying the time delay between pump and probe light, a reaction can be monitored as a function of time by probing the absorption changes after excitation has occurred with pump light, expressed by equation 2.2,

\[ \Delta OD = \Delta A = A(pump) - A(no\ pump) = -\log_{10}\frac{I(pump)}{I(no\ pump)} \]  

(2.2)

Figure 11 shows a sketch for ns transient absorption experiments. Specifically, a laser pulse (about 8-12 ns) is generated from a Q-switched Nd:YAG laser, which incorporates the dual-rod oscillators with two amplifier stages. Consequently, each pulse that undergoes the amplification produces output energies up to about 1250 mJ and emits a photon at 1064 nm, which then interacts with a nonlinear crystal to produce a secondary wave with a wavelength of 532 nm, called ‘double harmonic generation’. The resulting 532 nm wave can be mixed in the nonlinear crystal with the residual 1064 nm fundamental to produce a light at 355 nm, called ‘triple harmonic generation’. The 355 nm light then passes through an optical parametric oscillator (OPO), which converts it into a beam of arbitrary wavelength in the visible region (410-700 nm). The resulting visible light is then directed into the sample chamber and used to excite the sample (10 × 10 mm cuvette) with a right-angle regard to probe light, a Xe arc lamp that has a broad and strong output energy ranging from ultraviolet to near-infrared light. The probe light hits the sample, and passes through a detector in which the data is analyzed by either a charge-coupled-device (CCD) camera or a photomultiplier tube (PMT) detector coupled with a monochromator in the UV-Vis region (200-850 nm).
The CCD camera (in our case an iStar CCD 320) is an array of 1024 × 256 pixels, so it can monitor multiple wavelengths and analyze the whole spectrum of probe light at a specific delay time. The PMT instead is to monitor one single wavelength of the involving spectrum, which is selected with monochromator, as a function of time. This measurement generates a kinetic trace which is collected with a digital oscilloscope, ultimately sending it to the computer.

**IR Spectroscopy.** When involving the structural characterization of a sample, UV-Vis absorption measurements typically cannot give more information on the structure of the molecule. The IR spectrum of a molecule by contrast provides a valuable information to analyze the electron density and structural changes, since the change in dipole moment leads the vibrational modes to be IR active during the vibration. After absorption of light in the mid-IR region, vibrations involving chemical bonds in a molecule typically give distinct signals and narrow peaks at higher wavenumbers. This could be more easily assigned and investigated. In this thesis, the IR studies are involved the characteristic bands of carbonyls coordinated to the Fe centers in the synthetic diiron complexes. We know that carbon monoxide (CO) has a characteristic absorption band at 2143 cm$^{-1}$. When it is coordinated to a metal, the measured band can be found at a lower wavenumber. This is caused by the $\pi^*$-backbonding interaction, where the electrons are transferred from a d-orbital of the metal to the antibonding $\pi^*$ orbital of the CO. This leads to the strengthening of the metal-C bond and weakening of C-O bond, which is reflected in decreases of the stretching frequencies for the C-O bond. It indicates that the stretching frequency of the CO ligand is very sensitive to the electron density of the metal center, and therefore measuring the vibrational spectrum of CO is an excellent strategy to gain insights into the structures of a biomimetic diiron catalyst upon oxidation, reduction and protonation.

Combined the IR spectroscopy with flash photolysis technique, we could achieve better time resolution up to a few nanoseconds for IR absorption measurements [], compared to a modern FTIR spectrometer where one can measure on time scales of tens of milliseconds. In the setup of transient IR spectroscopy, we use the same pump light as mentioned in the UV-Vis setup to excite the sample. Two continuous-wave quantum cascade (QC) mid-IR QC lasers were equipped to provide the IR light for probing, instead of Xe arc lamp. The IR probe light is overlapped with the pump light in a suitable angle (see Figure 12). After the IR probe light passes through the sample, it is directed into a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Transient IR measurement does not provide an entire spectrum since the two mid-IR QC lasers are tunable with output wavelength between 1300-1965 cm$^{-1}$ and 1960-2150 cm$^{-1}$. In other words, the IR probe light itself is monochromatic. Thus, the MCT detector monitors the transient event at a tuned
one-single wavelength as function of time, and generates the kinetic trace that is collected with the same oscilloscope as used above.

![Diagram](image)

*Figure 12.* Simplified scheme of pump-probe experiment, probing in the mid-IR region.

### 2.2.3 Stopped-flow Rapid-mixing FT-IR Spectroscopy

In section 2.2.1, the simplest measurement in the FTIR spectrometer requires seconds for data acquisition. There is another measurement called ‘rapid-scan mode’ available on the same instrument, where many hundreds of spectra can rapidly be obtained over the period of the experiment. In this way, the observation time for a single spectrum can be down to the millisecond range [ref.].

In rapid-scan experiments, a liquid-nitrogen-cooled MCT detector is used to afford the required fast response time. Typically, spectra were collected at 4 cm\(^{-1}\) spectral resolution. How long one scan takes depends on the scanner velocity (frequency). Stopped-flow mixing coupled with rapid-scan FT-IR spectrometer (in our case a Bruker IFS 66v/S) represents a new experimental approach to explore reaction intermediates and kinetics in catalysis of proton reduction. Specific application of this approach can be found in Paper III.

