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INDUCTION AND PREVENTION OF ELECTRON TRANSPORT IN LANGMUIR-BLODGETT FILMS OF 3d-BASED METALLOSURFACTANTS: STUDIES ON CURRENT RECTIFICATION AND CORROSION INHIBITION

by

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DISertation

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DOCTOR OF PHILOSOPHY

2021

MAJOR: CHEMISTRY (Inorganic)

Approved By:

Advisor Date

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_________________________________
DEDICATION

To my parents, Ananda Weeraratne and Renuka Uduwara for their unconditional love, and to
my loving husband Chamath Gunasekara and my dearest daughter Sansa Gunasekara.
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Joining the Verani group was one of the best decisions I have ever made as a graduate student. Thank you very much Prof. Claudio Verani, for accepting me into your group. I am forever grateful for his endless support, encouragement, and guidance throughout my graduate studies. He identified my competencies and weaknesses, and he always gave advice and valuable suggestions to strengthen my personality as a researcher and as an individual. Not only that, he helped me immensely during my personal difficulties. Thank you once again for being a great mentor and being a role model to your students.

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CHAPTER 1: INTRODUCTION

Molecular metal-containing soft materials such as metallopolymers, metallosurfactants, and metallomesogens have gained a great deal of attention due to its, unique electronic and redox properties. New solid phase materials have been developed by using information obtained in the solution phase of the complexes. In order to transfer these complexes onto solid substrates, different film deposition techniques have been used in recent years, commonly including atomic layer deposition (ALD), self-assembly of monolayer (SAM), Langmuir-Blodgett technique (LB), and chemical vapor deposition (CVD). The Verani group is particularly interested in Langmuir-Blodgett deposition as it is more cost-effective, less destructive than other methods in the field, and allows for greater control over layer thickness. When designing and synthesizing complexes, hydrophobic and hydrophilic substituents are introduced to the molecule as the Langmuir-Blodgett technique requires. This thesis will describe the efforts that I have carried out to design and study new metallosurfactants for molecular electronics and corrosion inhibition. The two fields are complementary to each other in their requirements and goals. For rectification studies, we try to understand how to transport electrons between two electrodes, while for corrosion inhibition studies, we try to explore how to prevent electron transport between the external environment and the metal.

1.1. Molecular Electronic Devices

Most of the technological achievements of the past decade have depended immensely on microelectronics. Among these achievements, silicon-based integrated circuits have gained great attention. Smaller and less costly electronic devices with more efficient and effective functions would be the ultimate goal in the microelectronics industry. In 1965, Intel co-founder Gordon Moore proposed that the number of transistors per square inch on an integrated circuit doubles
approximately every two years and will continue into the foreseeable future.\textsuperscript{15} This significantly complicates the simultaneous miniaturization and optimization of future electric circuits. Silicon-based chips show some major limitations: when the oxide layers reach a thickness of three atoms they become poorly insulating and lead to charge leakage.\textsuperscript{16} Manufacturing smaller devices on chips are also very expensive.\textsuperscript{17} Alternative approaches must be used when synthesizing smaller chips in order to minimize these expenses and major limitations. To overcome limitations in the miniaturization process, the revolutionary idea of using molecules for electronics was first introduced by the Nobel Prize winner, Prof. Richard Feynman. In his 1959 talk, “There’s plenty of room at the Bottom”, he discussed how technical applications can be governed on a small scale.\textsuperscript{18} His idea was different from regular miniaturization processes as he had the idea of building electronics for information storage at an atomic or molecular level.\textsuperscript{18}

In 1974, Ari Aviram and Mark Ratner started the discussion about molecular-based electronics, using a hypothetical organic molecule that can be used as a rectifier.\textsuperscript{19} They were the first to introduce the notion of designing organic molecules for electronic devices.

Using organic molecules for electronic devices is more beneficial due to their ability to coordinate metals and fine-tune their electronic properties. One of the common methods used to build electronic devices and assess the electronic properties of the synthesized molecules is building metal\textemdash molecule\textemdash metal assemblies.\textsuperscript{20-24}

Electronic and redox properties of organic molecules can be improved by incorporating redox-active metals into the molecules. In some cases, introducing redox-active metals can decrease the separation between highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), which is important for electron transport. However,
limited studies have been done using metal-containing complexes. The following section will briefly describe the use of organic and metal comprising complexes as molecular rectifiers.

1.2. Molecular Rectifiers

Rectifiers are electrical devices that convert alternating current into direct current which allows electrical current to flow only in one direction (Figure 1.1). They are used in computers and other microelectronic devices. When the rectifiers are built with semiconductor materials they are known as semiconductor diodes, the most commonly used rectifier type. Semiconductor diodes consist of a p-n junction that has a positive “P-region” at one side and a negative “N-region” at the other. The positive P-region is constructed by doping group IV semiconductor materials such as silicon (Si) and germanium (Ge) with group III elements such as aluminum (Al), boron (B), and indium (In). These group III elements have only three electrons to share with neighboring group IV elements that result in holes in the semiconductor crystal. That results in an electron deficiency in the P-region, allowing it to act as the “Acceptor.” The negative N-region is constructed by doping group IV semiconductor materials with group V elements such as antimony.
(Sb) and phosphorus (P). The group V elements have five electrons to share with the neighboring group IV elements, resulting in a free electron in the crystal. Therefore, the N-region is electron-rich and acts as the “Donor.”

Molecular rectifiers are molecular devices that show unidirectional current flow. The organic molecule proposed by Aviram and Ratner\cite{Aviram96} for molecular rectification had the $[D$-$\sigma$-$A]$ structure, where D is one electron donor with relatively low first ionization potential ($I_D$), $\sigma$ is the saturated covalent sigma bridge, and A is one electron acceptor with relatively high first electron affinity ($A_A$). The first ionization potential is an approximation to the highest occupied molecular orbitals (HOMO) and the first electron affinity is an approximation to the lowest unoccupied molecular orbitals (LUMO). For an electron to transfer through the molecule, the HOMO and LUMO energies should be comparable to the Fermi levels of the metal electrodes. If this molecule is assembled between two electrodes $M_1$ and $M_2$ as shown in Figure 1.2, electrons will flow from the $M_2$ electrode to the $M_1$ electrode, because of the relative accessibility of the $[D^+$$\sigma$$-$$A^-]$ zwitterionic state. Electrons will not flow from $M_1$ to $M_2$, because the barrier to form the $[D^+$$\sigma$$-$$A^+]$ zwitterionic state would be higher. In order to achieve this electron transfer through this

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecule.png}
\caption{[D-$\sigma$-$A$] molecule proposed by Aviram and Ratner.}
\end{figure}
molecule, charge recombination must be avoided using the sigma bridge. The rectification ability of this organic molecule is theoretically proven, but it has never been synthesized.\textsuperscript{19-20}

Metzger proposed three basic mechanisms by which molecular rectification can take place, namely: Schottky (S-rectifier), Asymmetric (A-rectifier), and Unimolecular (U-rectifier). Among them, Schottky rectification is the most common rectification mechanism, which occurs due to interfacial dipole moments of two different electrodes (e.g., magnesium and platinum or gold and mercury) or covalent bonding of the self-assembled molecule to the electrode.\textsuperscript{26-31} Asymmetric and Unimolecular rectification depend on the frontier molecular orbital distribution of the molecule.

