COMPUTATIONAL CHEMISTRY STUDY OF IRON-BASED COMPLEXES FOR AQUEOUS REDOX FLOW BATTERIES

A Thesis

by

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This thesis meets the standards for scope and quality of Texas A&M University-Corpus Christi and is hereby approved.

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August 2021

ABSTRACT

Redox flow batteries (RFBs) are a new kind of battery with a great potential to store electricity from renewable energy sources like solar, wind, and tidal on a large scale. This project aims to discover new RFB active compounds that are eco-friendly and inexpensive to produce compared to vanadium, which is the current active compound for most commercial RFBs. This research focuses on iron-based organometallic complexes which are promising inexpensive and long-lived catholytes for aqueous RFBs. The long-term goal of this project is to discover new active compounds for aqueous redox flow battery (RFB).

When iron binds with bipyridine (a common ligand for organometallic complexes), it gives stability at near-neutral pH and high discharge potential (high energy density) relative to uncompleted ferrous/ferric ions. However, there are two major challenges with Iron tris(2,2'-bipyridine): low aqueous solubility and dimerization. In this research project, computational chemistry, mainly density functional theory (DFT), will be applied to predict properties of Iron tris(2,2'-bipyridine) for RFBs. Redox potentials are best predicted via computation of Gibbs free energies in a Born-Haber thermodynamic cycle. Due to a variety of functionals and basis sets that serve as inputs for quantum chemistry calculations, different approximations including BP89, PBE, PBE0, B3LYP, BHLYP, B3PW91 and CAM-B3LYP were performed to match redox potential and structural determinations from DFT with actual lab data. As a result, PBE0 functional with LANL2DZ/def2-TZVP basis set gave the most accurate information. Hence, it is applied for deeper study about molecular orbitals, electrostatic potential, and the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO)

In the pursuit of new RFB compounds, it is critical to understand the relationship of molecular structure, functional group properties, and electronic properties. Redox potential of 13 derivatives of bipyridine were calculated. We were able to plot the effects of substituents on bipyridine ligand on the complex's redox potentials by applying Hammett equation.

In addition, dimerization of Fe(bpy)₃SO₄, which leads to poor voltage efficiencies in batteries with this catholyte is studied in this research. Due to spin-crossover of the charged (oxidized) Fe (III) complex, it changes structural, vibrational, electronic, and magnetic properties of the molecule. Hence, it forms a dimer during discharge which leads to a drop in voltage efficiency. Preventing dimerization is important in RFB research because it maintain total voltage output of the redox flow battery. Due to spin-crossover phenomenon, broken symmetry was applied to describe the magnetic properties of dimer which is antiferromagnetic. In addition, the dimer undergoes two electron reductions to regenerate two Febpy2+ monomers, thus a modified Born-Haber thermodynamic cycle is applied in discharge reaction to estimate discharge potential of dimer.

DEDICATION

I would like to dedicate this thesis to my family, who have supported me throughout my Masters.

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CHAPTER I: INTRODUCTION

1.1 Electrical Energy Storage.

Recently, there is growing focus on developing solar, wind, hydro, tidal, geothermal, and biomass renewable energies. These sources of energy are powerful, clean, and unlimited. In addition, renewable energy is an alternative resource to fossil fuel-based energy, which causes global warming effect and other environmental harm. However, there is one problem while integrating renewables into our energy infrastructure, and that is their lack of energy storage. Without storage, the energy produced by these renewables must be immediately consumed and any excess amounts are wasted. Hence, renewable energy is intermittent and not of constant output and various means of energy storage are being investigated and studied. One of the most flexible and promising solutions to this problem is large-scale batteries.

Batteries are electrochemical devices which can store and interconvert electrical energy (electricity) and chemical energy. Lithium-based battery technology is what we use every day as they are ideally suited for portable applications (lightweight, high energy density). However, it is hard to extend the lithium-based battery to large scales such as grid storage due to the limitation of lithium in Earth's crust and the harmful environmental effects of Li extraction, as well as safety and cost concerns [1]. An alternative solution is the redox flow battery (RFB), which may be used to store renewable energy including solar, wind and tidal safely and at a low cost on the massive scale required [2].

1.2 Redox Flow Batteries (RFB)

Figure 1 shows conventional scheme of RFB; catholyte and anolyte are the redox active compounds dissolved in electrolyte solutions and stored in two different tanks with volumes selected as needed for the application. These solutions are pumped into the battery during

charge/discharge where they are separated by an ion-exchange membrane which allows ions to balance charge but prevents the mixing of active molecules. The core of the battery where redox reactions occur is called the stack, which can also be scaled as large as necessary for custom power requirements. Due to the unique system, many tanks connect to one stack and the solution can travel by pumps. This arrangement is effective for changing the input chemicals, long term use/maintenance, and ideal for large scale applications.



Figure 1: Redox Flow Battery System, adapted from [2]

There are two main classes of RFB depending on the solvent in which the active compounds are dissolved: aqueous and nonaqueous [3]. Non-aqueous solvents have a wider voltage window compared to water and thus higher energy density. However, non-aqueous solvents are sensitive to moisture and oxygen which might affect the performance of the battery. In addition, non-aqueous solvents are often expensive, flammable, and toxic, potential concerns for large scale batteries. On the other hand, aqueous solutions offer a high dielectric constant for high solubility of active compounds and background electrolyte (for solution conductivity) and very low cost. However, aqueous electrolytes have a limited potential window (about 1.8 V in practice) due to the electrolysis of water [4]. In this project, we seek high-performance aqueous electrolytes at mild, near-neutral pH (pH = 3-10) for RFB safety and to avoid corrosion issues in a large-scale application. Hence, active compounds with solubility in neutral water are chosen and tested.

For anolyte and catholyte, a huge number of conjugated compounds which are dissolvable in aqueous electrolyte have been tested for their RFB performance including quinones, viologens, alloxazines, phenazines, TEMPOs, and ferrocene [5]. According to figure 2, all these molecules have aromatic, π -conjugated structure which electrons can move freely (delocalization of π electrons). In addition, many anolyte compounds are known and actively studied, but there is a lack of suitable catholyte candidates. This project focuses on iron-based organometallic compounds which exhibit attractive qualities as catholytes for aqueous RFB but still possess some drawbacks that can be improved upon. Computational chemistry can be applied to study the effect of changing or modifying ligands on organometallic complexes for the prediction of redox potential, solubilities, and stability. This approach has been taken by several authors regarding allorganic compounds, but few computational studies focus on organometallics [10].



Figure 2: Solubility, redox potential, and pH conditions for potential active compounds for RFB. [5]

1.3 Advantage and Disadvantage of Redox Flow Battery

Separated tank and stack is a big advantage of RFB. In the long term, using active compounds are observed for any changing in structure. While ideally the active compounds should not degrade, they could easily be replaced after many years of service by exchange the electrolyte tank fluid. Moreover, the size of the tanks is adjustable depending on the purpose. A conventional battery such as the lithium-ion battery is limited in its size and capacity, which is not favorable for large scale energy storage. RFB maximize their performance by adding more tanks or increasing the stack size, which is easy to do for different sizes of renewable energy farms. Another advantage of aqueous RFB is safety. Active compounds are dissolved in water and transported into the stack for electron transfer, in comparison to Li-ion battery design; the risks of overcharge or over discharge reaction are minimized, which may lead to overheating and explosion in organic solvent-based batteries like Li-ion. RFB systems are easily monitored for performance and reactions are observed and evaluated to be replaced over time, keeping the system at best quality for the long-term use.

A disadvantage of the redox flow battery is the system. RFB system is complicated as there are pumps, sensor, flow tube, power management, stacks, and tanks. They are strictly connected and need to be maintained at its best quality as they are connected to each other. A single broken part might harm the whole system, so maintenance costs should be factored in for RFB.

1.4 Need for Iron complexation

Potential new compounds for RFB include organic and organometallic compounds that can be used in the anolyte or catholyte [3]. Our research is currently focused on improving the catholyte for RFB. Several metals have been employed as active compounds in RFB including vanadium,

4

zinc-bromine, iron-chromium [6]. Iron compounds are selected in this research because they are low-costing, safe materials, which are abundantly available on Earth's surface.

The ferric/ferrous redox couple is employed as the positive electrode reaction with a formal reduction potential of 0.77 V vs. SHE.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$
 E = 0.77V vs SHE

Ferric/ferrous ion cannot be used at a pH greater than 1.5 because Fe³⁺ will precipitate as ferric hydroxide [7]. To avoid deterioration of RFB and precipitation of ferric ions in mild pH solutions, various ligands can be bound with iron and create stable complexes. Nitrogenous organic ligands such as bipyridine or terpyridine bind tightly with iron in multi-dentate configurations, which enhances the stability and make it more suitable for secondary batteries. In addition, ligands can also improve the redox potential of iron. For example, bipyridine increases the redox potential of iron from 0.77 V vs SHE to 1.058 V vs SHE [8] which makes the battery more powerful.



1.5 Ligand Effects

Figure 3: Iron complex with different ligand [9]

Figure 3 shows the redox potential of different iron ligand complex. According to Lin et al. [9], iron tris(2,2'-bipyridine) has promising high positive discharge potentials of 1.058 V vs SHE and may operate under mild pH conditions. Despite the tunability of iron's redox potential, its complexes

do not necessarily have high solubilities in aqueous electrolyte compared to $Fe^{2+/3+}$ ions (solubility = 1 M in 0.5M H₂SO₄) [8]. Iron (II) tris(2,2'-bipyridine) (fig.4) is soluble up to 0.6 M in water but only 0.1 M in aqueous 1 M NaCl (a typical RFB supporting electrolyte solution) [9]. We hypothesize that yet to be explored additives to solution and/or direct modifications can be made to the bipyridine ligand, which will increase the derivative's solubility [11].