A schematic setup of the stopped-flow mixing system employed to the study of redox catalysts is shown in Figure 13. The driven gas-tight syringes (Hamilton) deliver the reactants to be studied, such as cobaltocene and biomimetic catalysts, through small internal diameter flexible Teflon tubes into the flow cell fitted with CaF\(_2\) windows, where reagents are mixed by a high efficiency T-format mixer. The driven stop syringe is triggered by an electric signal from the FTIR spectrometer, thus allowing precise time correlation between data acquisition and mixing time. In our experiments, the overall time for getting first spectrum is about 50 ms, which is equal to the sum of mixing time and scan time.
2.2.4 Electrochemical Methods

Electrochemistry is a powerful tool to the study of redox catalyst. The electrochemical behaviour of a catalyst can be studied by cyclic voltammetry (CV) and bulk electrolysis. CV describes an experiment where the potential is measured as function of time. This allows us to analyze redox potential of a system if the redox steps are stable over the time scales of measurement that is determined by the scan rate.

When combined electrochemistry with spectroscopic techniques, called spectroelectrochemical methods, it also affords deeper insights into reactivity of a catalyst. Yet, it in general has worse in time resolution than stopped-flow techniques. In the electrochemical experiments, an electrode can be regarded as electron donor. Thus, a catalytic system can be reduced to fewer components than discussed above. For example, only a catalyst and an acid are needed in electrocatalytic H2 formation. Those electron transfer reactions only occur on the electrode surface, which would
3. Results and Discussion

In this chapter, the mechanistic proposals for proton reduction catalyzed by structural mimics of FeFe-hydrogenase are presented. The results will be summarized into three parts in terms of the differences of their bridging head:

1) Photochemical reduction of FeFe(pdt)(CO)\textsubscript{6}
2) Proton-shuttling role of the azadithiolate ligand in second coordination sphere
3) Photochemical and chemical reduction on FeFe(Cl\textsubscript{2}-bdt)(CO)\textsubscript{6}

The presentations will only focus on addressing some kinds of central questions, i.e. what are the results and implication, as well as what has been done with the details given in the enclosed papers.

3.1 Photochemical reduction of FeFe(pdt)(CO)\textsubscript{6} (Paper I)

3.3.1 General considerations

As already mentioned before, FeFe(pdt)(CO)\textsubscript{6} (I) is the first member of a well-defined set of [(μ-SR):Fe\textsubscript{2}L] complexes inspired by FeFe-hydrogenase. To make the structure resemble the enzyme as close as possible, two CO ligands of hexacarbonyl can be replaced by electron donating ligands, such as cyanide (CN\textsuperscript{-}), trimethylphosphine (PMe\textsubscript{3}) etc. The first example that was used to catalyze protons reduction into molecular hydrogen was [FeFe(pdt)(CO)\textsubscript{4}(PMe\textsubscript{3})(CN)]\textsuperscript{+} compound, including one CN\textsuperscript{-} ligand and one PMe\textsubscript{3} ligand. Later on, proton reduction catalysis of the parent complex I has also been investigated extensively [ref.]. Despite various strategies have been undertaken towards better efficiency for hydrogen production [ref.], there still is a quite large discrepancy to date in comparison with the enzyme both at turnover frequency and overpotential [ref.]. Understanding the mechanism, especially the electron transfer chemistry in catalysis, is fundamental to the design of better artificial systems. For compound I, earlier spectro-/electrochemical studies showed that the major electron transfer step was a reversible one-electron step to give a singly reduced species I\textsuperscript{-}. However, the singly re-
duced state is unstable typically on the time scale of electrochemical experiments [ref.]. It has hence escaped characterization by direct spectroscopic observation and information regarding structure and reactivity of one-electron reduced intermediate has therefore been limited to results from computational studies and kinetic data indirectly inferred by electrochemistry from catalytic currents under turnover conditions. In contrast, photochemical reduction using laser flash-quench methods is an excellent solution to characterize those short-lived catalyst intermediates, because it in general has a higher time resolution compared to those of electrochemical techniques.

In this section, I will primarily address the structures of one-electron reduced intermediate of 1 triggered by the flash-quench-generated [Ru(dmb)₃]⁺ reductant, and subsequent reactivity with acids. The more details on reaction scheme and explanation of flash-quench techniques can be found in chapter 2.

3.1.2 One-electron reduced intermediates

In our methods, the reduction of complex 1 (E₀ = 1.60 V vs. Fc⁺/Fc in acetonitrile) [ref.] by flash-quench-generated [Ru(dmb)₃]⁺ (E₀ = 1.81 V) [ref.] typically takes place on the sub-microsecond time scales. Meanwhile, only 2 μM or 20 μM of transient concentration of reduced intermediate is generated depending on the optical path length. This excludes any kind of bimolecular transformation, such as disproportionation or dimerization of reduced catalyst 1⁻ as the half-life of these reactions will not be faster than several tens of microseconds under the conditions of flash-quench experiment. In addition, further reduction of 1⁻ will not be expected to occur, in that photoreductant [Ru(dmb)₃]⁺ (assuming 2 μM transient concentration) reacts with a large access of 1, minimizing the possibility of a double reduction caused by two subsequent encounters with [Ru(dmb)₃]⁺. This hence allows us to detect the one-electron reduced state during a long time window. The reduction reaction of complex 1 was also followed by transient mid-IR spectroscopy, where one uses the frequencies of carbonyl ligands as sensitive probe for electron densities of metal center and to geometry changes. Of major importance is that the shift of the CO frequencies allows us to identify the structures on singly reduced intermediate. Reduction of complex 1 with flash-quench-generated [Ru(dmb)₃]⁺ leads to the bleaches of all three absorption bands of 1 in the carbonyl region, accompanying rise of 1⁻ bands regularly shifted by 75-90 cm⁻¹ to lower frequencies, see Figure 8c. Such regular shift and similar spectral envelopes for 1 and 1⁻ indicate that the geometry does not change significantly upon reduction. This was also supported by earlier DFT
calculations\textsuperscript{[ref.]} in which the primary structural change on one-electron reduction of 1 is a lengthening of the distance of Fe-Fe bond by 0.28 Å but maintains an intact coordination sphere.