Asymmetric rectification relies on the asymmetric distribution of the HOMO and LUMO energy levels relative to the metal Fermi levels. In Figure 1.3, LUMO of the acceptor moiety is energetically comparable to the electrode Fermi level compared to HOMO, therefore LUMO of the acceptor moiety accepts an electron from the M\textsubscript{1} electrode and donates it to the M\textsubscript{2} electrode. Only LUMO orbitals are involved in the electron transfer process.\textsuperscript{32-38} Baranger and Whitesides have reported that the HOMO alone can carry the electron transfer process when the HOMO is closer to the electrode fermi level.\textsuperscript{39-40}

\textbf{Figure 1.3.} Schematic representation of an asymmetric (A) current rectification mechanism.
The Unimolecular rectification involves molecules with well-defined donor and acceptor moieties with LUMOs and HOMOs. In this mechanism, the LUMO of the acceptor moiety accepts an electron from the M₂ electrode and then HOMO of the donor moiety donates an electron to the M₁ electrodes. Due to the lower energy difference between LUMO and HOMO, excited electrons in LUMO will transfer to HOMO and that will facilitate the upcoming electron flow. In this mechanism, both HOMO and LUMO orbitals are involved (Figure 1.4).³²-³³, ⁴¹-⁴³ Rectification behavior of a particular system can be evaluated using the rectification ratio (RR). The rectification ratio can be obtained by dividing the current at the negative potential by the current at the positive potential.⁴³

\[
RR = \frac{|I_{at -V_o}|}{|I_{at +V_o}|} \quad (\text{Equation 1.1})
\]

To consider a system as a rectifier, the rectification ratio should be ≥2. As such, the higher the rectification ratio the more precise the control of current.

When developing molecular devices, another important parameter that should be considered is how the molecules are assembled between two metal electrodes. To build effective molecular rectifiers, defect free and closely packed films are essential. Langmuir-Blodgett and

---

**Figure 1.4.** Schematic representation of an unimolecular (U) current rectification mechanism.
self-assembly techniques are widely used methods when developing molecular devices. Initially, molecular rectifiers were built using LB multilayers. But due to the formation of Schottky barriers at the metal|molecule junction and higher thickness, devices made with monolayers are more beneficial. The work done by Ashwell$^{44}$ and Metzger$^{34, 45}$ has shown that LB technique can form defect free, well ordered films. Also, the film formation ability of the molecules can be altered by changing the substituents of the ligand. LB monolayers physisorbed onto the metal electrodes via weak Van der Waals interactions. After the deposition, the rectification ability of the films was studied by sandwiching the monolayers between two metal electrodes to form metal|molecule|metal assemblies.

1.3.1. Organic Molecules as Rectifiers

Purely organic systems have been extensively studied as molecular rectifiers due to the feasibility of electron transport through delocalized 2p orbitals of the aromatic rings in the organic molecules. Molecular rectification was first experimentally achieved by Ashwell et al.$^{46}$ in 1990 by using LB monolayers of π-bridged hexadecylquinolinium-tricyanoquinodimethanide ($\text{C}_{16}\text{H}_{33}\text{Q}-\pi\text{-3CNQ}$) system (Figure 1.5). Due to the existence of a π bridge between the donor (D)
and acceptor (A) moieties, this system is different from the Aviram and Ratner theoretical model. First rectification has been detected between asymmetrical electrodes (Mg and Pt electrodes), and it was remeasured and confirmed by Metzger and co-workers using symmetrical electrodes (first by Al electrodes, then by Au electrodes). The results suggested that electron transfer takes place from the tricyanoquinodimethanide part (A⁻) to the (n-hexadecyl) quinolinium part (D⁺) of the molecule. They have studied devices containing LB monolayers and multilayers and concluded that devices containing monolayers show a higher rectification ratio compared to multilayer devices. For this system, the proposed mechanism of rectification is different from the Aviram and Ratner model. In this system, first the ground-state zwitterion D⁺-π-A⁻ undergoes intervalence charge transfer to produce the neutral form D-π-A, then an electron transfers from an electrode to form the original zwitterion D⁺-π-A⁻. Over the past years, Metzger and co-workers have studied zwitterionic molecules with different alkyl chains with the same quinolinium tricyanoquinodimethanide chromophore, fullerenes containing molecules, and molecules containing iodide for rectification (Figure 1.6). To avoid Schottky barriers, rectification has been studied by sandwiching LB monolayers between Al electrodes and later between Au electrodes. From experimental and theoretical calculations, all the molecules were identified as Unimolecular rectifiers.

Besides these studies, a few other groups have also investigated rectification using organic molecules. In 2004, Yu et al. reported rectification with two thiophene–thiazole diblock oligomers. These molecular diodes contain two different thiol protection groups. One end of the oligomer bound to an Au electrode after deprotonation and the other end bound to an Au nanoparticle (Figure 1.7a). Rectification was studied using a scanning tunneling spectrooscope (STS) and they observed that rectifying direction can be controlled by the orientation of the
oligomer between the electrodes. Also, they observed that by adding acid, rectification can be reversed due to the protonation of the pyrimidine rings. In 2005, Bryce, Heath, and coworkers discussed a rectifier that is an analog to the model of the Aviram–Ratner unimolecular rectifier (TTF-s-TCNQ). The molecule they studied has very strong electron-donor (tetrathiafulvalene) and -acceptor(tetracyanoquinodimethane) moieties and they are separated by a saturated aliphatic linker. Theoretical calculations showed extremely small HOMO–LUMO gap which is necessary for rectification. In the same year Weber, Mayor, and co-workers reported that they observed rectification with an asymmetric molecular rod consisting of one tetrafluorophenyl group at one end, and a plain phenyl group at the other end, but no rectification observed with symmetric