Figure 4: Iron-tris(2,2'-bipyridine)

Beside shifting the reduction potential, ligands have potential to enhance the solubilities of the complex at mild pH. According to Popov et al. [10], imine nitrogen atoms could be used to increase solubility of iron complex. However, the impact of ligand substitution on redox properties is still underestimated. Therefore, in this research different ligands like phenanthroline, terpyridine and their derivatives are complexed with iron to observe their effects on the electrochemistry of the complex [9]. Due to the many possible ligands, configurations, and solubility-enhancing additives possible, computational chemistry is a valuable tool for predicting important properties before doing deeper tests in the lab. By using computational chemistry calculations, experiments are accelerated because time for synthesis and testing is reduced to a few promising pre-identified

compounds. In addition, computational experiments also reduce the waste of material from wet lab. Thus, this project will focus on the use of computational chemistry to predict properties of iron-based complexes for RFB.





An electrochemical study of iron complexes for RFB mainly focuses on the movement of electrons during a redox reaction. From cyclic voltammetry (CV) graph (fig.5), molecules with both reduction and oxidation peaks are chosen. This demonstrates abilities for



charge and discharge of battery, so it is suitable for secondary battery. Iron tris(2,2'-bipyridne) is one example. Then, the average energy potential of reduction and oxidation is recorded as base data for computational study. It proves the reliability of DFT data. E_{redox} of new complex is calculated by DFT and CV is used to confirm reversible ability of new complex.

CHAPTER II: DENSITY FUNCTIONAL THEORY

Computational science has been used for several decades to study molecular structure and solve chemical problems. The benefit of computer simulations is in time and cost savings in a wet laboratory. Due to the expense and difficulty of wet lab experiments, performing computational experiments and predictions is excellent for studying molecular transformations, predicting/interpreting spectroscopic data, geometry optimization, frequency calculation, potential energy surface, transition structure and redox potential energy. In computational science, there are generally two major classes of calculations: molecular dynamics and quantum mechanical approaches. In molecular dynamics, atom and molecules are simulated on a computer to obtain their physical movements. Usually, molecular dynamics is applied in complex systems with a vast number of particles. On the other hand, for small molecules including the iron comple xes discussed above, quantum mechanics is the computational method of choice. It gives energetic information for different transition states of iron complexes and its reaction pathway.

2.1 Quantum Chemistry:

Quantum Chemistry (QC) is a branch of chemistry focuses on determining the electron structure within atoms and molecules. Specifically, QC is theoretical chemistry, and it calculates a molecule's properties including geometry, electronic energy, electric dipole moment, charge distribution, vibrational frequency, etc [11]. Then, it can be used to predict the mechanism of reactions and analyze electronic reorganization during the reactions. In the history of computational chemistry, different programs, algorithms and models for simulating electronic structure have been created depending on the purpose of research and systems under study. Hence, it is important to understand and select the appropriate methods to model and analyze molecule while saving time and computational resources (cost). In QC, the Schrödinger equation is used to describe characteristic of electron:

Quantum science

Semi-

empirical Parameter

Figure 6: Three methods to approach

Schrodinger equation

Ab initio

Wavefunction

Schodinger equation

DFT

Electron density

$$\widehat{H}\psi = E \psi \tag{1}$$

where $\boldsymbol{\psi}$ is the wavefunction, $\boldsymbol{\hat{H}}$ is the

Hamiltonian operator and *E* is the energy of the given system. Application of \hat{H} to the wavefunction determines the energy of system, E, known as the eigenvalue to the Hamiltonian. The major goal in computational chemistry calculations is solving the Schrodinger equation to determine the minimum energy of a chemical

system. Figure 6 shows three different methods to approach solution of this equation: *Ab initio*, semi-empirical and Density Functional Theory (DFT). In *ab initio* and semi-empirical, the Hamiltonian operator is written as



where r_{ij} is electronic coordinates and Z_{ab} is nuclear coordinates. The *ab initio* method, meaning "from first principles", is most accurate and gives a good result of electron behavior, spin and relationship between electron-electron, and electron-nuclear interactions. However, due to its complicated equation, it requires high power computer which is expensive and time consuming. Semi-empirical methods require input parameters derived from experiments before running a calculation. So, the accuracy of this method depends on a database which is used to parameterize the performance. In DFT, the wavefunction is replaced by electron probability density function or electron density function [12]. Because nuclei are relatively large and slow, electrons are considered as moving in the field of fixed nuclei (Born-Oppenheimer approximation). Then, the nuclear kinetic energy is assumed as zero. Hence, the Hamiltonian is reduced into a simpler form.

DFT calculations are popular recently due to its computational efficiency and accuracy, with results approaching the accuracy of *Ab initio* and semi-empirical but with significantly faster processing times. That is the reason why a lot of research is applying DFT in recent years (figure 7) [13].

To compute the energy of a chemical system which is dictated by the electron distribution and density, DFT uses functionals (functions of other functions) to determine molecular properties after starting with certain molecular coordinates and orbitals defined by a chosen basis set. Because



of its popularity, many different functionals, and basis functions have been created to improve the performance of DFT for modeling specific chemical systems. There is no combination of functionals/basis set for any system, thus a lot of test, comparison, and evaluation (validation with experimental data) is required to figure out the best one for this research.

2.2 Density Functional Theory

In DFT, the main idea is to describe a many-body interacting system via partial density and not via many-body wave function [14]. Since an N-body system is replaced by three spatial



Figure 8: Jaccob's ladder of functionals approximation

coordinates through particle density, the total time required for calculation is reduced significantly. Hohenberg-Kohn (HK) theory is the first one considered system as its ground state density. Combining with Born-Oppenheimer (BO) approximation, and Kohn-Sham (KS) theory, DFT was improved to solve by approximation the exchange-correlation (XC) energy (E_{xe)}. There are four levels of approximations to solve E_{xe} (fig.8) which are Local Density Approximation (LDA), Generalized of Gradient Approximation (GGA), Meta-GGA (MGGA) functionals, and Hybrid Functional.

2.3 Exchange-correlation energy (E_{xc}) functional

In DFT calculation, Hohenberg-Kohn theory (1964) is used to explain electron density [15]. The first Hohenberg–Kohn theorem states that 'the ground state of any interacting many particle systems with a given fixed inter-particle interaction is a unique functional of the electron density n(r)'. It is written in the equations:

$$\widehat{H}\psi = E\psi \tag{3}$$

With
$$\widehat{H} = \widehat{T} + \widehat{E_{ext}} + \widehat{V_{ee}}(1)$$
 (4)

$$\widehat{H} = \left[\sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_i} \nabla^2 \right) + \sum_{i=1}^{N} E_{ext}(r_i) + \sum_{i>j}^{N} V_{ee}(r_i, r_j) \right]$$
(5)

 \hat{T} is the kinetic energy operator, $\vec{E_{ext}}$ is external energy operator and $\vec{V_{ee}}$ is electronelectron interaction operator which contributes to the total energy of the system [16]. *r* represents properties of electron in its ground state, and it is a variable. Hence, each electron in the system is identified and added to sum up to the total energy. However, this equation is unsolvable. Hence, the Kohn-Sham (1965) formalism was developed to solve this equation. In the Kohn-Sham approach, electrons are divided into 2 types: non-interacting electron and interacting. For noninteracting electrons, the Hamiltonian operator is used as approximation wavefunction for the others. And for the interactive electrons, the exact Hamiltonian is applied to determine each electron energy. Because non-interacting electrons are in the ground state, which is exceedingly difficult to calculate. As the result, an approximation is used to describe non-interacting electrons. The equation is rewritten as

$$\widehat{H} = \widehat{T_s} + \widehat{J} + \widehat{E_{ext}} + \widehat{E_{xc}}$$
(6)

from equation (5) and (7)

$$\widehat{E_{xc}} = \widehat{T} - \widehat{T_s} + \widehat{V_{ee}} - \widehat{J}$$
(7)

with $\widehat{T_s}$ is the kinetic energy operator of non-interacting electrons in the system and \widehat{J} is the classical Coulombic electron – electron interaction. \widehat{J} is a known value and $\widehat{T_s}$ is identified by equation

$$\widehat{T}_{s} = \sum_{i=1}^{N} \left\langle \psi_{i} \left| -\frac{1}{2} \nabla^{2} \right| \psi_{i} \right\rangle \tag{8}$$

2.4 Local density approximation (LDA)

The local density approximation (LDA) [17] is the simplest method to solve E_{xc} . In LDA, E_{xc} is determined by the exchange-correlation of an electron in a homogeneous electron gas of the same density:

$$E_{xc}^{LDA}[n(r)] = \int \varepsilon z_{xc}(n(r))n(r)dr$$
(9)

with ε_{xc} is the exchange-correlation energy of each particle in the system. In LDA, exchange energy is $Cr^{1/3}$ and correlation energy is parametrized [18]. LDA treats the system as homogeneous, but iron complexes are more complicated than homogeneous. Electron in different position has their own significant features like binding energy, spin direction, etc. As the result, we cannot use LDA in iron – ligand calculation research.