The IR spectra of 1 and 1\textsuperscript{-} were also compared with those of analogous bdt-bridged complexes 2 and 2\textsuperscript{-}, see Figure 8d. IR spectra of 1 and 2 in the starting state have very similar shape, and the latter slightly shifts all three bands by 5-10 cm\textsuperscript{-1} to higher frequencies due to the electron withdrawing effect of the aromatic dithiolate ligand. However, the singly reduced species feature evident spectral dissimilarities. IR spectrum of 2 shows an irregular shift upon reduction, and therefore 2\textsuperscript{-} has four resolved bands instead of only three in the starting state. Compared to an intact coordination sphere for 1, 2\textsuperscript{-} undergoes structural changes that is attributed to the breaking of one of the S-Fe bonds \textsuperscript{[ref.]}]. The comparison is in fact valuable as the structural differences might result in different protonation behaviors, which may affect the catalytic performance.

\textbf{Figure 8.} Top panels: UV-Vis spectra of a) complex 1 (\textsuperscript{[\textbullet]} and its singly reduced product 1\textsuperscript{-} (\textsuperscript{[\textcdot]} and b) complex 2 (\textsuperscript{[\textbullet]} and its singly reduced product 2\textsuperscript{-} (\textsuperscript{[\textcdot]}). Bottom panels: IR spectra of c) complex 1 (\textsuperscript{[\textbullet]} and its singly reduced product 1\textsuperscript{-} (\textsuperscript{[\textcdot]} and d) complex 2 (\textsuperscript{[\textbullet]} and its singly reduced product 2\textsuperscript{-} (\textsuperscript{[\textcdot]}). Copyright 2018.

3.1.2 Kinetic Behaviors of Protonation and Detection of Reduced-protonated Species
The reactivity of singly reduced species of complex 1 towards acids of different strength was investigated by transient nanosecond UV-Vis- and mid-IR-spectroscopy. The acids examined in this investigation include p-toluenesulfonic acid (pKa ~ 8.6), trichloroacetic acid (pKa ~ 10.7) and dichloroacetic acid (pKa ~ 13.3). For catalysis of proton reduction with complex 1, the protonation reaction of singly reduce species 1^- as second step in the overall catalytic cycle has been proposed frequently by electrochemical techniques. This means that the reaction rate for this step should be faster than dimerization or disproportionation of 1^- under electrochemical experiment conditions. However, it is typically hard to measure the exact rate constant for protonation of reduced catalyst using electrochemical techniques [ref.]. With flash-quench methods, we could provide direct measurements for protonation reaction by following kinetic traces of singly reduced species signals. In figure 9, with addition of acid the accelerated decay at 700 nm, which is one of absorption bands of 1^-, is an implication of protonating the reduced catalyst. Fitting the decay with exponential function gives the pseudo-first-order rate constants $k_{obs}$ for protonation reaction, and plotting $k_{obs}$ as function of acid concentration gives the second order rate constant of protonation. The rate constants with three acids examined in this investigation can be found in paper I.

Figure 9. Left column: Normalized kinetic traces at 700 nm (original ΔOD ca. 0.015) with selected concentrations of DCA (a), TCA (b) and TsOH (c) together with biexponential (rise-and-decay) fits. The decay component gave the pseudo-first order rate constant ($k_{obs}$) for protonation of 1^- kobs. Right column: Plots of pseudo-first order
rate constants $k_{obs}$ determined from the 700 nm traces vs. concentration of DCA (d), TCA (e) and TsOH (f). Reproduced by permission from ref. [#]. Copyright The American Chemical Society © 2018.

Surprisingly, the protonation rate constant of $1^-$ is comparable to that of $2^-$, because we expected that the protonation of $2^-$ should be slower due to the less electron donating bdt-bridging ligand. This could be attributed to two factors:

1) Reduction of $2$ with deligation of S-Fe bond undergoes structural changes (see above) and gives a more open structure, and therefore make the protonation more facile;

2) Protonation of $2^-$ could occur at sulfur site;

3) Reduction of $1$ significantly lengthens the distance of Fe-Fe bond, leading to be slower for protonation of $1^-$ relative to that of $2^-$, since the protonation of reduced catalyst corresponds to the two metal centers to give a bridging hydride, see these structure implications in Figure 10.