Figure 1.6. Unimolecular rectifiers by Metzger and co-workers. (a) zwitterionic molecules with different alkyl chains (b) fullerenes containing molecules (c) iodide containing molecules.
molecular rods with identical groups at the ends. Then another study done by Ashwell and coworkers\textsuperscript{55} in 2005 found that the direction of rectification can be changed when hydrophobic tail is substituted to either the acceptor [D–π–A–C\textsubscript{16}H\textsubscript{33}] or the donor [A–π–D–C\textsubscript{16}H\textsubscript{33}] group (Figure 1.7b). In 2016, Jurchescu et al.\textsuperscript{56} studied current rectification of self-assembled monolayers of nine new alkylated silane molecules using metal/monolayer/metal configuration, with a silicon bottom contact and a eutectic gallium-indium liquid metal (EGaIn) top contact. They found that rectification ratio increases with the increase of the strength of the molecular dipole moment and it is reduced with increasing molecular length. The Garg group\textsuperscript{57} reported self-assembled monolayers of new porphyrin-based systems as molecular rectifiers in 2016. They observed that a porphyrin molecule with an eleven-carbon alkyl chain linker showed a higher rectification ratio (RR) relative to a system that had a six-carbon alkyl chain linker. That can be possibly due to the compact packing of the molecule with an eleven-carbon alkyl chain.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.7.png}
\caption{(a) Thiophene–thiazole diblock oligomer from Yu group (b) [D–π–A–C\textsubscript{16}H\textsubscript{33}] and [A–π–D–C\textsubscript{16}H\textsubscript{33}] from Ashwell and coworkers.}
\end{figure}
and coworkers$^{58}$ have performed a theoretical calculation to study the rectification of azafullerene system ($4\text{TPA}-C_{60}$). This molecule had behaved as a unimolecular rectifier with a rectification ratio of 145 at a bias of $\pm 1$ V. This study was influenced by the study done by Van Dyck and Ratner$^{24}$ in 2015. Brudvig and coworkers$^{59}$ examined conductance and rectification properties of a series of N-phenylbenzamide (NPBA) derivatives. They selected NPBA from a large number of computationally screened molecular diode structures. Functionalization of the NPBA 4-carboxamido-aniline moiety with electron donating methoxy groups, demonstrated enhanced conductance and rectification. The use of electron donating group raised the energy of the HOMO close to the Fermi level and made electron transport easier, resulting in amplification of the rectification behavior. In 2017, Nijhuis et al.$^{60}$ reported electron transport across donor–acceptor self-assembled monolayers (SAMs). Their systems consisted of a polychlorotriphenylmethyl (PTM) electron-acceptor moiety and an electron-donor ferrocene (Fc) unit. The rectification behavior of the system is influenced by nonradical and radical forms of PTM. Junctions with nonradical units rectified currents through the highest occupied molecular orbital (HOMO), whereas junctions with radical units have a new accessible state, a single-unoccupied molecular orbital (SUMO), which turned rectification off. As recently as in 2020, Yu and Hu$^{61}$ reported rectification using a self-assembled monolayer (D-SAM) structure. They constructed a $\text{Au}\|\text{S-(CH}_2\text{)}_6\text{-ferrocene}\|\text{SAM-2}\|\text{Au}”$ junction with various chemical structures of SAM-2. They observed the charge transport mechanism transition from tunneling to hopping during the rectification, which caused current fluctuation. This study was inspired by the pioneering work done by Whitesides et al.$^{62}$ in 2001. More details about organic molecular rectifiers are summarized in a series of sophisticated reviews by Metzger.$^{32-34, 43, 63}$
1.3.1. Coordination Complexes as Rectifiers

Rectification of coordination complexes are not much investigated. The most studied molecules include modified phthalocyanins, polypyridines and porphyrins. In 1994 Pietro et al.\textsuperscript{64} discovered non-Schottky-type rectification in a junction comprising of Ni\textsuperscript{2+} and Cu\textsuperscript{2+} phthalocyanins. In 2007, Ren et al.\textsuperscript{65} studied the use of both symmetric and unsymmetric bis-alkynyl diruthenium compounds for current rectification and found that energetic alignment of frontier orbitals of the unsymmetric compound favors directional electron flow, which is a necessary requirement for unimolecular rectification. In the same year, Liu group\textsuperscript{39} introduced an organometallic cobaltocene molecular rectifier that exhibited high current at low bias voltage. They observed a good rectification ratio of about 10 at bias voltage of 0.5V. In 2008, Yu and coworkers\textsuperscript{66} reported unimolecular current rectification of a device made with a hexa-coordinated ruthenium(II) complex (Figure 1.8). Even though this molecule has \( C_2 \) axis of symmetry, the molecular rectification was explained by the presence of a permanent dipole moment perpendicular to the molecular wire ligand. Due to the ligand planarity acquired upon metalation, they have observed higher rectification ratios with the complex compared to the free ligand. In 2015, Ghoshal et al.\textsuperscript{31} reported the first metal–organic framework base current rectifier. They have studied a metal–organic framework (MOF) of cadmium(II) for current rectification and it behaved as a

![Hexa-coordinated ruthenium(II) complex introduce by Yu group.](image-url)
Schottky rectifier with rectification ratio of ~100 at applied bias of ±10V. As recent as in 2017, Chen group\textsuperscript{67} presented a quasi-molecular rectifier with a biazulene-bridged cobalt-coordinated framework. Devices were prepared forming thin films on Au electrodes by a layer-by-layer dip-coating method. The molecule exhibited excellent stability and a rectification ratio as high as 5.7.

The Verani group has contributed to this field by developing several coordination complexes as current rectifiers. In 2013, we published our first molecular rectifier which was a phenolate-rich asymmetric Fe(III) complex based on the redox-active [N$_2$O$_3$] framework (Figure 1.9a).\textsuperscript{68} The Au|LB[Fe$^{III}$(L$^{N2O3}$)]|Au devices demonstrated asymmetric current response with a rectification ratio ranging from 4.5 to 12 between −2 to +2 V and from 2.9 to 37 between −4 to +4 V.

\textbf{Figure 1.9.} Five-coordinate HSFe$^{III}$ molecular rectifiers and Cu$^{II}$ insulator.
V, respectively. This complex favors unimolecular rectification mechanism. We postulated that the phenolate part of this complex behaves as the electron donor (D) and the metal center act as electron acceptor (A) during rectification. In 2014, we introduced another Fe(III) containing molecular rectifier with a \([\text{N}_2\text{O}_2]\) framework (Figure 1.9). This complex shows asymmetric rectification with a rectification ratio ranging from 4 to 29 at a bias potential of \(\pm 2\) V and from 2 to 31 at a bias potential of \(\pm 4\) V. Frontier molecular energy levels of the rectifying \(\text{HS}^3\text{d}^5 \text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}\) complex was compared with a structurally similar nonrectifying \(3\text{d}^9 \text{Cu}^{\text{II}}(\text{L}^\text{N}_2\text{O}_2)\) complex (Figure 1.9c) and have demonstrated that SOMO energy of the \(\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}\) is energetically comparable with the Fermi energy of the electrode while SOMO energy of the \(\text{Cu}^{\text{II}}(\text{L}^\text{N}_2\text{O}_2)\) is energetically high. So electron transfer can happen through the SOMO of the \(\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}\), but not with the \(\text{Cu}^{\text{II}}(\text{L}^\text{N}_2\text{O}_2)\), which explains the asymmetric current rectification of the \(\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}\) complex (Figure 1.10). Rectification of the \(\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}\) was confirmed by Metzger using dissimilar electrodes. In 2016, we performed a systematic study to evaluate the...
roles of electronic structure on the mechanisms for current rectification. This study was conducted with four, five-coordinate iron(III) complexes with [N2O2Cl] and [N2O3] coordination spheres. We found that the two complexes with apical phenolato support unimolecular mechanisms and two complexes with apical chlorido ligands favor asymmetric mechanisms. Then in 2018, we teamed up with Metzger and reported rectification of HSFeIII complex [FeIII(LN3O)(OMe)2] (Figure 1.9). All the other rectifiers we reported earlier had phenolate groups, but this complex contains pyridines as well. By introducing electron deficient pyridine groups to the ligand framework we postulated that it would lower the SOMO energy levels and enable directional electron transfer. Rectification was first measured using Au electrodes and then we opted to use Au and gallium indium eutectic electrodes (Figure 1.11). Recently, we observed rectification of new bimetallic Fe(III) hydrophobe (Figure 1.9e), bisphenolate and trisphenolate chromium(III) and oxovanadium(IV) complexes, more details about these rectifiers are described in Chapters 3 and 4.

Figure 1.11. [FeIIILN3O)(OMe)2] in EGaIn|Lb|Au assemblies.