2.5 Generalized Gradient Approximation

The LDA assumption that all electrons are same leads to underestimation of the exchange energy and over-estimation of the correlation energy. To fix this problem, the spatial gradient of the electron density was added to equation which extends this calculation to more realistic nonhomogeneous electron densities. The new form of GGA is [19]

$$E_{xc}^{GGA}[n_{\downarrow},n_{\uparrow}] = \int \varepsilon_{xc}(n_{\downarrow},n_{\uparrow},\nabla n_{\downarrow},\nabla n_{\uparrow})n(r)d^{3}r$$
(10)

Where n_{\downarrow} , n_{\uparrow} illustrate spin-up and spin-down densities. Perdew and Wang [30] successfully produced highly accurate atomization energies and extended it to various system. Within each approximation method, various specific functionals have been developed to treat chemical systems. Examples of commonly used GGA functionals are BP86 [20][21], BLYP [20][22], PW91[23][24][31], PBE [19]. Paier and Kresse[25] mentioned in their paper PBE represent for non-empirical GGA. It performs well in calculating ionization energy and atomization energy of transition metal and specially iron. In addition, PBE is a good method for new compound study for which we do not have any parameters.

2.6 Meta - Generalized Gradient Approximation

According to Perdew [26], one problem of GGA functionals is electron's selfinteracting error. Each electron interacts with the total electron density and itself. meta-GGA is an improvement of GGA but still maintains all GGA features. The most popular approximation of Meta-GGA is TPSS which was found by Tao, Perdew, Staroverov, and Scuseria. Recently, it has been applied to study equilibrium geometries, bond energies, spin-inversion, and excited energy of transitional metal system. In an article of Jensen [27], study of spin-crossover iron complexes with TPSS and meta hybrid 10% -exchange functional TPSSh was successfully performed. It reached 11 kJ/mol for enthalpies of spin crossover which is close to actual data (10 kJ/mol). Due to its accuracy, TPSS and TPSSh are applied in spin crossover study of this research which explains the creation of dimer.

2.7 Hybrid Functional

Hybrid functionals are more reliable than GGA in some calculation which have specific properties like atomization enthalpies, and vibrational frequency. Thus, the hybrid functional was introduced as linear combination of Hartree-Fock theory and an exchange-correlation energy. Depending on material and purpose of project, a different amount of HF is adjusted to enhance the result. One of the most well-known and popular approximations is B3LYP (Becke, 3-parameter, Lee-Yang-Parr). It was introduced by Becke in 1993 [28] and is illustrated as

$$E_{xc}^{B3LYP} = E_x^{LDA} + 0.20(E_x^{HF} - E_x^{LDA}) + 0.72(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + 0.81(E_c^{GGA} - E_c^{LDA})$$
(11)

B3LYP is used widely in calculating Iron tris(2,2-bipyridine). Bruce et al [29] successfully optimized the molecular structure of $Fe(bpy)_3^{2+}$ using B3LYP and showed that bond lengths and angles were in close agreement with experimental XRD crystal data, showing a 97% percent match. Lawson et al [30] applied B3LYP to explain characteristic of Iron (III) tris(2,2'-bipyridine) in low spin state and high spin state which is highly relevant to this research. High spin state and low spin state play an important role in redox energy and transformations of this iron complex.

However, another study explains the failure of B3LYP in calculating properties of the bipyridine ligand. According to Milko and Iron [31], B3LYP treated Iron (III) Tris(2,2'-bipyridine) as closed-shell system (no unpaired electron) which is inaccurate. Spin-crossover happens in iron (III) complexes and leads to 5 unpaired electrons (open-shell systems). But they also emphasized that B3LYP has significant problems in handling open-shell systems. Hence, B3LYP and some of other popular hybrid functionals (Table 1) are performed in this research. In addition, different molecular properties of different types of molecules requires different functional approximation to determine the most accuracy results. Thus, the scientific literature is extremely useful for finding which functionals/basis sets might work best for different classes of chemicals as well as for validating computations by comparison to previously published experimental results.

Hybrid Functional	% Hartree	Application	
	Fock		
B3LYP [20]	20	Good for organic molecule	
		• Show error for transitional metal and large	
		molecule	
PBE0 [32]	25	• Give good result for the gap of Ionization energy	
		and electron affinity (HOMO-LUMO)	
B3PW91[33] [34]	20	• Fulfills the uniform electron gas limit	
BHLYP [35]	50	• Improving chemical kinetic calculation, and	
		reaction barrier height [35]	
		• Having problem with transition metal and spin	
		state split	
I contraction of the second			

Table 1: Hybrid Functional Approximation

Rappoport et al. [36] mention that while calculating transition metal energies, the energy gap between low spin state and high spin state increased as the increasing of HF amount. When there is only GGA (%HF=0), the system is too much covalency. Moreover, when % HF is high (50% in BHLYP), it leads to too little covalency. As a result, the percentage of Hartree-Fock mixing in hybrid functionals (see above) was found to be optimized in the 10 to 20% range. The paper also mentioned that PBE, PBE0 and TPSS were suitable for transition metal studies. Whereas LYP or LYP hybrid forms should not be applied because its parameter overestimates correlation energy.

2.8 Different direction in DFT development:

2.8.1 Basis sets

Another very important parameter in setting up Kohn-Sham equations is selection of appropriate basis sets. In DFT, a basis set represents the wavefunction of an electron.





By applying basis set, calculation is more accurate and accelerated [37]. A couple of specific basis sets have been identified to be particularly applicable to the research on iron complexes in this thesis research. In addition, Fe is a 3d⁶ transition metal, so DFT and Triple-Zeta Valence with Polarization (def2-TZVP) is advanced enough for this calculation based on figure 9. Moreover, in Yang et al [38] mentions that Los Alamos National Laboratory 2 double zeta (LANL2DZ) and def2-TZVP combination is widely applied to redox calculations of transition metal complexes. LANL2DZ concentrates on iron core and def2-TZVP (Triple-Zeta Valence with Polarization) is an Ahlrich's-type basis set that has been proven to be accurate for C and N atoms. LANL2DZ contains effective core potential (ECP), so it prevents the interaction between core and valence electron. As the result, it reduces core functions which leads to decrease of computational effort. In a paper of Pettersson et al [39], by applying ECP in heavy molecule and its cluster, it reduces 50% in CPU time and disk storage, so the calculation is accelerated. Finally, the more functions (atomic orbitals) included in a basis set give a better description of the molecular/electronic structure.

2.8.2 Dispersion Correction

Correction accounts for van der Waals forces that is especially important for modeling inter- and intra-molecular interactions, especially in spin-crossover study. Kepp et al. [40] showed that functionals with more than 20% HF exchange were much more accurate when using the D3BJ correct. Especially it reduces error in energies calculation of low spin state in iron complexes.

2.9 Simulation of the solution phase

The major inaccuracies in Born-Haber thermochemical calculations, and DFT calculations in general, is in modelling the influence of the solvent for determining solvation free energies [41]. Most calculations are typically performed on a molecule in the gas phase. However, solvents play a huge role in influencing the redox potential through non-covalent interactions with the dissolved active compounds, for example via hydrogen bonding in water. These interactions influence the electronic properties and ultimately the redox potential of the compound. Ideally, solvent molecules (water in our case) in at least the first solvation shell would be included explicitly (individually) in the model and calculation. Unfortunately, it is computationally too expensive to model so many water molecules along with the main compound. Since electrochemistry of the iron tris(2,2'-bipyridine) complex occurs in the solution phase, the solvent medium in which it is dissolved needs to be modeled and included in calculations to give a true representation of the molecular environment and more accurate final energies. Hence, an implicit solvent model (dielectric continuum) such as CPCM is often applied for solution-phase calculations in Born-Haber redox potential predictions. Solvents are modeled based on their dielectric constant. In addition, dielectric constant of water (80) is used in most of calculation. However, some other dielectric constant including dichloromethane (CH2Cl2), 8.93; acetone, 20.7; acetonitrile (CH3CN), 36.64; dimethyl sulfoxide (DMSO), 46.7 are used to obtain the impact of solvent on the molecule.

2.10 Literature review

Zhang et al. [42] predicted the redox potential of 1710 quinone and hydroquinone derivatives by thermodynamic cycle. In addition, DFT was applied to figure out the solution-phase Gibbs free



Figure 10: Thermodynamic cycle was used to predict redox potential and solubility of organic molecule [42]

energy changes (ΔG_{red} and ΔG_{ox}) during the reduction or oxidation processes. Then, the theoretical redox potentials (ΔE^{o}) and solvation free energies of the redox couples (ΔG_{solv}) were calculated as figure 10. Moreover, ΔG_{solv} was used to determine solubility and stability of organic molecules. Thermodynamic cycle is reported as a most positive method for redox potential prediction.

Shikha et al. [43] reported DFT study about geometry and energy of iron complex in different state of charge. Fe (II) complex is in singlet spin state. However, when complex was oxidized from 2+ charge state to 3+ charge stage, it switched from low spin to high spin state. The article also emphasized that high spin state of iron (III) is preferred in solution. As the result, bond

distance between Fe and N is longer and energy is higher. To study about spin-crossover phenomenon, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in different spin state of iron was obtained and analyzed. HOMO and LUMO is powerful tool to study about changing of structure and energy during spin crossover.

Flores-Leonar et al. [44] analyzed the structural and energetic changes during spin crossover by DFT. According to the article, Fe (III) complex in high spin state is not stable in solution. Moreover, Fe -N distance increases which can suggest the possibility of the bond being broken. This points out that Fe (III) complexes tend to switch to high spin state and unstable in aqueous solution. As the result, ligand is attacked by water and forms dimers.