![Figure 10. Structural indication of all three states of [Fe$_2$(pdt)(CO)$_6$] (1) and [Fe$_2$(bdt)(CO)$_6$] (2).](image)

The protonation states are also transient intermediates in catalysis of proton reduction. Detecting the reduced-protonated species could be a good strategy to understand the kinetic bottlenecks limiting the catalytic efficiency. The singly reduced intermediate $1^-$ can be easily detected using flash-quench methods coupled with mid-IR probing, see the transient IR spectrum in Figure 9. However, this is challenging for detection of reduced protonated species, because the protonation of $1^-$ to form $1H$ leads to a shift in the IR spectrum back to higher frequencies where the neutral complex $1$ is bleaching.

3.2 Proton-shuttling Role of Azadithiolate (adt) Lig-
3.2.1 General
Since the pedant amine in the azadithiolate (adt) bridge was regarded as potential proton relay for facilitating either protonation of iron center or proton-hydride interaction in catalysis of [FeFe]-hydrogenase, mimicking the function of proton relays in the active site of this enzyme has become a routine design principle in the development of synthetic molecular electrocatalysts for H₂ evolution. In this manner, DuBois and co-workers perhaps provide the most impressive confirmation of the proton relay functions of amines in catalysis of proton reduction by synthetic Nickel (Ni)-containing catalysts [ref.]. Upon reduction, one of their catalysts could convert to a transition state that contains a proton on a pendant amine of the second coordination sphere and a hydride on the Ni center [ref.], see Figure 6b in chapter 1. Regarding structural mimics of FeFe-hydrogenase with adt ligand the same role has been more recently proposed in an electrochemical and computational study by Gloaguen and co-workers. Their studies pointed out that the superior catalytic performance of adt-based complexes relative to their pdt- and bdt-based analogues was attributed to formation of hydride intermediate by proton shuttling from the nitrogen site of adt ligand [ref.]. The work presented in this section was therein intrigued whether the proposed role of adt ligand as proton relay and the formation of terminal hydride intermediates in these model complexes could be inferred from direct spectroscopic observation.

In this section, I will address those electron and proton transfer reactions of diiron complexes, FeFe(adt)(CO)₆ (3) and [FeFe(adt)(CO)₄(PMe₃)₂] (4), with the adt ligand investigated by time resolved IR and UV-Vis spectroscopy to elucidate whether the amine functionality relays protons to the metal center in catalytic H₂ formation.

3.2.2 FeFe(adt)(CO)₆ complex

_Laser flash photolysis._ The redox potential of complex 3 is very similar to that of complex 1, and therefore we could use the same experimental procedure as that presented in section 3.1 to initiate one-electron reduction of complex 3 (see reaction equations below); more details about the reaction scheme were explained in chapter 2.

\[
[Ru(dmb)₃]^{2+} + TTF \xrightarrow{k_2} [Ru(dmb)₃]^+ + TTF^+ \quad (1)
\]
\[
[Ru(dmb)₃]^+ + 3 \xrightarrow{k_{ET1}} [Ru(dmb)₃]^{2+} + 3^- \quad (2)
\]
\[
3^- + TTF^+ \xrightarrow{k_{Rec1}} 3 + TTF \quad (3)
\]

The resulting electronic absorption bands of 3* (390 nm, 580 nm and 700 nm) and its vibrational spectrum in the carbonyl region (2006 cm⁻¹, 1945 cm⁻¹ and 1910 cm⁻¹, Fig. 11a) resemble closely those of 1*. Yet, unlike complexes 1 and 2, where protonation must be initiated by a reduction step, complex 3 contains...
a protonable NH group that allows us to investigate either an ET/PT or a PT/ET mechanism depending on the strength of the acid.

With weaker acid such as CICH\textsubscript{2}COOH (pK\textsubscript{a} = 15.3 in acetonitrile), it catalyzes H\textsubscript{2} production via an ET/PT mechanism, while a stronger acid such as 2, 5-dichlorobenzenesulfonic acid (Cl\textsubscript{2}BSA, pK\textsubscript{a} = 6.7) gives a PT/ET sequence. Our experimental data suggest that no matter what mechanism is involved, the initial protonation occurs at adt-N site, see the IR spectra in Figure 11b, c. This excludes the possibility of a ET/PT route that results in direct formation of a hydride complex, 3Hy, without involvement of nitrogen site, as has been presented by Gloaguen et al. based on predicted pK\textsubscript{a} values of 18.8 (bridging hydride), 17.1 (terminal hydride) and 13.8 (adt-N protonation) with DFT calculations [ref.]. The protonation of the adt-N site results in a shift of about 20 cm\textsuperscript{-1} to higher wavenumber of the v\textsubscript{C-O} bands, characteristic of ligand-based protonation [ref.]. Both ET/PT and PT/ET mechanisms produce the same initial product 3H (2025, 1965 and 1935 cm\textsuperscript{-1}). 3H formed by ET/PT sequence decays with second-order kinetics, which is attributed to a charge recombination of 3H with TTF\textsuperscript{+} in a diffusion-controlled reaction, and no tautomerization from 3H to 3Hy was observed on the time scales of charge recombination. The decay of 3H generated by a PT/ET route with Cl\textsubscript{2}BSA is on the other hand much faster than the former. The accelerated decay cannot be assigned to a tautomerization process. This is because 3Hy can be expected to have carbonyl frequencies different from the starting material 3H\textsuperscript{+} by 20 cm\textsuperscript{-1} (see Table 1), which would be readily detected in the transient IR absorption spectra. Instead, it could be attributed to the direct metal protonation of 3H by the external acid yielding 3H\textsuperscript{Hy+}, with a second-order rate constant of 6 x 10\textsuperscript{7} M\textsuperscript{-1}s\textsuperscript{-1}. It is a little surprising that the metal protonation of 3H by Cl\textsubscript{2}BSA occurs with a similar rate constant as metal protonation of the pdt analogue 1-.
(\(k_{PT} = 7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}\)) by TsOH. Although both complexes are in the same Fe\((2,0)\) oxidation state, the electron density at Fe core is expected to be substantially decreased upon adt ligand protonation in 3H, and this effect will be explained below.