Coordination complexes show promising results in molecular electronics compared to their organic analogs. Our group has successfully developed a few nanoscale molecular rectifiers based on asymmetric five- and six-coordinated iron(III) complexes. This enabled us to conclude that
rectification proceeds via singly-occupied molecular orbitals (SOMOs) of the metal. Therefore, the spatial and energetic modulation of the frontier molecular orbitals is an essential step towards the design of diode-like molecules with electron transport properties. In order to modulate the Fermi/SOMO and Fermi/HOMO gap, we have synthesized amphiphilic metal complexes with different ligands and metal ions.

1.5. Corrosion Inhibition

Corrosion is a thermodynamically driven spontaneous process caused by an electrochemical or chemical reaction between the metal and the surrounding environment. Both metal and environmental conditions around the metal determines the rate and the type of the corrosion. Except for noble metals, almost all metals readily undergo corrosion and convert into more chemically stable forms, such as sulfides, oxides, and hydroxides. For this thesis, I will only discuss iron and aluminum corrosion. We studied iron and aluminum corrosion inhibition with those compounds with 3d\textsuperscript{10} metal ions that fails at electron transport.

1.5.1. Impact of Corrosion

As a result of corrosion, metals lose their useful properties, and that has a huge impact on human safety, environment, and financial costs. In 2011, Hansson reported in his article several case studies of corrosion related injuries and deaths. He reported that in 1984, a chemical plant explosion in India caused the death of 23,000 people and this is by far the worst corrosion related disaster in terms of human deaths. This accident happened due to steel pipe corrosion.\textsuperscript{73} There are many other corrosion related cases reported in the literature that had a huge impact on human lives.\textsuperscript{73-75} Corrosion does not only have an impact on human lives but is also harmful to the environment. In 2006, Papavinasam et al. reported that 15\% of all pipeline related incidents in the
United States between 1994 to 2000 were due to internal corrosion of pipelines. Oil leaks that occur from corroded pipelines have caused detrimental effects on wildlife.\(^{76}\)

In 1930, Rohrman referred to corrosion as a “billion dollar thief,” therefore understanding the cost of corrosion has gained a great deal of attention among corrosion scientists and engineers for over many decades.\(^{77}\) The first systematic study on the cost of corrosion was performed by H. H. Uhlig in 1949, where he projected that annual direct cost of corrosion in the United States to be 5.427 billion US dollars at that time.\(^{78-80}\) In 1971, a pioneering study done by T.P Hoar developed a method to investigate the cost of corrosion in 10 individual industries in the United Kingdom. He estimated that the total cost of corrosion in each sector was about 1365 million pounds and 310 million pounds of which could have been avoided with corrosion inhibition.\(^{81}\) In 1978, NBS Battelle report, which is considered as another important corrosion study revealed at that time total corrosion cost per year in the USA was 70 billion US dollars (4.5% of GNP, gross national product) and anti-corrosion techniques would prevent 14% of the corrosion cost.\(^{82-83}\) In 1998, the National Association of Corrosion Engineers (NACE) conducted a study combining both Uhlig and Hoar methods and found that the total direct cost of corrosion was $276 billion per year (3.1% of GDP, gross domestic product).\(^{84}\) At the 1\(^{st}\) Global Corrosion Summit held in New Delhi, India in 2011, India reported that their annual corrosion cost was about 45 billion US dollars. Annual global corrosion cost was first studied by NACE in 2016 where they reported that the annual cost of corrosion (worldwide) is about US $2.5 trillion which constitutes about 3.4% of the global GDP.\(^{85}\) They also found in their study that the use of corrosion inhibition techniques can save 15-35% of the cost of damage, between $375-875 billion (USD). This study was performed by analyzing available corrosion data from different regions of the world.\(^{86}\)
1.5.2. Corrosion Mechanisms

1.5.2.1. Mechanisms of Iron Corrosion

Iron is the fourth most common element in the earth's crust and has been utilized all around the world for about 6000 years. It is one of the cheapest and strongest metals and it played a huge role during the industrial revolution. Iron can be used to make a much stronger material called carbon steel when combined with varying amounts of carbon and minute amounts of some other metals such as nickel, vanadium, tungsten, and manganese. Iron and steel are used in a wide range of applications such as structural components, industrial pipes, and kitchen appliances. However, when exposed to aggressive environments, they corrode severely, resulting in substantial economic losses and potential environmental problems. It has been projected that 25% of all the steel produced in the US is used to replace the steel lost by corrosion.

Corrosion of iron to form rust is a familiar process to everyone. Rusting occurs when iron reacts with moisture in the environment to form hydrated iron oxide or Fe$_2$O$_3$.xH$_2$O. Water can penetrate through this corrosion product and it can further corrode the metal and disintegrate it. The extent of the corrosion depends on the composition of the metal and the surrounding environment. The fundamental reaction for iron corrosion was first pointed out by Whitney in 1903 (Equation 1.2),

$$\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H} \quad \text{(Equation 1.2)}$$

Then Walker stated the function of oxygen during the corrosion reaction and how hydrogen eliminates during the process using the following reactions (Equation 1.2-1.3),

$$2\text{H} + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{(Equation 1.2)}$$

$$2\text{H} \rightarrow \text{H}_2 \text{(gas)} \quad \text{(Equation 1.3)}$$
This fundamental reaction can be further explained by using electrochemical anodic and cathodic reactions. In the anodic reaction, iron will be oxidized to form ferrous ions (Equation 1.4).

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (\text{Equation 1.4})
\]

Depending on the acidity and degree of aeration of the solution, several possible cathodic reactions can occur. In deaerated solutions like in the bottom of rivers, the following reduction reactions can take place (Equation 1.5-1.6),

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (\text{Equation 1.5})
\]

\[
\text{H}_2\text{O} + 2e^- \rightarrow 2(\text{OH})^- + \text{H}_2 \quad (\text{Equation 1.6})
\]

Combining anodic and cathodic reactions, the following reaction can take place (Equation 1.7),

\[
\text{Fe}^{2+} + (\text{OH})^- \rightarrow \text{Fe(OH)}_2 \quad (\text{Equation 1.7})
\]

In aerated solutions, two alternative cathodic reduction reactions can take place that involves dissolved oxygen (Equation 1.8-1.9),

\[
\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(\text{aq}) \quad (\text{Equation 1.8})
\]

\[
\text{O}_2(g) + 2\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{OH}^-(\text{aq}) \quad (\text{Equation 1.9})
\]

The anodic, cathodic products combine and form white ferrous hydroxide. This reaction happens much faster in aerated conditions.

If there is limited oxygen present, these two reactions can occur (Equation 1.10-1.11),

\[
6\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}_3\text{O}_4. \text{H}_2\text{O} \quad (\text{green hydrated magnetite}) \quad (\text{Equation 1.10})
\]

\[
\text{Fe}_3\text{O}_4. \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{Fe}_3\text{O}_4 \quad (\text{black magnetite}) \quad (\text{Equation 1.11})
\]
Black magnetite which forms during the above process is more stable and does not propagate rapidly as other forms of rust. When more oxygen is present, the following reaction can take place, which will result in the formation of red/brown rust (Equation 1.12).

$$4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \text{ (red/brown rust)} \quad (\text{Equation 1.12})$$

The color of the corrosion product depends on the oxygen and moisture content in the environment. Iron corrosion can take place in different ways. The most common type of iron corrosion is uniform corrosion. Iron or steel undergo uniform corrosion when it is exposed to an open atmosphere, natural waters, and soils.