Chen et al. [45] applied broken symmetry approach in DFT (DFT-BS) in calculate oxobridged diiron (III) systems. Due to 5 unpaired electrons for each iron (III) with high spin state, it is a challenge to explain the magnetic properties. By applying DFT – BS, calculation of iron (III) dimers was successfully performed. Fe-O-Fe angle was 148.1° which is same as X-ray crystallography analysis of iron complex. It also gives Fe-O bond distance in 1.73 Å to 1.83 Å which close to 1.765 Å of crystal. Applying DFT-BS in dimer of iron calculation enhances the accuracy of result, so it is a positive method for this research.

2.11 Thermodynamic cycle in redox potential study

Computational chemistry has been applied to predict the redox potential of many types of compounds. Specifically, in RFB research Lin et al. [46] developed a database whereby 1000 organic molecules were screened, and their redox potentials were calculated.



Figure 11: Gibbs free energy in each phase of the cycle is determined for redox potential calculation.

The well-known Born-Haber thermodynamic cycle (Fig.11) is generally accepted as the most accurate computational method for the prediction of redox potentials and applied to find the redox potential iron complex in aqueous environment [47]. The formula is used to calculate the redox potential ($E_{red}^{1/2}$) is

$$E_{\rm red}^{1/2} = \Delta G_{\rm (s)}/nF - C \tag{12}$$

where $\Delta G_{(s)}$ is the overall reaction of the standard Gibbs free energy, respectively, *n* is the number of electrons in the redox process, *F* is the Faraday constant (96485 C/mol), and *C* is a constant, which is based on the reference electrode [48][49].

To determine the Gibbs free energy in each phase of the cycle, frequency calculations using DFT are applied, which generates information on a compound's thermochemistry. To determine the redox potential of a compound, typically four calculations need to be performed after generating an initial molecular structure: (i) geometry optimization and frequency calculation of *gas-phase oxidized* form of compound, (ii) frequency calculation of *solution-phase oxidized* compound, (iii) geometry optimization and frequency calculation of *gas-phase reduced* form of compound, (iv) frequency calculation of *solution-phase reduced* compound. From subtraction of the computed free energies of calculations (i) and (ii), $\Delta G_{(s,ox)}$ can be determined. Similarly, (iii) and (iv) give $\Delta G_{(s,red)}$, (i) and (iii) give $\Delta G_{(g,ox)}$, and (ii) and (iv) give $\Delta G_{(s,red)}$. Then $\Delta G_{(solv)}$ is determined by equation:

$$\Delta G_{(\text{solv})} = \Delta G_{(\text{g,ox})} + \Delta G_{(\text{s,red})} - \Delta G_{(\text{s,ox})}.$$
(13)

2.12 Summary

Recently, most research about redox flow battery uses DFT instead of *Ab initio* even though both are good for quantum study for several reasons. First, the calculation is faster and less resource-intensive compared to other methods such as *Ab initio* calculations since some empirical information can be used. Furthermore, in DFT calculations, each electron is identified, and its characteristics calculated with respect to all other electrons, so all electron behavior will be observed and studied. In this research, DFT is used to describe the effect of gaining or losing electrons on iron which lead to different performances of the complex in redox flow batteries.

Density functional theory (DFT) is applied to study about model the three relevant forms of iron tris(2,2'-bipyridine) (2+, 3+ and dimer) in order to provide a theoretical framework through which solubility of the monomer might be improve and its propensity to dimerization in the oxidized form could be inhibited. DFT will be used to calculate different aspect including geometry, vibrational frequency, energy, redox flow potential, HOMO-LUMO, and electron density.

CHAPTER III: OXO-BRIDGED DIIRON BIS(2,2'-BIPYRIDINE) DIMER





To study the process of $Fe(bpy)_3^{3+}$ dimerization into $Fe_2O(bpy)_4Cl_2$, the iron (II) complex $Fe(bpy)_3SO_4$ is first dissolved in 2 M sodium chloride solution. An operando Bulk Electrolysis system is set up and running at the same time with UV-vis. In this experiment, changing of the peak illustrates the behavior of electron during redox reaction. However, during reduce reaction, there is a huge drop in voltage from 1.058 V in SHE to 0.3 V in SHE. Figure 12

shows a low voltage plateau during discharge which does not affect the overall capacity of the RFB, but it lowers the discharge voltage severely. As a result, the battery cannot output full power. In this research, we performed several deep studies of oxo bridge iron bis(2,2'bipyridine) to understand the reason behind this voltage loss and ultimately try to prevent it.

Ruan et al. [51] and others have noted that this phenomenon is due to the dimerization of $Fe(bpy)_{3^{3^+}}$. The new structure (Fig.13) is a oxo-bridged diiron bis(2,2'-bipyridine). Oxo-bridged iron complexes (Fe-O-Fe) have been known for decades and have biochemical importance, such as in the protein [52]. In water, the electron-deficient iron (III) complex is unstable and tends to be attacked by water to form [(bpy)₂(Cl)Fe(III)-O-Fe(III)-(Cl)(bpy)₂].


Figure 13: Dimer form of iron complex

Ruan et al. [51] explain this dimerization by reaction equation

Charge:
$$[Fe(bpy)_3]^{2+} \rightarrow [Fe(bpy)_3]^{3+} + e^- E = 1.03 V vs. SHE$$

 $2[Fe(bpy)_3]^{3+} + 2Cl^- + H_2O \rightarrow [Fe_2(bpy)_4OCl_2]^{2+} + 2Hbpy^+$
Discharge: $[Fe_2(bpy)_4OCl_2]^{2+} + 2Hbpy^+ + 2e^- \rightarrow 2[Fe(bpy)_3]^{2+} + 2Cl^- + H_2O$
 $E = 1.03 V vs. SHE$

Even though capacity is maintained at same level, dimerization still degrades the battery in terms of a compromised voltage output and poor voltage efficiency:

$$VE = \frac{\text{average discharge voltage}}{\text{average charge voltage}}$$
(14)

Voltage efficiency is a critical factor to the performance of RFB and should be always maximized. Under typical performance conditions (i.e., 20 mA/cm^2 discharging), most RFB from the literature exhibit VE's around 60-70%, whereas VE in RFB using the Fe(bpy)₃SO₄ catholyte are only 64% by our experiments. Luckily, the voltage loss is not due to irreversible degradation in the battery; the original Fe(bpy)₃SO₄ species is perfectly regenerated after the discharge phase.

Thus, the battery can cycle for thousands of times in theory, and only the voltage loss issue needs to be addressed.

3.2 Magnetic exchange couplings in binuclear iron (III) complexes

One explanation for the forming of dimerization is spin crossover (SCO) in Fe (III) (fig14). [53]. The SCO between paramagnetic high -spin state (HS) and diamagnetic low-spin state (LS) can be induced by temperature, pressure, light, and other stimulation. $Fe(bpy)_{3^{2+}}$ is in low spin state, however, when this 6d species is oxidized to the Fe (III) 5d species, the high-spin electron arrangement becomes energetically favorable to the low-spin Fe (III). Thus, the oxidized complex can undergo spin crossover from LS to HS.



Figure 14: Increasing of bond length and energy with Fe3+ switch from LS to HS

Once in the HS form, the bond length between Fe-N increases 0.2 Å and energy is excited to higher level (Fig14). As the result O_2 ligands are significant more stable than bipyridine. Hence, oxo-bridge is formed to stabilize high oxidation states of iron [54]. In addition, among the paramagnetic state, Fe (III) dimers tend to be stable through an antiferromagnetic coupled arrangement. It has 5d electron spin up and 5d electron spin down on the other side. Due to magnetic moment of two metal center affecting the molecule, magnetic exchange coupling (J) is applied to study about oxo-bridge iron complex. To describe about magnetic properties of binuclear transition metal complexes, Heisenberg-Dirac-van Vleck spin Hamiltonian is used [55]

$$H = 2J_{12}S_1S_2$$
(15)

With J_{12} is the spin coupling constant and S_1 and S_2 are the spin operators for the two respective metal centers. This equation is solved by applying broken symmetry approach in DFT (DFT-BS), which is described as

$$J_{12} = \frac{E^{BS} - E^{HS}}{\langle S \rangle_{HS}^2 - \langle S \rangle_{BS}^2} \tag{16}$$

According to Korcharing et al, DFT-BS determined negative J constant (J<0), so antiferromagnetic exchange coupling is found in the oxo-bridge iron complex (fig.15). In addition, DFT-BS also carries out total energy of high spin state, localization of orbitals, and subsequent BS calculations of the low spin state with the broken spatial and spin symmetry [56]. It is more convenient comparing to conventional DFT in iron cluster calculation.



Figure 15: Antiferromagnetic exchange coupling of dimer

The major goal of this part of the thesis research is to better understand the energetics of dimerization (spin stabilization via exchange coupling constant). With this information, we might gain insight into how to disrupt dimer stabilization and force $Fe(bpy)_3^{3+}$ to remain in the monomer state. This will allow an RFB utilizing $Fe(bpy)_3$ as a catholyte to produce full power during the entire discharge phase.