Table 1. IR data of different oxidation states in the carbonyl frequencies region.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Wavenumber/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2073, 2034, 1994</td>
</tr>
<tr>
<td>3(^-)</td>
<td>2005, 1945, 1915</td>
</tr>
<tr>
<td>3H(^+)</td>
<td>2090, 2051, 1945</td>
</tr>
<tr>
<td>3H</td>
<td>2025, 1965, 1935</td>
</tr>
<tr>
<td>3Hy</td>
<td>2073, 2034, 1995</td>
</tr>
<tr>
<td>3HHy(^+)</td>
<td>2090, 2051, 1994</td>
</tr>
</tbody>
</table>

\(^a\) Predictable data: protonation of the Fe-Fe bond would be expected to essentially compensate for the increase in electron density upon 1e\(^-\) reduction (see paper 1).

![IR spectra and kinetic traces](image)

\(\text{Figure 12. Transient IR spectra (red) with spectra of the starting state (black) and kinetic traces with fits for the indicated reactions induced by reduction with flash-quench generated Ru(dmb)3\(^+\). a) Reduction of 1 to 1\(^-\): b) Formation of 1H by protonation of 1\(^-\) with Cl\(_2\)CCOOH (15 mM) following reduction of 1. c) Formation of 1H by reduction of 1H\(^+\) following protonation of 1 with Cl\(_2\)BSA (3 mM) and subsequent protonation of 1H to 1HHy\(^+\).}

\(\text{Stopped-flow chemical reduction. Because tautomerization of 3H to 3Hy had been proposed as an explicit step in catalytic cycle for reduction of stronger acids,\([6]\) the reactivity of 3H on longer time scales was addressed by complementary experiments with rapid-mixing transient IR spectroscopy. As illustrated in Figure 13, reduction of 3H\(^+\) (E\(^0\) = 1.20 V) with cobaltocene (E\(^0\) =
1.32 V) yields \( 3\text{H} \) (2020, 1960 and 1935 cm\(^{-1}\)) that decays with a rate constant on the order of \( 1 \text{ s}^{-1} \). The decay of \( 3\text{H} \) yields a product that can be assigned to the recovery of parent complex 3, most likely via either a bimolecular reaction between two \( 3\text{H} \) entities that results in the release of \( \text{H}_2 \) or a first-order loss of the \( \text{H} \) atom from \( 3\text{H} \) [ref.], see Figure 14.

\[ \text{Figure 13.} \text{ a) Rapid scan IR spectra in acetonitrile between 50 ms (red) and 3 s (black) after } 3\text{H}^+ \text{ with cobaltocene; Kinetic traces with mono-exponential fits monitoring decay of } 3\text{H} \text{ at 1960 cm}^{-1} \text{ (b) and formation of } 3 \text{ at 2034 cm}^{-1}. \]

\[ \text{Figure 14.} \text{ Bimolecular reaction between two } 3\text{H} \text{ entities together with release of } \text{H}_2 \text{ and loss of } \text{H} \text{ atom from } 3\text{H}. \]

Alternatively, the observed decay on these time scales indicates a tautomerization process of \( 3\text{H} \) to \( 3\text{Hy} \), which may be spectrally very similar to the parent complex 3. Irrespective of the assignment, indicating either turnover or tautomerization, the observation of \( 3\text{H} \) being stable on these time scales puts in either case an upper limit on the order of \( 1 \text{ s}^{-1} \) on the rate constant of tautomerization. For the electrochemical \( \text{H}_2 \) formation with 3, pseudo first order catalytic rate constant on the order of \( 10^3 \) to \( 10^4 \text{ s}^{-1} \) have been determined and
the proposed mechanism involves intramolecular isomerization of $3H$ to $3Hy$ according to computational results []. To account for the observed turnover frequencies the tautomerization rate constant would have to exceed the upper limit determined from the direct observation of $3H$ by several orders of magnitude. Our results however exclude that the catalytic cycle passes through a tautomerization step. Instead, the electrochemical reaction most likely involves the formation of $3HHy^+$ by direct protonation of $3H$ from the external acid. This is due to the fact that the acid concentration is much larger in these experiments, same manner as in the flash photolysis experiments.

Regarding the superior catalytic performance of complex 3 in direct comparison with its pdt (1) and bdt (2) analogues, protonation at nitrogen site shifts the reduction potential by about 300 mV to a less negative position, and therefore lowers the overpotential in the catalytic cycle [ref.]. In principle, shift of about 300 mV in reduction potential for the $3H^+/3H$ compared to $1/1^-$ should drop in $pK_a$ by about 5 upon adt protonation. However, the lowered driving force for protonation of adt-protonated catalyst does not slow down the catalytic rate constant (see above), which is faster by one to two orders of magnitude than that expected. This could be hence attributed to the fact that the barrier for metal protonation might be lowered by structural changes at Fe core induced by the adt ligand protonation. A second possibility is that the bridging hydride undergoes a structural rearrangement forming a transient intermediate with a terminally bound hydride ligand that is more active for catalysis [], as shown in Figure 15. The follow-up reaction of intramolecular hydride/proton coupling could precede the release of $H_2$ more rapidly relative to its pdt (1) and bdt (2) analogues.