![Schematic overview of the iron corrosion process when oxygen present.](image)

**Figure 1.12.** Schematic overview of the iron corrosion process when oxygen present.

**1.5.2.2. Mechanisms of Aluminum Corrosion**

Aluminum and aluminum alloys are used in a wide range of applications, from household appliances to structural components of airplanes due to its specific properties such as high strength and low weight. Aluminum is protected by its naturally occurring oxide film on its surface in wide range of media, but many studies have shown that this oxide layer can be destroyed and metal can be corroded when exposed to many acidic, alkaline, and especially chloride containing solutions. The corrosion potentials for aluminum are more negative than those of many metals, so when aluminum or aluminum alloys are in contact with other metals with more positive...
corrosion potentials it would result in galvanic corrosion. Another serious type of corrosion that aluminum alloys undergo is intergranular corrosion, which occurs at grain boundaries. This is a type of localized corrosion where grain boundaries act as anodes and grain interior being a cathode. As a result of this corrosion, exfoliation is seen along grain boundaries. Pitting corrosion is a frequent type of corrosion that is mostly seen in aluminum or aluminum alloys when exposed to chloride mediums. Pitting corrosion is detailed in the next section.

i. Corrosion of aluminum in chloride solution

Pitting corrosion is a localized corrosion, where metal dissolute and forms irregular shape pits on the metal surface. This is the most dangerous type of aluminum corrosion because corrosion products can cover the pits and it is difficult to predict where and when this type of corrosion may occur. Pitting corrosion takes place in the presence of aggressive ions such as chloride, bromide, and iodide ions. Among these anions it has been generally accepted that chloride has the highest tendency to attack the oxide layer on aluminum due to its small size and high mobility. Pitting corrosion begins with the chloride ions penetrating through the natural oxide layer through defects or migration via oxygen vacancies, replacing oxygen atoms of the oxide film. When the chloride ions reach the Al\(_2\)O\(_3\)|Al\(^0\) interface, that results in dissolution of aluminum into aluminum chloride. Then due to excess chloride ions, aluminum chloride converts into a soluble anionic tetrahedral [Al\(^{III}\)Cl\(_4\)\(^-\)] complex, which can then hydrolyze to form hydroxide and acid. This creates a more acidic (pH = 3–4) environment around the anode. Reactions occur at the anodic sites, (Equation 1.13-1.14),

\[
\text{Al(s)} \rightleftharpoons \text{Al}^{3+} + 3e^- \quad (\text{Equation 1.13})
\]

\[
[\text{Al}^{III}\text{Cl}_4]^- + 3\text{H}_2\text{O} \rightleftharpoons [\text{Al}^{III}(\text{OH})_3] + 3\text{H}^+ + 4\text{Cl}^- \quad (\text{Equation 1.14})
\]
Possible reactions at the cathodic sites include the following, *(Equation 1.15-1.16)*,

\[ 3H^+ + 3e ⇌ 3/2H_2 \text{ (Equation 1.15)} \]

\[ 1/2O_2 + H_2O + 2e ⇌ 2(OH)^- \text{ (Equation 1.16)} \]

Due to the dissolution of aluminum, blisters are formed during this process. Hydrogen gas evolution causes these blisters to erupt and form pits on the surface.\(^{119}\) Oxygen plays a crucial role during the corrosion, forming hydroxide ions which make cathodic sites more alkaline. Aluminum hydroxide forms at the cathodic site and accumulates at the rim of the pits as corn shaped precipitates.\(^{80}\)

![Figure 1.13. Schematic overview of the aluminum corrosion process when chloride present.](image)

**ii. Corrosion of aluminum in alkaline solution**

Aluminum is thermodynamically stable in pH range from 5-8.5 due to the amorphous oxide layer formation on the surface. But in alkaline solutions like sodium and potassium hydroxide, aluminum corrosion can be seen, and it has become a huge problem in the performance of aluminum-air batteries. Pyun and Moon proposed a mechanism for aluminum corrosion in alkaline solutions using electrochemical techniques.\(^{120}\) They proposed that alkaline corrosion begins with the migration of the hydroxide ions through the oxygen vacancies in the oxide layer.\(^{121}\) The
dissolution of aluminum begins with the formation of an aluminum hydroxide film (Equation 1.17).\textsuperscript{122-123}

\[
\text{Al} + \text{OH}^- \rightleftharpoons \text{Al(OH)}_3 + 3e^- \quad (\text{Equation 1.17})
\]

Hydroxide ions then attack the aluminum hydroxide dissolving the film, forming soluble aluminate ions (Equation 1.18).

\[
\text{Al(OH)}_3 + \text{OH}^- \rightleftharpoons \text{Al(OH)}_4^- \quad (\text{Equation 1.18})
\]

The partial anodic dissolution reaction can be obtained by the combination of hydroxide film formation and dissolution reactions (Equation 1.19).

\[
\text{Al} + 4\text{OH}^- \rightleftharpoons \text{Al(OH)}_4^- + 3e^- \quad (\text{Equation 1.19})
\]

Electrons produced by the anodic reaction are consumed by oxygen and/or water. The reactions can be represented by Equation 1.20-1.21.

\[
\frac{3}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} + 3e^- \rightleftharpoons 3(\text{OH})^- \quad (\text{Equation 1.20})
\]

\[
3\text{H}_2\text{O} + 3e^- \rightleftharpoons \frac{3}{2}\text{H}_2 + 3\text{OH}^- \quad (\text{Equation 1.21})
\]

Experimental findings show that during the corrosion process in alkaline solutions gas bubbles evolve from the aluminum surface, suggesting that alkaline aluminum corrosion proceeds mainly by water reduction.

iii. Corrosion of aluminum in acidic solution

Obot et al,\textsuperscript{124} has reported the aluminum dissolution mechanism in acid solution. The reactions can be represented by Equation 1.22-1.25.

\[
\text{Al} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}_{ads} + \text{H}^+ + 3e^- \quad (\text{Equation 1.22})
\]
AlOH$_{ads}$ + 5H$_2$O + H$^+$ ⇌ Al$^{3+}$.6H$_2$O + 2e$^-$ (Equation 1.23)

Al$^{3+}$ + H$_2$O ⇌ [AlOH]$^{2+}$ + H$^+$ (Equation 1.24)

[AlOH]$^{2+}$ + X$^-$ ⇌ [AlOHX]$^+$ (Equation 1.25)

The soluble cationic complex formed during this process causes the metal dissolution. The rate of the dissolution of aluminum depends on the anion(X$^-$) concentration in the solution.