CHAPTER IV: EXPERIMENTAL METHODOLOGY

4.1 Computational resources:

All calculations are performed with ORCA 4.2 open-source computational chemistry program as it is flexible and an easy program to perform DFT calculation. DFT experiments processed using TAMUCC's Tsunami high performance computing (HPC) cluster, which contains 1 head node, 44 cpu nodes, and 4 gpu nodes. Each node contains two Xeon processors, 256 GB of memory, and 1 TB of local disk storage. The tsunami cluster also has 10 TB of disk space for programs and 11.7 TB for memory. Simple Linux Utility for Resource Management (SLURM) is applied to handle all jobs. SLURM program helps to manage and perform tasks on HPC. By using the HPC, calculations can be performed in parallel for significant reductions in computation time. The HPC was granted in a previous multi-departmental collaboration at TAMUCC by the National Science Foundation.

4.2 Geometry study:

All DFT input files are generated by Avogadro software after drawing the molecular structure of interest and pre-optimizing the geometry using Avogadro's molecular mechanics UFF force field (Fig. 16).



Figure 16: $Fe(bpy)_{3^{2+}}$ and input parameter

Computational experiments started by exploring the iron - bipyridine ligand. Typical code

used for an input file is shown in Figure 17.

! PBE Def2-TZVP def2/j D3BJ LANL2DZ RIJCOSX AutoAux Grid5 Nofinalgrid GridX4 NofinalgridX opt freq tightSCF printmos xyzfile UNO UCO

%scf Maxiter 500 end %pal nprocs = 16 end %output Print[P_OrbEn] 0 end *xyz 3 2 -molecule coordinate-*

Figure 17: DFT parameter

This file contains all description of the $Fe(bpy)_3^{2+}$ complex nuclear coordinates, charge, multiplicity, and other computational parameters (table 2).

! Functional basis set ECP auxiliary basis set(s) dispersion correction speed-up algorithm

grid selection scf tolerance	geometry c	optimization f	requency	orbital analys	is
	8	Pulling			

Parameter	Explanation		
CAM-B3LYP	Density functionals		
	It can be B3LYP, BP86, PBE, PBE0, B3PW91, CAM-B3LYP,		
	ωB97X, etc		
Def2-TZVP and LANL2DZ	Basis sets		
	Def2-TZVP is applied for C, N and H atoms. LANL2DZ is		
	applied for Fe core which contain ECP		
Def2/j	Auxiliary basis sets are needed to approximate Coulomb		
	energies in basis sets of split valences, triple zeta valence and		
	quadruple zeta valence.		
D3BJ	Dispersion correction accounts for van der Waals forces		
RIJCOSX Grid4X	Approximation for Coulomb and HF Exchange		
Nofinalgridx	It can speed up the calculation		
Autoaux Grid5 nofinalgrid	Automatically generate auxiliary basis sets		
	It is required in RIJCOSX method to provide good fit for basis		
	set		
Freq	Vibrational frequency		
Opt	Geometry optimization		

TightSCF	Request tight convergence for vibrational frequency
UCO	Corresponding orbital
	Useful for analyzing spin-couple system
UNO	Quasi-restricted orbital
	Analyze open-shell single-ion metal complex

Table 2: DFT codes

Different density functionals including B3LYP, BP86, PBE, PBE0, B3PW91, CAM-B3LYP, ω B97X were used to calculate geometries and thermochemistry for redox potential prediction. Each functional is combined with basis sets, typically 6-31G**, LANL2DZ, def2-SVP and def2-TZVP. During calculations, ORCA 4.2 builds an output file which contains all results of the calculation. Optimizing output file was analyzed for deeper study including geometry study, vibrational frequency, the highest occupied molecular orbital to the lowest unoccupied molecular orbital (HOMO \rightarrow LUMO), and electrostatic potential study.

4.3 Redox potential study

To predict redox potentials computationally, a series of different calculations needs to be performed. Different combination of functional and basis set is determined again with $Fe(bpy)_3^{2+}$. Optimization calculations find the minimum energy molecular structure, then subsequent frequency calculations generate thermochemistry data at the same levels of theory of the geometry optimization. In addition, the LANL2DZ basis set is used for Fe because it uses Effective core potentials aka pseudo-potentials for the transition metal's core electrons.



Figure 18: Born-Haber Cycle is applied to predict redox potential of iron complexes

The goal of the redox potential calculation is to fill out all information for a Born-Haber cycle (Figure 18). Calculations are performed to determine the Gibbs free energy changes of the gas phase and the solution-phase of the oxidized and reduced species. These values are then used to calculate the overall standard Gibbs free energy by equation (17):

$$\Delta G_{solv}^{o,redox} = \Delta G_{gas}^{o,redox} + \Delta G_s^o(red) - \Delta G_s^o(Ox)$$
(17)

Then, Nernst equation is applied to determined redox potential of one electron.

$$\Delta G_{solv}^{o,redox} = -nFE_{cal}^{o} \tag{18}$$

Where *n* is, *F* is the Faraday constant, 96485 C/mol, and E^0 is redox potential. This method will be used to predict redox potentials of iron tris(2,2'-bipyridine) 2+, 3+, its dimer, and Fecomplexes using functionalized bipyridines. To validate our method, results from our Born-Haber redox potential calculations will be compared to published experimental results for various wellstudied organometallic species.

4.4 Synthesis of iron tris(2,2'-bipyridine) complexes for UV-vis and FTIR study.

Generally, 5 gram of ferrous sulfate is dissolved is 50 mL of water and excess ligand is added in 50 ml of acetonitrile with the ratio >3 ligand:1 iron [51]. Then, slowly mix the two solutions together and stir for 2 hours. When the ligands bind with iron, they form a strongly colored solution (red with bipyridine). All solution will be eliminated by rotary evaporator and the complex is washed again with CH_2Cl_2 to remove excess uncoordinated bipyridine before drying under vacuum. The new iron-ligand complex is analyzed via cyclic voltammetry, UV-vis and FTIR. These experimental data will be used to confirm the accuracy of DFT calculations.



4.5 Cyclic voltammetry study

Figure 19: Cyclic Voltammetry

In the cyclic voltammetry study, the iron complex Fe(bpy)₃SO₄ is dissolved in 2 M NaCl solution. A three-electrode system is used, with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/AgCl reference electrode to determine the redox potential and reversibility of the organometallic complex

A generic cyclic voltammogram is shown in Figure 19. Compounds suitable as active redox species (anolyte or catholyte) in RFB need to have reversible reduction/oxidation peaks which reflect its charge and discharge abilities. The two peaks need to be close together, approaching E_{a} - $E_{c} = 59$ mV of an ideally reversible redox couple, and with a peak current ratio approaching 1 indicating no side reactions. These parameters indicate that there is little to no kinetic energy barrier during the redox reactions resulting in low overpotential energy loss when charging/discharging an RFB. Data in this experiment was compared with DFT results to prove the reliability of our computational methodology. Cyclic voltammetry will be used to evaluate different Fe-complexes using bipyridine functionalized in electrolyte if any positive result is obtained.

4.6 Highest occupied molecular orbital (HOMO) - the lowest unoccupied molecular orbital (LUMO) calculation

Due to the transformation of Fe (III) to a dimer complex (Fig. 20), HOMO and LUMO of Fe (II) complex, Fe (III) complex in low spin state, high spin state and dimer in water solvation were obtained. Geometry optimization was performed first to reach the most stable structure. Then, visualization and printing calculations were performed to evaluate the molecular orbitals and Avogadro was used to analyze the molecule structure and orbitals. In these HOMO-LUMO calculations, bond lengths and angles of the iron complex and its dimer were analyzed in different charge state including 2+, 3+ low spin, 3+ high spin and dimer high spin. In addition, the electrostatic potential across the molecules in their highest occupied molecular orbital state and lowest unoccupied molecular orbital state were obtained.



Figure 20: Transformation of Iron complex to dimer.

4.7 Electrostatic potential map (EPM)

Electrostatic potential is also an important molecular property regarding electron density and distribution. In this study, EPMs were generated to show electron density in the Fe (II) complex, the Fe (III) complex in low and high spin states, and in the Fe (III) dimer. Geometry results from the previous study were used to determine energy density within molecule. ORCA 4.2 and HPC plotted electrostatic potential map and converted result to a .gbw file. gbw file cannot open on Multiwfn directly, so orca_2mkl is used to convert .gbw file to molden input. Then, Multiwfn use molden input to generate output data containing EPM of Fe (II) complex, Fe (III) complex in low spin state, high spin state and dimerization. There are 3 .pdb file for each molecule generated by Multiwfn. Finally, VMD is a visualization tool for the final construction and analysis of electrostatic potential maps. It combines 3 .pdb file together and plot electrostatic potential maps. 4.8 Oxo-bridge Iron Bis(2,2'bipyridine)



Figure 21: Dimer form of Iron complex

Iron (III) tris(2,2'-bipyridine) is not stable in water and spin-crossover occurs which switches the iron (III) complex from low spin state to high spin state. As the result it creates a dimer form (fig.20) which lowers the output voltage battery. In this research, density functional theory (DFT) will be performed to collect data on geometry, vibrational frequency, HOMO-LUMO, and electrostatic

potential. Due to the novelty of this study, different functional and basis set were tested and compared for the best result.