**Figure 15.** $H_2$ elimination from $3HHy^+$ through a transient intermediate with terminally bound hydride ligand.

### 3.3.3 FeFe(adt)(CO)$_4$(PMe$_3$)$_2$ complex

In case of complex 3, the reason why the amine of adt ligand does not serve as a proton shuttle to metal center could also be the poor basicity of hexacarbonyl metal core, or the low driving force for tautomerization of $3H$ to $3Hy$. In this context, we introduce trimethylphosphine (PMe$_3$) ligands at the diiron center to prepare complex 4 (see figure 16), and also mimic the electron do-
nating CN ligand in the active site of [FeFe]-hydrogenase enzyme. The introduction of PMe₃ ligands significantly increases the electron density of the Fe core, which would allow us to investigate the possibility of the amine functionality working as proton relay to metal core. Indeed, previous experimental studies for complex 4 showed that tautomerization of 4H⁺ to 4Hy⁺ can be catalyzed by chloride ions, but the rate is extremely slow (k_{tauto.} = 2 \text{ M}^{-1}\text{s}^{-1}) [ref].

Figure 16. Structural indications of complex 4 in different oxidation states

We are by contrast interested in the tautomerization upon reduction of 4H⁺ induced by a laser flash-quench-generated photoreductant, even without the help of chloride ions as catalysts. The protonation of complex 4 (E⁰ = -2.19 V vs. Fc⁺/Fc) in adt ligand shifts the reduction potential by about 610 mV to milder potentials, with 4H⁺ formation (E⁰ = -1.58 V) [ref]. Thus, the flash-quench-generated [Ru(dmb)₃]⁺ (E⁰ = 1.81 V) is thermodynamically able to reduce 4H⁺. A larger driving force for tautomerization of 4H to 4Hy would be expected upon reduction. This allows us to study a potential PCET process if the tautomerization of 4H to 4Hy is rapid enough. The complex 4 is protonated by Cl-anilinium (pKₐ = 9.7) to prepare the 4H⁺, which combined with sensitizer [Ru(dmb)₃]²⁺ and electron donor TTF constitutes the solution for flash-quench experiments. The UV-Vis transient spectra shown in Figure 17 were obtained. The transient spectra shows that besides the typical TTF⁺ (435, 580 nm) and [Ru(dmb)₃]⁺ (510 nm) absorption, a small absorption band at 715
nm was observed that is assigned to $4H$. $4H$ decays with second-order kinetics on the time scale of about 100 $\mu$s, which is typical for charge recombination of $4H$ and $\text{TTF}^+$ under those conditions (Figure 18). It is apparent that the tautomerization of $4H$ to $4Hy$ does not occur on these time scales. Thus, the potential tautomerization is expected to occur on the longer time scales. Such experiments would be addressed with stopped-flow techniques in the future work.

Figure 17. Transient UV-Vis absorption spectra of samples containing 50 $\mu$M sensitizer $[\text{Ru(dmb)}_3]^2+$, 1.0 mM electron donor TTF and 100 $\mu$M catalyst $4H^+$ (prepared by adding 2 equivalents Cl-anilinium), exciting at 465 nm with 10 mJ/pulse.

Figure 18. kinetic traces collected at 715 nm with a second order fit, which shows a charge recombination of $4H$ with TTF$^+$.

Since complex 4, on the other hand, can directly react with acids to selectively prepare three protonated states, i.e. $4H^+$, $4Hy^+$ and $4HHy^+$ [ref.], this allows one to obtain the different intermediates upon reduction of protonated precursors. One example is that the stable hydride $4Hy^+$ ($E^0 = -1.10 \text{ V}$) can be readily reduced to $4Hy$ by flash-quench-generated $[\text{Ru(dmb)}_3]^+$ reductant, and the
transient IR spectrum shown in Figure 19 was obtained. The laser flash-induced reduction of 4H⁺ results in bleaching of its two bands (2033, 1992 cm⁻¹) and appearance of three bands of the product 4H that essentially match the spectrum of the parent complex 4 (1981, 1943 and 1908 cm⁻¹). This observation provides solid proof of the general notion that the IR spectrum of a one-electron reduced hydride species should be very similar to that of parent complex, thereby leading to complete cancellation of transient IR absorption when reduced hydride is generated from the parent complex, as presented in previous sections for complexes 1, 2 and 3.

Figure 19. Reduction of 4H₂⁺ to 4H by electron transfer from flash-quench generated [Ru(dmb)₃]⁺. Transient IR spectrum 1 µs after the laser flash (red) and IR spectra of 4 (black) and 4H₂⁺ (blue).

Future work. It was found that the ligand protonation product 4H⁺ can be immediately excited with visible light (532 nm). The excitation of 4H⁺ results in the bleaching of its three bands, and concomitant rise of new peaks, shown in figure 20. In general, a homogeneous photocatalytic system for H₂ formation need to be mad up of sensitizer, electron donor and a catalyst. It would be by contrast interesting studying a novel route of which one can be used as unsensitized photocatalyst for H₂ production.
Figure 20. Transient IR absorption spectrum of 4H⁺ (a) and (b) kinetic transients after laser excitation with 532 nm.