1.6. Common Inhibitors

There are different corrosion protection techniques. Among them, the use of corrosion protection coatings and corrosion inhibitors are the most common.$^{125-126}$ Corrosion protection coating consists of a three layer protective coating system. Chrome-based conversion coating is used as the first layer that provides corrosion protection and it is in direct contact with the metal surface and primer is the second layer consisting of both chromated and non-chromated pigments enclosed in an epoxy resin which is the principal corrosion protector. A top coater is the barrier against extreme environmental influences.$^{127-128}$ However, due to the high environmental impact of these chrome-based coatings, the REACH, European Union regulation has decided to limit/restrict their use.$^{129}$ Therefore, many researchers have focused on developing corrosion inhibitors. Corrosion inhibitors are a special group of substances that can be adsorbed on the surface of the metal and form a thin film that prevents corrosion. Surfactants and organic molecules are well known organic inhibitors used for achieving such protection.$^{130-137}$

1.6.1. Surfactants as Inhibitors

Surfactants are a special class of corrosion inhibitors that have been extensively studied in recent years.$^{92, 138-142}$ Surfactants are amphiphilic molecules with hydrophobic and hydrophilic molecular sections. They have been used in corrosion inhibition for iron,$^{134, 143-148}$ aluminum,$^{149-}$
copper, and magnesium surfaces. As discussed in the recent review by Free et al. the “amphiphilic nature of surfactant molecules creates an affinity for adsorption at interfaces such as metal/metal oxide–water interface.” As such, when the surfactant adsorbs onto metallic surfaces it forms a barrier that inhibits corrosion. The adsorption of surfactants onto metallic surfaces depends on several factors, such as concentration of the surfactant, composition of the solution, properties of the surfactant and the surface, and the electrochemical potential of the surface. When evaluating the surfactant concentration on the effect of metal corrosion inhibition on the surface, aggregation concentration (sac) and critical micelle concentration (cmc) are two important parameters. The concentration at which a monolayer formed on the metal surface is termed as sac and the concentration at which molecules start to form aggregates in solution is termed as cmc. In 2016 the Free group studied how the surfactant concentration affects corrosion inhibition on steel surfaces using benzalkonium chloride (BAC) surfactants. From the electrochemical measurements and DFT calculations, they found that when the surfactant concentration increases to sac, corrosion inhibition increases due to the formation of a complete

Figure 1.14. General examples of (a) cationic (b) anionic (c) non-ionic (d) amphoteric and (e) gemini surfactants.
They also discovered that, when the concentration further increases inhibition efficiency slightly increases due to the formation of multilayers/micelles of surfactants which covers the surface more.

Depending on the charge of the hydrophilic section of the surfactants, they can be classified as cationic, anionic, amphoteric, or non-ionic surfactants. Some of the structures of the surfactants are described in Figure 1.14. The use of charges determines how the surfactant adsorbs onto the metallic surface. The inhibition mechanism of the cationic surfactants has been studied by many groups.\(^{[172-181]}\) In 2013, Yildirim group\(^{[182]}\) reported corrosion inhibition mechanism on carbon steel using amide-based cationic surfactants. According to their studies, when the metal surface is positively charged, negatively charged chloride and/or bromide ions can be adsorbed onto the metal in acidic solutions. That will facilitate cationic surfactants to adsorb onto the metal surface via electrostatic interactions forming a monomolecular layer below and at \(\text{cmc}\). The hydrophobic section of the surfactant also plays an important role during corrosion inhibition. They lie perpendicular to the metal surface forming non-polar interactions between the hydrocarbon chains forming a better protective layer (Figure 1.15). Yildirim group also found in their study that if the hydrocarbon chain is too long, the surfactants become less soluble in acidic medium and that leads to reduction of the inhibitor activity. In 2017, Masroor group\(^{[87]}\) studied how the absorption of the cationic surfactants change with varying temperatures. The study was performed using iminium surfactant, which undergoes physico-chemical adsorption with the metal surface. They have found in their study that inhibition efficiency increases with increase in temperature. At high temperatures, chemisorption is favorable due to a lower kinetic energy barrier which causes increase in inhibition efficiency.
As early as 1999, Zhao et al. studied corrosion inhibition and adsorption of anion surfactants on aluminum surfaces in 1M HCl. The weight loss method was used in this study. According to the results, the highest corrosion resistance was observed at its cms and adsorption of the surfactants accorded with the Langmuir equation, with the hydrophilic group facing the aluminum and hydrophobic group facing the solution. In 2013, Venkatesha et al. studied corrosion inhibition of self-assembled monolayers (SAM) of anionic sodium oleate surfactants on steel in saline water. This study revealed that sodium oleate can successfully form monolayers on carbon steel and show anticorrosive character by forming a barrier between the surface and media. In 2014, Javadian et al. investigated the synergistic inhibition offered by cationic and anionic surfactants on the corrosion of mild steel in 2M HCl solution. They used cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) as corrosion inhibitors. They found from the impedance and polarization curves that SDS/CTAB mixtures show high inhibition efficiency compared to SDS and CTAB alone. This shows that compared to the adsorption of single cationic

Figure 1.15. Corrosion inhibition mechanism on carbon steel using cationic surfactants.

![Corrosion inhibition mechanism](image-url)
and anionic surfactants, mixtures of cationic and anionic surfactants exhibit synergism at the solid–liquid interfaces.

In recent years, gemini surfactants have gained a great deal of attention as a promising anticorrosion candidate compared to conventional surfactants due to their unique structure and more efficient surface properties.\textsuperscript{91, 134, 138, 185-189} Gemini surfactants are composed of two identical surfactant molecules that are linked by a spacer group.\textsuperscript{130, 190} In 2013, Verani group\textsuperscript{191} reported electronic and interfacial behavior of two copper(II) gemini surfactants with azide and thiocyanate spacer groups. Isothermal compression curves of both gemini surfactants showed excellent film formation ability with high collapse pressures. Qiu et al.\textsuperscript{192} studied the effect of the spacer length on adsorption on carbon steel in 1 M HCl. According to his study when the spacer group is longer both hydrophillic groups there is adsorption onto the metal, whereas with a shorter spacer group only one hydrophilic group adsorbs onto the surface while the other group becomes free in the solution. In 2001, El Achouri group\textsuperscript{189} studied a series of 1,2-ethane bis(dimethyl alkyl (C\textsubscript{n}H\textsubscript{2n+1})