To calculate redox potential of the dimer, a modified form of the Born-Haber cycle (Fig.22) is applied:

Optimization and frequency calculations are applied to calculate ΔG_{solv} of each oxidized compound in water and gas. Conventional DFT is applied for most of calculation except dimer. Broken symmetry is used to determine dimer properties due to it magnetic properties. Same process is applied for reduced compounds including Fe[(bpy)₃]²⁺, Cl⁻, and H₂O. All data are put together as shown above to calculate $\Delta G_{(aq)}$. The spin state of electrons in the Fe(bpy)₃³⁺ and dimer forms play a significant role in dimerization. To handle energy stabilization in binuclear organometallic complexes, broken symmetry calculations can lead to greater insight into spin energetics. ORCA is particularly useful in running BS calculations.

$$\begin{array}{c} \Delta G(_{gas}) \\ [Fe_{2}(bpy)_{4}OCl_{2}]^{2+} + 2HBpy^{+} + 2 \ e^{-} \rightarrow 2Fe[(bpy)_{3}]^{2+} + 2 \ Cl^{-} + H_{2}O \\ \Delta G_{solv}(1) & \qquad \Delta G_{solv}(2) & \qquad \Delta G_{solv}(3) & \qquad \Delta G_{solv}(4) & \qquad \downarrow & \qquad \Delta G_{solv}(5) \\ [Fe_{2}(bpy)_{4}OCl_{2}]^{2+} + 2HBpy^{+} + 2 \ e^{-} \rightarrow 2Fe[(bpy)_{3}]^{2+} + 2 \ Cl^{-} + H_{2}O \\ \Delta G(_{aq}) \end{array}$$

Figure 22: Thermodynamic cycle of bi-nuclear oxo-bridge complex

CHAPTER V: RESULTS AND DISCUSSION

5.1 Study about Functional and Redox potential prediction

5.1.1 Cyclic voltammetry

Figure 23 shows the cyclic voltammetry result of $Fe(bpy)_3SO_4$ in 1M of NaCl with $E_{redox} = 1.05$ V vs SHE. It matches with Ruan et al. data [51]. Iron tris(2,2'-bipyridine) has peaks corresponding to its oxidation (anodic peak) to the Fe (III) complex and reduction (cathodic peak) back to the Fe(II) complex. The potential splitting between the 2 peaks is about 65 mV which is suitable for secondary battery. In addition, the ratio of cathodic and anodic peak equals one which reflects all Fe²⁺ oxidized to Fe³⁺ during the charging process can reduce back to its previous form.



Figure 23: The cyclic voltammogram of 4mM Fe(bpy)3SO4 in 1M NaCl at 50mV/s on a glassy carbon working electrode.

Over the short time scale of CV (~20 s), hardly any dimerization can occur, and the redox event appears to have excellent reversibility. However, when the Fe (III) complex remains in solution for longer durations (minutes to hours) dimerization takes place, which is a major focus of this work. Fe(bpy)₃²⁺ is known as a promising RFB catholyte because it has a high redox potential, works in a wide range of pH (3-9), and does not undergo irreversible degradation [57]. Hence,

 $Fe(bpy)_{3}^{2+}$ is used widely in electrochemical energy studies. In addition, the observed redox potential of $Fe(bpy)_{3}^{2+}$ is just slightly lower than electrolyte breakdown limit, 1.23 V vs SHE. Thus, Iron tris(2,2'-bipyridine) maximizes the voltage output for the catholyte side of the battery without triggering oxygen evolution.

5.1.2 Geometry study:

The first important calculation to perform is in confirmation of the stable geometry of the $Fe(bpy)_3^{2+}$. To best match experimental data, different functionals were screened for their accuracy to reproduce the $Fe(bpy)_3^{2+}$ crystal form. Comparison of the average Fe-N bond lengths can be used quantify the accuracy of different computational inputs.

Functional	Types of Functional	% HF	Average Fe-N	% Error
			bond length (Å)	
Crystal			1.967	
PBE0	Hybrid-GGA	25	1.968	0.05
B3LYP	Hybrid-GGA	20	1.986	0.97
B3PW91	Hybrid-GGA	20	1.960	0.36
ωB97X	Long-range Hybrid	40	2.017	2.54
	GGA			
CAM-	Long-range Hybrid	20	1.990	1.17
B3LYP	GGA			
BP86	GGA	0	1.945	1.12
PBE	GGA	0	1.958	0.46

Table 3: Different Functional combining with LANL2DZ/def2-TZVP in Fe(bpy) ₃ ²⁺ geometry
calculation.

Table 3 shows results of calculation compared with the crystal structure of Fe(bpy)₃²⁺ from the X-ray structure database [58]. PBE0, PBE, and B3PW91 functional gave the best result with only 0.05%, 0.36%, and 0.46% error respectively. CAM-B3LYP and B3LYP also give a positive result which is about 1% error. As PBE is a pure GGA and non-empirical functional, so PBE and its hybrid PBE0 result do not depend on any parameterized data. Hence, PBE and PBE0 is a generally well-performing functional for general organometallic systems, which require computational studies for deeper insight. In addition, B3LYP and CAM-B3LYP have not shown great accuracy in geometry study. According to Lawson [30], LYP parameter usually give longer metal - ligand distance comparing to other DFT functionals. For example, B3PW91 is a hybrid functional which is similar with B3LYP. However, it replaced the LYP correlation energy parameter with that of Perdew and Wang and it gave better result. Hence, LYP is poorly parametrized for approximating the correlation energy which overestimates bond distance. That is the reason why B3LYP hybrid and CAM-B3LYP are not suited to geometry study.



Figure 24: % Error vs % HF

In conclusion, PBE, PBE0, B3PW91, are the best methods to calculate bond distance and angle. Owing to their accuracy in predicting the geometry of $Fe(bpy)_{3}^{2+}$, these functionals will also be applied to $Fe(bpy)_{3}^{3+}$, whose crystal structure is not known due to its instability. HOMO-LUMO energy levels and electrostatic potential will also be derived from these calculations.

5.1.3 Redox potential study:

In redox potential calculation, the output file (fig. 25) carried out all information including Gibbs free energy changes of the gas phase and the solution-phase of the oxidized and reduced species, redox potential vs Li electrode, SHE electrode and Aa/AgCl electrode

Variable Name	Value	Evaluation String
EGASPHASEOX	-1607.3206384488	TTHERMOEnergy.INNERENERGYU[2]
GGASPHASEOX	-1607.4010196611	TTHERMOEnergy.FREEENERGYG[2]
UGASPHASEOX	-1607.8454175522	TTHERMOEnergy.ELENERGY[2]
HGASPHASEOX	-1607.3196942398	TTHERMOEnergy.ENTHALPYH[2]
ZPEGASPHASEOX	0.4974788286	TTHERMOEnergy.ZPE[2]
ELIQUIDPHASEOX	-1607.7665785597	TTHERMOEnergy.INNERENERGYU[3]
GLIQUIDPHASEOX	-1607.8476736449	TTHERMOEnergy.FREEENERGYG[3]
HLIQUIDPHASEOX	-1607.7656343506	TTHERMOEnergy.ENTHALPYH[3]
ZPELIQUIDPHASEOX	0.4949586975	TTHERMOEnergy.ZPE[3]
EGASPHASERED1	-1607.7591108551	TTHERMOEnergy.INNERENERGYU[5]
GGASPHASERED1	-1607.8394667413	TTHERMOEnergy.FREEENERGYG[5]
UGASPHASERED1	-1608.2830501621	TTHERMOEnergy.ELENERGY[5]
HGASPHASERED1	-1607.7581666460	TTHERMOEnergy.ENTHALPYH[5]
ZPEGASPHASERED1	0.4964321307	TTHERMOEnergy.ZPE[5]
ELIQUIDPHASERED1	-1607.9637705465	TTHERMOEnergy.INNERENERGYU[6]
GLIQUIDPHASERED1	-1608.0449777223	TTHERMOEnergy.FREEENERGYG[6]
HLIQUIDPHASERED1	-1607.9628263375	TTHERMOEnergy.ENTHALPYH[6]
ZPELIQUIDPHASERED1	0.4947100871	TTHERMOEnergy.ZPE[6]
DG_SOLVOX_	-1.4383776370	ELIQUIDPHASEOX-ZPELIQUIDPHASEOX-EGASPHASEOX-ZPEGASPHASEOX
DG SOLVRED1	-1.1958019092	ELIQUIDPHASERED1 - ZPELIQUIDPHASERED1 - EGASPHASERED1 - ZPEGASPHASERED
DG_SOLVOX_KJMOL	-3776.4604859432	DG_SOLVOX_*2625.5
DG SOLVRED1 KJMOL	-3139.5779126043	DG SOLVRED1 *2625.5
DDG_SOLV1_	0.2425757278	DG_SOLVRED1DG_SOLVOX_
DDG_SOLV1_KJMOL	636.8825733389	DDG_SOLV1_*2625.5
DG_GAS1_	-0.4384724063	EGASPHASERED1-EGASPHASEOX
DDG_SOLV1_EV	6.6008251595	DDG_SOLV1_*27.2114
DG_GAS1_EV	-11.9314480368	DG_GAS1_*27.2114
DG_GAS1_KJMOL	-1151.2093027406	DG_GAS1_*2625.5
DG_REDOX1_	-514.3267294017	(DG_GAS1_+DDG_SOLV1_)*2625.5
E1_REDOXVSLI_	4.0906392642	(-DG_REDOX1_/96.485)-1.24
E1_REDOXVSFC_	0.7056392642	E1_REDOXVSLI3.385
E1_REDOXVSSHE_	1.0506392642	E1_REDOXVSLI3.04
E1_REDOXVSAG_	0.8266392642	E1_REDOXVSSHE0.224
IP1	-11.9085960010	(UGASPHASERED1-UGASPHASEOX)*27.2114
EA1	-11.9314480341	- (HGASPHASEOX-HGASPHASERED1)*27.2114
H_0XS0LV_	-43749.5537825679	HLIQUIDPHASEOX*27.2114
H_RED1SOLV_	-43754.9196526002	HLIQUIDPHASERED1*27.2114
G_OXSOLV_	-43751.7861866208	GLIQUIDPHASEOX*27.2114
G_RED1SOLV_	-43757.1551067926	GLIQUIDPHASERED1*27.2114
****ORCA TERM	INATED NORMALLY****	
TOTAL RUN TIME: 0 days 15 hours 26 minutes	50 seconds 320 msec	