3.3 Photochemical and Chemical Reduction of FeFe(Cl₂-bdt)(CO)₆ Complex

3.3.1 General

In section 3.1, we compared the IR spectra of one-electron reduced intermediates for FeFe(pdt)(CO)₆ (1) and FeFe(bdt)(CO)₆ (2) to identify their structural differences, which are then applied to elucidate their different protonation behavior. For electrochemical studies that I did not discuss in the previous sections, complex 1 undergoes an initial quasi-reversible one-electron reduction at about -1.6 V versus Fe⁺⁺/Fc in acetonitrile, and a second irreversible reduction of 1 occurs at about 0.6 V more negative than the initial reduction [ref.]. The complex 3, adt-analogue, has a similar electrochemical behaviour with that of 1. In comparison, complex 2 having the benzenedithiolate (bdt) ligand is directly reduced to its dianion in a reversible two-electron process with a milder reduction potential (E⁰ = -1.32 V) [ref.]. The milder reduction
potential has been explained in an electronic effect study of bdt bound to transition metals by Lichtenberger and co-workers [ref.], who demonstrated that the bdt ligand has an ability to buffer the change in electron density at diiron core upon reduction, and therefore minimizing the changes in electron energies. The buffering is attributed to the ability of the benzenedithiolate to adapt its geometry relative to the diiron center to the change in electron configuration. The geometry change upon reduction is confirmed by our experimental data and DFT calculations in which the IR spectrum is not only shifted to lower wavenumber, but also shows a different shape compared to the spectrum for the oxidized form [ref.]. As a result, the reduction potentials of the two one-electron processes are inverted, which means that the second reduction is thermodynamically more favorable than first one, leading to an overall two-electron reduction observed by cyclic voltammetry (CV). Thus, the coupling of a bdt ligand with the diiron core in molecules analogues to the active site of the enzyme should have benefits for saving thermodynamic cost and stabilizing the reduced states in the overall catalytic cycle. The reduction potential of the two-electron process is further shifted to more positive values by the installation of electron-withdrawing chloro-groups in ortho-position of bdt ligand. The resulting FeFe(μ-Cl,bdt)(CO)₆ complex (5, E⁰ = -1.2 V vs. Fc⁺/Fc) essentially maintains an intact structure geometry and has the same electrochemical properties as the parent complex 2, and it has been demonstrated capable of catalyzing the hydrogen production both in electrochemical and visible-driven photochemical experiments [ref.]. However, the introduction of the electron-withdrawing chloro groups is expected to slow down those protonation steps in catalytic cycle. This provides a possibility to characterize more catalytic key intermediates, and therefore allows us to understand the fundamental steps in proton reduction catalysis of complex 5 via spectroscopic techniques with resolution ranging from nanosecond to seconds time scales.

3.3.2 Detection of Catalytic Key Intermediates of Complex 5

Since the properties of complex 5 is very similar to that of parent complex 2, photochemical one-electron reduction can be readily achieved using flash-quench techniques. Complexes 2 and 5 both in the neutral and reduced states feature very similar IR spectra with minor shift of all bands in the complex 5 by about 5 cm⁻¹ to higher wavenumbers due to the electron withdrawing effect of chloro groups, as shown in Figure 21.

Electrochemical or chemical reduction of complex 5 yields a doubly reduced intermediate. Compared to the electrochemical reduction in which the reactions only occur on the electrode surface, chemical reduction of complex 5 by a reducing agent can occur in homogeneous solution. Thus, the two-electron reduction of complex 5 and subsequent protonation steps presented in this thesis are addressed by the rapid-mixing transient IR spectroscopy. Reduction of complex 5 with cobaltocene (E° = -1.33 V) immediately yields the doubly reduced species, [5]^2-, gives a shift of about 120 cm\(^{-1}\) towards lower wavenumber (1968, 1918 and 1872 cm\(^{-1}\)), together with appearance of a peak at 1685 cm\(^{-1}\) that is typically assigned to the formation of a bridging carbonyl (see Figure 22, blue curve). This species is stable over several seconds with the IR stopped-flow experiments, and its dimerization which subsequently evolves into a more complex spectrum can be detected on the longer time scales.

[5]^2- is a much stronger base than [5], with a pK\(_a\) on the order of 19 or greater [\textit{ref.}]. It can be easily protonated, cleanly the one product [5H]^+ when it is generated in the presence of acids such as pentachlorophenol (pK\(_a\) ≈ 18.4 in acetonitrile) or benzoic acid (pK\(_a\) ≈ 20.3) [\textit{ref.}]. The single protonation of [5]^2- shifts all bands by about 80 cm\(^{-1}\) to higher wavenumbers (2046, 2000, 1964 and 1766 cm\(^{-1}\), Figure 22), and both [5]^2- and [5H]^+ feature the same spectral shape. These points suggest the formation of a bridging hydride ligand for [5H]^+ but the bridging carbonyl still remains, instead of moving back to a terminal position as in the [5] and [5]^+ states (see the structural indications in Figure 23, [5H]^+). This provides direct spectroscopic evidence, for the first time, characterizing the doubly reduced intermediate with single protonation.
Figure 22. Rapid scan FT-IR spectra in acetonitrile after reduction of 5 or 5/Cl₃-phenol with cobaltocene. (Black) Starting state, 5; (Blue) Doubly reduced intermediate, [5]²⁻; (Pink) Doubly-reduced singly-protonated species, [5H]⁺

Figure 23. Structural indications of complex 5 in different oxidation states.