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure116.png}
\caption{Mode of adsorption of gemini surfactants.}
\end{figure}
ammonium bromide, (where N=10, 12, and 14), for iron corrosion inhibition in HCl. They found that all gemini surfactants are good cathodic inhibitors for iron corrosion and they also proposed three different modes of adsorption at different concentrations. As described in Figure 1.16a, at low concentration adsorption of gemini surfactant takes place horizontally by electrostatic interaction of quaternary nitrogen atom (N+) on cathodic sites and counter ion (Cl-) adsorbed on the anodic sites. As the concentration increases, perpendicular binding takes place due to the inter hydrophobic chain interactions (Figure 1.16b). At high concentrations, surfactants form bimolecular layers on the iron surface (Figure 1.16c). In 2011 Mahdavian et al.193 did a study to compare the corrosion protection ability of the cationic gemini surfactant and the corresponding monomeric surfactant on mild steel in 1M HCl. Polarization measurements reveal that both surfactants act as mixed type inhibitors and the gemini surfactant shows superior corrosion inhibition even at low concentrations. They proposed that strong corrosion inhibition of the gemini surfactants is due to the formation of closely packed well developed bilayers on the steel surface compared to monomeric surfactants. A similar study has been performed by Hegazy et al.194 using novel cationic and gemini surfactants on carbon steel in 0.5 M H2SO4 solution. They also found in their study that gemini surfactants show higher corrosion inhibition efficiency compared to cationic surfactants at the same concentration and temperature. This can be attributed to the presence of many adsorption centers and higher dipole moment of the gemini surfactant. In 2010, Arami et al.181 did a study to investigate the synergistic effect of the gemini surfactants with halide salts (NaCl, NaBr, and NaI) on steel in HCl. From electrochemical and weight loss measurements they found that gemini surfactants in combination with halide salts show higher inhibition efficiency when compared to gemini surfactants alone. This has been explained using two different adsorption models, known as competitive or co-operative adsorption. In competitive adsorption,
halide anions and surfactant cations adsorb at different sites, and in co-operative adsorption halide anions adsorb on the metal surface, then surfactant cations adsorb on anions. Either way, the adsorption of both anions and cations leads to an increase in corrosion inhibition. In 2015 Zhang et al.\textsuperscript{195} studied corrosion inhibition of quaternary ammonium gemini surfactant containing an ester spacer on carbon steel. They reported that when increasing the concentration below the $cmc$, corrosion inhibition efficiency increases rapidly and when the concentration exceeds its $cmc$, increasing concentration led to small changes in the corrosion inhibition efficiency. This behavior was explained using the surface adsorption mechanism. They proposed that at low concentration gemini surfactant adsorbs onto the metal surface through two ammonium groups ($N^+$) and when concentration of the inhibitor increases, inter hydrophobic interactions increase which leads to desorption of one or both ammonium groups. When the concentration further increases beyond $cmc$, surfactants form multilayers which will have a slight effect on the corrosion inhibition. This is because monolayers are already sufficient for significant corrosion inhibition. In 2020, gemini surfactants, propanediyl-1,3-bis(N,N-dimethyl-N-dodecylammonium bromide) and propanediyl-1,3-bis(N,N-dihydroxyethyl-N-dodecylammonium bromide), abbreviated as PDDB and PDHDB was prepared by Chen et al.\textsuperscript{196} to study the effect of hydroxyls at the headgroup of gemini surfactants for corrosion inhibition on carbon steel in 1M HCl solution. The results confirmed that PDHDB gemini surfactant with hydroxyl group has better corrosion inhibition compared to PDDB due to chemisorption of the hydroxyl group onto the metal surface. More information about the corrosion inhibition efficiency of gemini surfactants are described in an elegant review by Heakal et al.\textsuperscript{130}
1.6.2. Organic Molecules as Inhibitors

![Chemical structures (a) to (e)]

These structures represent commonly studied organic corrosion inhibitors. (Figure 1.17)

Organic molecules have been widely studied as corrosion inhibitors for iron and aluminum surfaces due to the fact that they contain heteroatoms (N, O, S, and P) and π electrons which can serve as adsorption centers during metal-inhibitor interactions (Figure 1.17). The adsorbed organic films insulate the metallic surface from aggressive surroundings and protect the metal from dissolution. Organic molecules are adsorbed onto the metal surface via electrostatic interactions (physisorption) or by sharing of π and non-bonding electrons between the organic molecule and metallic d-orbitals (chemisorption) or by the association of both. To date, organic molecules containing azoles, Schiff base, pyridine, and other heterocycles have been extensively reported. In this thesis, I have discussed a few major works on organic corrosion inhibitors containing O, N, S, and P. Organic corrosion inhibitors have been studied a lot, but there were very limited studies that have been done to understand how they bind to oxidized metal surfaces and how small structural changes affect the inhibition efficiency until the 1990s. The Tasker group has performed several studies to understand the modes of action of known
organic corrosion inhibitors by synthesizing the polynuclear complexes involving known organic active compounds. This was a new approach at that time to understand the surface interactions by the use of structural motifs found in such model complexes. In 1998, they studied surface interactions of organic corrosion inhibitor (3-(4-methylbenzoyl)-propionic acid) (HL) produced by Ciba Specialty Chemicals. By synthesizing two model iron complexes they learned that firstly the ligand binds to the metal sites by carboxylate head group and form hydrogen bonds between the ketone and the hydroxide group of the metal oxide hydroxide surface. Then by computer modeling further verified efficient packing of the organic molecules above the surface, which is important for effective inhibition. In 1999, they did another study to understand the mode of action of 5-nonylsalicylaldoxime (referred to as P50) on iron surfaces. According to the model structure, they postulate that P50 forms a tetranuclear cluster complex at the metal surface. This study revealed that polyfunctional ligands form compact polymeric complexes at the metal surface which is beneficial for corrosion inhibition.

Many N-heterocyclic compounds have been studied as effective corrosion inhibitors on iron and aluminum surfaces. Among them, azoles are the most common. In 2002, Gu et al. studied corrosion inhibition efficiency of benzotriazole (BTAH) on iron surfaces in an acidic and saline medium using electrochemical and Surface-Enhanced Raman Spectroscopy studies. From these studies, they observed that BTAH shows higher inhibition efficiency in the saline medium than in the acidic medium. In the saline medium, BTAH forms Fe(II)-BTA complex on the iron surface. The triazole ring of the BTAH molecule is responsible for forming the iron-nitrogen coordinate bonds. A cleavage of NH bond occurs during the chemisorption of BTAH with the iron surface (Figure 1.18). In the acidic medium, protonated BTAH$_{2}^{-}$ cations physisorbed onto the negatively charged surface. At potentials more positive than the potential of zero charge, SO$_{4}^{2-}$
ions interact with the positively charged iron surface and at more negative potentials, BTAH$_2^+$ interact with the negatively charged iron surface. The low inhibitive effect in the acidic medium can be explained by the weak electrostatic interactions. In 2019, Zhang et al.$^{233}$ performed quantum chemical calculations to study the relationship between the inhibition efficiency and molecular structure of triazole. The adsorption activity of the inhibitor molecule can be determined by the energy difference of the molecular orbitals ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$). Decrease in energy difference will result in an increase in adsorption activity, which makes it more easily adsorbable. According to the calculations the protonated form has a smaller $\Delta E$, therefore protonated triazole can easily adsorb onto the metal surface via electrostatic interactions. In addition, the protonated form of the triazole has the lowest $E_{\text{LUMO}}$ value and the neutral form has the highest $E_{\text{HOMO}}$. That means the neutral form has a stronger donating ability. Therefore, the neutral triazole molecule chemisorbs to the metal surface through donating unpaired electrons of heteroatoms and $\pi$ electrons.

**Figure 1.18.** Benzotriazole inhibition mechanism in saline medium proposed by Gu group.
Schiff bases are another class of organic compounds that are extensively studied to prevent corrosion. In 2019, Shah group reported\textsuperscript{234} anticorrosive activity of novel Schiff base compounds for aluminum alloys in acidic medium (Figure 1.19). They have proposed a mechanism for corrosion inhibition from the observations drawn from electrochemical and theoretical calculations. The Schiff base molecule prevents corrosion by adsorbing onto the aluminum surface. Unshared electrons on the N of the azomethine C=\(N\) and \(\pi\) electrons of the double bonds share electrons with the p electrons of the aluminum and form covalent bonds. In addition, molecules adsorb onto the metal surface by donor-acceptor interactions between the \(\pi\) electrons of benzene rings and vacant p-orbitals of the aluminum. They observed that Schiff bases can be adsorbed on the aluminum via the neutral or protonated form, so that aluminum can be protected from the acidic environment. The use of organic molecules as corrosion inhibitors has attracted many researchers over the years, so there are several reviews on organic corrosion inhibitors for iron and aluminum in acidic and alkaline solutions.\textsuperscript{114, 235-237}

![Schiff base compound](image)

\(R= H\)
\(R= OCH_3\)
\(R= OC_2H_5\)

**Figure 1.19.** Schiff base compound studied by Shah group.
1.7. The Role of Metal Ions as Corrosion Inhibitors

1.7.1. Corrosion Inhibition of Iron Surfaces

From an early point in corrosion science, the use of metal ions was explored in corrosion inhibition, either by using (i) metal ions with organic inhibitors or (ii) as discrete coordinating compounds.