Figure 25: Output file of Eredox

Redox potential energy is calculated with Lithium electrode. However, in most report, redox potential is measured with Standard Hydrogen electrode (SHE) or Ag/AgCl. Hence, E_{redox}

is converted to these reference electrodes to match with actual data.

$$E_{SHE} = E_{Li} - 3.04 V$$
 (19)

$$E_{Ag/Agcl} = E_{Li} - 0.224 V$$
 (20)

With 3.04 V and 0.224 V are potential of lithium versus SHE and Ag/AgCl respectively. Table 4 shows results of redox potential prediction for E_{redox} with different functionals. In this calculation, CAM-B3LYP gave the most accurate result at 1.05 V vs. SHE compared to the experimental data (1.058 V vs SHE). Even though CAM-B3LYP performed badly in bond length and bond angle calculation, it performed much better in the redox potential determination. The coulomb-attenuating method (CAM) increases the amount of Becke exchange [56], so it reduces errors of atomization, ionization, and the total atomic energies. Hence, CAM is a significant improvement of B3LYP in calculation atomization energies in this research.

From geometry study and redox potential study of Fe(bpy)₃²⁺, different functional is good for specific calculation. For example, in research relating to bond length, angle, and molecule structure, PBE, PBE0 and B3PW91 is good choice. On the other hand, PBE0 and B3PW91 functional underestimate energies of molecule, which made CAM-B3LYP becomes the better candidate. This long range functional is highly accurate in energy calculations. The long-range feature increases the fraction of the exchange parameter. Overall, B3LYP is not suited to our research because it gave significant error in both geometry and redox potential prediction. Moreover, PBE cannot match with actual value but % error is low, so PBE is a good functional for general study that we have not had any experimental data.

Basis set	LAN	LANL2DZ LAN		Def2-TZVP	LANL2DZ/ 6-31G	
	Voltage vs SHE (V)	Processing Time (h)	Voltage vs SHE (V)	Processing Time (h)	Voltage vs SHE (V)	Processing Time (h)
PBE	1.07	11	1.07 V	11	1.07	11
PBE0	0.91	14	0.91 V	13	0.91	14
B3PW91	0.97	13	0.97 V	10	0.97	14
BP86	1.15	11	1.15 V	10	1.15	11
CAM- B3LYP	1.05	15	1.05 V	14	1.05	18
B3LYP	0.89	14	0.89 V	12	0.89	14

Table 4: Calculated redox potential of Fe(bpy)32+ with different functionals and basis set In addition, a mix of basis sets can be applied to calculate redox potential of Fe(bpy) $_{3}^{2+}$ and obtain the influence of basis set on the calculations (fig 26).

This part of research is an extension of a project from a paper by Yang [38]. Usually, bigger size of basis set requires more CPU time. However, this paper mentions that combination of basis set improves the result and CPU time. In this research, LANL2DZ and LANL2DZ combined with 6-31G and TZVP were processed to evaluate this information. LANL2DZ is applied for iron metal. Due to EPC correction of LANL2DZ, it is applied to determine iron core of complex. In addition, def2-TZVP is a good basis set for valence bond which is aromatic structure. The result is interesting. CAM-B3LYP performs well in calculating the redox potential as the table above. By changing basis set, it does not affect much E_{redox} but slightly decrease CPU time. To validate the accuracy of this method, we calculated the redox potential of iron – terpyridine (tpy) complex and iron - phenanthroline (phen) and compared them to literature values [9] (Table S1). In this paper, the author measured redox potentials for both iron-ligand complexes as 1.069 V vs SHE. In our calculation, PBE give more accurate data with 1.068 V vs SHE for iron-Tpy and 1.069 vs SHE for iron-terpyridine and 1.11 vs

SHE for iron- phenanthroline ligand. Overall, both functionals are able to match the actual data with low error. PBE generally have good result in this calculation, so it is applied for further study which we have not have any information yet.



Figure 26: Calculated redox potential of $Fe(bpy)_{3^{2+}}$ with different functional and basis set

5.1.4 Substituents study:



Figure 27: Different position for functional group

Since unfunctionalized bipyridine-based Fe complexes do not have high solubility in aqueous electrolytes, different functional groups can be added to make the complex more polar and thus enhance solubility

(Fig.27). To illustrate, functional groups which might make ligands more polar will be added in R_2 , and R_3 of bipyridine. For R_1 and R_4 positions, functional group will make complexation less effective because of steric hindrance upon chelation with iron in a pseudo-octahedral orientation. [3]. As a result, the ligands are unable to bind strongly with iron and create a stable complex. Because PBE functional gave 1.07 V vs SHE, and it also performs well for general molecule, PBE was applied to study about bipyridine derivative. LANL2DZ is applied to determine iron core combines while def2-TVDZ were applied to calculate C, H and N atoms.



CI

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5







9





12





In this study, the redox potential was calculated for iron complexes made of derivatives of bipyridine and other related compounds that could, in theory, be synthesized. The bipyridine structures are based on chemicals available from Ambeed.com.



Figure 29: Redox potential of iron bipyridine derivative

Understanding the impact of functional group on redox potential is important to predict new materials for RFB and improve redox active molecules. Several groups have performed computational studies on the effect that adding various functional groups to a core molecular structure has on redox potential. For example. Lin et al. [46] applied this study on anthraquinone and observed the effect of electron-donating and electron-withdrawing groups on redox potential. We computed E_{redox} of 14 iron-based complexes with ligands that are derivatives of bipyridine. Functional groups such as carbonyl, amine, hydroxyl, aldehyde, methyl, and halogens were explored (Fig. 28). These groups are either electron withdrawing groups (EWG) or electron donating (EDG), which are known to shift redox potentials in a predictable direction; typically, EWGs shift the redox potential positively (harder to oxidize) and EDGs shift it negatively (easier to oxidize). An ideal derivative would have a high redox potential that does not overlap with water and also have high polarity for better aqueous solubility (energy density in battery).

Fig 29 shows the redox potential of the theoretical iron complexes studied. When hydroxyl or amine group is added to the bpy core, the redox potential is reduced, but when aldehyde or carbonyl are added, they increase the redox potential. This aligns with the predictions above that could be made based on Hammett constants of the functional groups (fig.30).



Figure 30: Substituent constant vs Redox potential

In conclusion, there are 7 derivatives enhance redox potential of iron complex. However, 5 of them pass the limitation of electrolyte. When the redox potential of active compound is higher than oxygen, water will be oxidized first. It will be converted to O_2 which reduces energy efficiency, and the gas evolution may damage the battery system. Hence, we cannot use 5 of them; nevertheless, they may be of interest to the non-aqueous RFB community, where organic solvents permit the use of electrolytes with more extreme redox potentials compared to water. On the other hand, 5 derivatives decrease redox potential. A moderate decrease with a substantial increase in solubility may be acceptable, but a major decrease of >0.5 V in E_{redox} is not worth future study.

Only terpyridine, phenanthroline and phenanthroline-epoxy gave positive result which acceptably enhance redox potential. Unfortunately, these three ligands are not practical to use in RFB since they are difficult to synthesize, so it would be prohibitively expensive to build large scale batteries based on these catholytes.

5.2 Study about Oxo-bridged Diiron Bis(2,2'-bipyridine) dimer

5.2.1 Electrostatic potential map (EPM)

Molecular electrostatic potential maps are used to describe molecule size, shape, and reactive sides. Red represents electron-rich areas, which is relatively negatively charged, while blue shows electron-deficient regions, which are relatively positively charged, and green regions are neutral [60].



Figure 31: Electrostatic potential map

Figure 31 shows distribution of electron in Fe(bpy)₂²⁺ is stable in water solvent and tend to be non-polar. The color bar scale is adjusted to 25 kcal/ mol to 50 kcal/mol for monomer and 150 kcal/ mol to 200 kcal/mol for the dimer. It shows an amount of energy per number of atoms. From this information, electrophilic and nucleophilic sides can be identified. Red color is close to iron core which means iron is electron donor and ligand is electron acceptor. When it is in oxid ized form and spin crossover happens, 5 unpair electron created magnetic field which make molecule more electrophilic. We can see from Figure 31 that electron distribution is extended to ligand. It contrasts to pi accepted bond of ligand [54]. As the result, Fe(bpy)₃³⁺ attracts nucleophilic water molecule. A dimer is formed to stabilize the high spin monomer. In addition, all information is performed by PBE0 due to its accuracy in ionization energy and atomization energy calculation. Moreover, DFT broken symmetry is applied in dimer to describe its magnetic properties. Basis set in this determination is a combination of LANL2DZ and def2-TZVP.