3.3.3 Catalytic Turnover Processes with Stronger Acids

[5H]⁺ can not be further protonated by weak acid as presented above, and is thereby a significantly weaker base than the doubly reduced species [5]²⁻. Thus, for proton reduction catalysis from weak acids, [5H]⁺ needs to be further
reduced to \([5H]^2\) that undergoes electrophilic attack from external proton, followed by the dissociation of molecular hydrogen from the complex without an energy barrier [ref.]. Upon inspection of cyclic voltammetry, however, it is clear that the catalytic current occurs near at -1.94 V, giving rise to a large thermodynamic cost (overpotential) of about 0.8 V. Instead, when the catalyst is reduced by two-electrons in the presence of stronger acids such as TsOH (pKa ~ 8.6), the doubly reduced species \([5]^2\) is rapidly protonated, which is not resolved under the current experimental conditions, and the resulting \([5H]^-\) can react with the second proton. \([5H]^-\) is decaying with a rate constant on the time scales of seconds, followed by regeneration of the starting complex \(5\), as shown in Figure 24a. This suggests that the catalysis closes the cycle by facile release of H\(_2\) from the two-electron two-proton intermediate, with the second protonation as the rate-limiting step; more details about the mechanism will be discussed in the following section. The decay of \([5H]^-\) and the rise of starting complex \(5\) were increasingly accelerated with increasing amount of TsOH concentration (Figure 24b, c). The observed pseudo first-order rate constants are proportional to the concentration of TsOH, leading to a second order rate constant of 57 M\(^{-1}\)s\(^{-1}\) (turnover frequency, TOF) for catalytic molecular hydrogen formation (Figure 24d). The same measurements were repeated using acids spanning over several pKa units to estimate the hydricity of the \([5H]^-\). With Cl\(_2\)BSA (pKa ~ 6.7), the catalysis is faster as expected, and the catalytic turnover process is not resolved with acid concentration up to 6 mM under the stopped-flow IR conditions, observing the complete recovery of starting complex \(5\); the time-resolved IR spectra with different concentrations of Cl\(_2\)BSA can be found in the enclosed paper. The Cl\(_3\)CCOOH (pKa ~ 10.7), the moderately strong acid, does essentially not catalyze the formation of H\(_2\), and more complex spectra were observed with either higher concentration or longer time scales. The detailed mechanism will be discussed in the following section.
Figure 24. a) Rapid scan FT-IR spectra showing the disappearance of [5H]- followed by recovery of starting complex 5 in acetonitrile between 32 ms (pink) and 8 s (black) after mixing of 5/TsOH (1 mM / 12 mM) with cobaltocene (3 mM). b) The decay of [5H]- at 1964 cm⁻¹ and c) recovery of 5 at 2049 cm⁻¹ were accelerated with increasing TsOH concentration. d) The plot of pseudo first order rate constant vs. TsOH concentration.

3.3.4 Mechanistic Aspects for Catalytic H2 Formation

In principle, there are three pathways that can be followed for reactivity of [5H]+ towards H2 formation, given in Figure 25. The first one in Figure 25 involves the direct protonation of [5H]+, which subsequently leads to the dihydrogen formation and H2 release, regenerating the starting complex 5 (heterolytic pathway, ①). Second, the bimolecular reaction of [5H]+ itself forms [5] together with H2 release (homolytic pathway, ②) [ref.]. Yet, our results remarkably support the heterolytic pathway when using TsOH or Cl2BSA as proton source, and the rate-limiting step is the coupling of the [5H]+ with an additional proton, a precursor step forming the dihydrogen bond. The kinetic site of protonation in [5H]+ is the hydride ligand, and not sterically favorable in the metal center. In addition, our experimental results rule out the possibility of which the [5- (η²-H2)] intermediate formed could convert into a stable dihydride that has been proposed in the literature [ref.]. No catalytic turnover was observed with Cl3CCOOH, indicating that the pKa value of [5H]+ is less than 10. More complex IR spectra were detected on longer time scales. This is because the equilibrium rate constant between [5H]+ and [5]²⁻ is too small,
leading to the deprotonation of $[5\text{H}]^+$ to again form $[5]^2-$ that involves a dimerization process. The dimerization is accelerated with assistance of acid compared to that without acid. Further reduction of $[5\text{H}]^+$ is not thermodynamically favored under our experimental conditions, but it has been investigated in an electrochemical and computational study by Lichtenberger et.al.

\[ \begin{align*}
[5] & \quad \xleftrightarrow{e^-} \quad [5]^\cdot \\
[5]^\cdot & \quad \xleftrightarrow{e^-} \quad [5]^2- \\
[5]^2- & \quad \xleftrightarrow{H^+} \quad [5] + H_2 \\
[5-H]^2- & \quad \xleftrightarrow{e^-} \quad [5-H]^\cdot \\
[5-H]^\cdot & \quad \xleftrightarrow{H^+} \quad [5] + H_2 \\
[5]^\cdot & \quad \xleftrightarrow{\text{H}_2} \quad [5]^- + H_2
\end{align*} \]

*Figure 25.* Three possible pathways of reactivity of $[5\text{H}]^+$ towards ultimately $H_2$ formation.