5.2.2 HOMO-LUMO

In redox potential studies, the highest occupied molecular orbital is related to the reduced form when molecule ready to donate an electron and the lowest unoccupied molecular orbital reveals the oxidized form which molecule can obtain an electron [59]. The energy gap between HOMO and LUMO reveals the amount of energy require for the oxidation and reduction process and is proportional to redox potential. Mendez – Heznandez et al. [60] plotted a linear graph reflecting the relationship between $E_{HOMO/LUMO}$ and redox potential of 70 organic molecules. It is a useful tool for large molecules which cannot calculated by Born-Haber cycle. In addition, it demonstrated the close relationship between $E_{HOMO/LUMO}$ and E_{redox} .



HOMO-LUMO

Figure 32: HOMO and LUMO data in different states

Figure 32 shows clearly distribution of electron density in 2+, 3+ low spin, 3+ high spins and dimer of iron complexes. While iron 2+ is a low spin state, HOMO graph show that iron is electron donor and ligand is electron acceptor. This structure is stable due to pi back-bonding interaction which is showed in MO diagram of metal and ligand. When iron switches from low spin to high spin, an electron from iron is excited to ligand pi nonbonding. It is explained as metal to ligand charge transfer.



Figure 33: Metal to ligand charge transfer

Then, the ligand gains more pi donating electrons, so pi donor ligands lie lower in energy than the pi acceptor ligands [61]. As the result, bipyridine has both pi donor and pi acceptor character which makes the energy of pi* orbital approximately equal to the energy of the metal d orbital. This is illustrated in LUMO of iron 3+ high spin state. The iron complex turns nucleophilic and the strength between ligand and metal is weaker. In addition, the bond length between iron and ligand increases 0.02 Å when the spin crossover phenomena happen. Then, oxygen plays as a nucleophilic molecule and attacks the bond between iron and bipyridine. Finally, oxo-bridge diiron is a stable form of complex in high spin state.

5.2.3 Broken symmetry in calculating dimer

Geometry and redox potential tests for the dimer were processed first to evaluate the

		Average Fe-O distance (Å)	Fe – O – Fe angle (°)
	Crystal	1.7819	166.95
No broken	PBE0	1.843	147.7
symmetry	BHLYP	1.827	146.4
	B3LYP	1.852	148
Broken symmetry	PBE0	1.794	156.2
	B3LYP	1.8	157.1
	B3LYP/G	1.791	156.6
	CAM-B3LYP	1.844	1.477
	B3PW91	1.787	156.5

accuracy of functionals and basis sets.

Table 5: Geometry study of dimer.

According to Lawson et al. [30], the GGA functional is a good approximation for the ground state, however, high spin state iron requires 10 to 20% of HF. Different functionals were tested to prove the reliability of this information. From table 4, most of GGA cannot converge energy in our study. In addition, when we applied broken symmetry correction, data is improved which close to crystal information. In this experiment (table 5), B3PW91 gave the closest information which is 1.794 Å and 156.2° Fe-O-Fe angle. The average bond length between iron metal and ligand is increased 0.02 Å when molecule in high spin state. As above information, the promotion of 2 electrons from nonbonding metallic level of octahedral Fe into an antibonding level octahedral Fe is the main reason for this increasing. Hence, magnetic field which is created by magnetic moment of 2 Fe³⁺ on both sides has an effect on molecule structure.

Predicting redox potential energy is important in this research. It is used to prove the reliable data of DFT-BS in calculate energy of dimer complex. In order to obtain accurate redox potential (E) calculations, Born-Haber cycle is applied in in discharge reaction as mentioned above.

Functional	HF%	E _{redox} vs SHE
B3LYP/G	15	0.6
B3LYP	20	0.4
PBE0	25	0.63
CAM-B3LYP	20	0.54
B3PW91	20	0.56

 Table 6: Predicting redox potential of dimer

In table 6, PBE0 showed the closest result 0.6 V vs SHE comparing to our wet lab data which is 0.6 V vs SHE. Our data also matched the redox potential of Barbara et al. [62]. Because dimers have two iron metal centers linked by oxo-bridge, the redox potential of one center is influenced by the other. And when one iron is reduced, charge delocalizes toward to the other center. As the result, the second side is thermodynamically harder to reduce than the first. Hence, E_{redox} drops significantly during discharge. In addition, the cyclic voltammetry is divided into 2 one-electron processes, so we cannot calculate the redox potential directly through Born-Haber cycle. By applying Born-Haber cycle into discharge reaction as mentioned above, we are able to get the redox potential of dimer by DFT-BS. DFT-BS has an important role in describing the magnetic field which is created by 5 unpaired electrons on two sides.

Magnetic moment and exchange coupling constant J of dimer is carried out by broken symmetry calculation. According to Werner et al. [63], higher electron density of the oxo-bridge illustrates stronger antiferromagnetic coupling. Table 7 shows a negative J value which means dimer is stable under antiferromagnetic contribution. Combined with LUMO data, this shows that electrons delocalize to iron metal and the oxo-bridge. As a result, a stable molecule is created which require a large amount of energy to reduce the dimer back to iron (II). Understanding the relationship between J constant and dimer structure can prevent forming of dimer. We hypothesize several methods to reduce the J constant. First, adding a substituent in bipyridine which helps increase pi acceptor energy. So, molecule will not turn to electrophilic compound in high spin state and attract oxygen ligand. Second, a different factor is added including salt, dielectric constant to observe their influence on J constant value. By reducing the J value, the dimer will be weaker and require less energy to revert back to its original form.

Functional	E _{HS} (Eh)	E _{BS} (Eh)	$\Delta E (eV)$	J (cm ⁻¹)	Fe-Fe
					Distance (Å)
PBE0	-2330.54	-2330.58	1.13	-315.98	3.505
B3LYP	-2330.61	-2330.61	0.16	-45.37	3.522
CAM-B3LYP	-2331.75	-2331.80	1.46	-412.45	3.509
B3PW91	-2332.31	-2332.39	2.07	-576.53	3.492
B3LYP/G	-2376.71	-2376.72	0.22	-70.48	3.521

Table 7: Predicting exchange coupling constant

In addition, B3LYP performed well in this calculation which gave -45.37 cm⁻¹ in J value. There is a big difference in the J constant result between different functionals. According to Werner's work on many iron-base complexes, the J constant is in the range 0>J>-150 cm⁻¹. Hence, we need to test the functional and basis set again to get better results.

CHAPTER VI: CONCLUSION AND FUTURE WORK

6.1 Summary:

In summary, we applied different functional and basis set of DFT to calculate characteristics of iron-base complex. In our research, different functionals performed well in specific calculations. In geometry study, PBE and PBE0 were able to match Fe-N prediction with crystal structure Fe(bpy)₃²⁺ which is 1.967 Å. In addition, Born-Haber cycle is a straightforward method to carry out redox potential. And CAM-B3LYP is a good functional for this calculation which estimated 1.05 V vs SHE. Moreover, PBE0 also gave 1.07 V vs SHE which is close to actual data. Due to PBE0 giving high accuracy in most calculations, it is applied to HOMO-LUMO, electrostatic potential, and substituents study.

In study of the dimer, we were able to predict the redox potential of the dimer by applying Born-Haber cycle in discharge reaction and carry out redox potential for 2 electron reducing reaction. In addition, we applied broken symmetry correction in our calculation to describe magnetic properties of the dimer which improved our data. Redox potential prediction is 0.6V vs SHE which is matched with wet lab data. PBE0, LANL2DZ/Def2-TZVP and DFT-BS is used in most dimer calculations.

Finally, HOMO-LUMO calculation, exchange coupling constant J and electrostatic potential are determined and used to explain spin crossover phenomena. Understanding the dimer can prevent its formation and keep the iron complex in monomer form. As the result, voltage efficiency of battery is maintained.

6.2 Future work

In this project, DFT is used to understand oxo-bridge diiron. Several functional and basis sets were tested to figure out best method for dimer calculation, which is PBE0, LANL2DZ/Def2-TZVP and DFT-BS. In addition, understanding about dimer structure can prevent it from forming. Future work for dimer study is:

- More functional and basis set will be tested on different iron ligand complexed to validate the methods.
- Different substituent will be added to bipyridine ligand and observe their effect on the oxobridge through exchange coupling constant J.
- Study about relationship between dielectric constant and exchange coupling constant J

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LIST OF SYMBOLS AND ABBREVIATIONS

BPY	bipyridine
B3LYP	Becke, three-parameter, Lee-Yang-Parr
BLYP	Becke, Lee, Yang and Parr
BP86	Becke and Perdew
BO	Born-Oppenheimer
CV	Cyclic Voltammetry
DFT	Density Functional Theory
ECP	Effective core potential
EPM	Electrostatic potential map
EWG	Electron withdrawing groups
EDG	Electron donating groups
GGA	Generalized Gradient Approximation
НОМО	Highest occupied molecular orbital
HF	Hartree-Fork
HPC	High performance computing
HS	High-spin state
KS	Kohn-Sham
LANL2DZ	Los Alamos National Laboratory 2 double zeta
LDA	Local Density Approximation
LUMO	Lowest unoccupied molecular orbital
LS	Low-spin state
TPSS	Tao, Perdew, Staroverov, and Scuseria

TZVP	Triple-Zeta Valence with Polarization
TPY	Terpyridine
PBE	Perdew, Burke, Ernzerhof
PBE0	Hybrid functional of Perdew, Burke, Ernzerhof
PHEN	Phenanthroline
PW91	Perdew and Wang
QC	Quantum chemistry
RFB	Redox flow battery
SCO	Spin crossover
SLURM	Simple Linux Utility for Resource Management
SHE	Standard hydrogen electrode
VE	Voltage efficiency
XC	Exchange-correlation