(i) Metals ions with organic inhibitors

To address the challenges of poor and moderate inhibition ability of corrosion inhibitors, metal cations have been used from early on. The use of metal cations with organic or inorganic inhibitors known as synergism. Synergism can be described as an effective method to improve the inhibitive force of the inhibitor. Transition metal cations have been extensively investigated for possible synergistic effects with organic inhibitors. In 1956, Gatos has reported that oxidizing agents (Fe$^{3+}$, Ce$^{4+}$, Cr$_2$O$_7^{2-}$) increase the corrosion rate of iron in 1N H$_2$SO$_4$, 1N HCl, and 1N acetic acid while reducing agents (Sn$^{2+}$, As$^{3+}$, Zn$^{2+}$) decrease the corrosion rate. Among all the cations, zinc ions have been the most explored. That is due to the ease of being replaced by cations high up in the electrochemical series. The only stable oxidation state of zinc is the +2 state and these ions readily hydrate and form complexes with halide, ammonia, and cyanide. Several studies have proposed that in alkaline and neutral solutions, Zn$^{2+}$-inhibitor complex forms in the solution. When the metal(M) is introduced to the solution, the Zn$^{2+}$-inhibitor complex dissociates and forms a more stable metal-inhibitor complex near local anodic regions. Released Zn$^{2+}$ forms Zn(OH)$_2$ near the cathodic region (Equation 1.26-1.27).

$$\text{Zn}^{2+}\text{-inhibitor} + M \rightarrow M\text{-inhibitor} + \text{Zn}^{2+} \text{ (anodic region)} \quad \text{(Equation 1.26)}$$

$$\text{Zn}^{2+} + 2\text{OH} \rightarrow \text{Zn(OH)}_2 \quad \text{(cathodic region)} \quad \text{(Equation 1.27)}$$
As early as 1986, a study done by Hirakawa et al. showed that using Zn$^{2+}$ ions with 1-hydroxyethyliden-1,1-diphosphonic acid (HEDP) increases the inhibition efficiency on iron due to the formation of a Fe-HEDP and Zn(OH)$_2$ protective film. In 2005 for the first time, Demadis studied the molecular structure of Zn-HDTMP organic–inorganic hybrid [HDTMP-hexamethylenediaminetetras(methylene phosphonate)] and its anticorrosion effect on steel. The Zn center is found in a distorted octahedral environment of phosphonate oxygens. Experimental studies have shown that when generated in situ, this complex acts as a corrosion inhibitor by forming a protective film. Many studies$^{125, 242-245}$ have also shown that synergistic combination of Zn$^{2+}$ and AMP [AMP- amino-tris(methylene phosphonate)] (Figure 1.20) exhibit superior inhibition efficiency than Zn$^{2+}$ and AMP alone. However, these studies have not discussed the identity of the inhibitor species. In 2007, Demadis et al.$^{246}$ has done a more detailed study on the inhibitor species and they found that inhibitor species consist of Zn and P in approximately 1:3 ratio and Fe was also present originating from the metal. In 2008, Amar group$^{247}$ studied the synergistic effect of Zn$^{2+}$ and piperidin-1-yl-phosphonic acid (PPA) on iron using electrochemical techniques and weight loss methods. They observed that a combination of PPA and Zn$^{2+}$ shows excellent inhibition efficiency. Also, they performed Fourier transform infrared (FTIR) spectrum

![Figure 1.20. AMP [AMP- amino-tris(methylene phosphonate)].](image-url)
of the protective film and found phosphonates zinc salt formation. This supports the proposed mechanism of metal-inhibitor complex and Zn(OH)$_2$ formation at the cathodic and anodic sites, respectively.

Concentration of the Zn$^{2+}$ ions in the solutions plays a major role on the inhibitor’s efficiency. In 1998, Rajendran reported$^{239}$ that formulation comprising of 300 ppm sodium salt of phenyl phosphonic acid (PPA) and 50 ppm Zn$^{2+}$ ions show 95% inhibition efficiency and it decreased as the Zn$^{2+}$ ion concentration was greater than or equal to 100 ppm. They have explained that at higher concentrations more Zn$^{2+}$-inhibitor complex is formed and it becomes difficult to diffuse from solution to the metal surface so that metal-inhibitor protective film is not sufficiently formed. The pH of the environment has a significant influence on the inhibitor-zinc formulation which affects the inhibition efficiency. Rao et al.$^{248}$ investigated the influence of the pH variation on the inhibition efficiency of phosphonate, Zn$^{2+}$, and ascorbate formulation and noticed that it is effective only in the pH range of 5-8. They found that pH$\geq$9, due to the higher concentration of OH$^-$ ions in the solution, leads to the formation of [Zn(II)-inhibitor-OH] complex, which may not contribute to the formation of protective film on the metal surface. At pH$\leq$4, ligands will be in the protonated form and do not coordinate with the Zn(II) as deprotonated ligands. Also, enough amount of Zn(OH)$_2$ will not be formed at the cathodic sites, hence the inhibitor may not be effective at pH$\leq$4. The corrosion inhibition efficiency of the inhibitor-zinc mixture also depends on the immersion time. In 2009, Rajendran et al.$^{249}$ documented that inhibition efficiency decreases with time due to the destruction of the protective film by the corrosive chloride ions present in the solution. According to the authors, there is a competition between the formation of FeCl$_2$ and Fe-inhibitor complex and with time formation of FeCl$_2$ is more favored than the formation of Fe-inhibitor film, hence inhibitor efficiency decreases with time.
There are many literature reports on the synergistic effect of Cu$^{2+}$ and organic corrosion inhibitors. Yin group studied the corrosion inhibition effect of carboxymethylchitosan (CMCT) and Cu$^{2+}$ on steel corrosion in HCl. They have observed a significant reduction of corrosion when a mixture of CMCT+ Cu$^{2+}$ is used. CMCT can adsorb onto the metal surface by donating a lone pair of electrons to vacant d-orbitals of the metal forming donor-acceptor bonds. Cu$^{2+}$ acts as a bridge to attach more CMCT rings, so that it can make a more compact film on the steel surface, leading to higher inhibition efficiency.

Benzotriazole is a well-known corrosion inhibitor for copper and its alloys. Therefore, several researchers have studied the synergistic effect of Benzotriazole and Cu$^{2+}$ on corrosion inhibition on iron. In 2003, Ayeta et al. studied synergistic effects of benzotriazole and copper ions on iron corrosion using electrochemical impedance spectroscopy (EIS), polarization curves, and weight loss methods. They found that an increase in the concentration of either Cu$^{2+}$ or benzotriazole increased the synergistic effect. Due to the standard electrode potential of Cu$^{2+}$/Cu compared to Fe$^{2+}$/Fe, it can reduce to metallic copper in two consecutive steps. First Cu$^{2+}$ will reduce to Cu$^{+}$ and then to metallic copper. This will result in the formation of a Cu(I)BTA complex on the iron surface. This Cu(I)BTA complex can polymerize and form a polymeric [Cu(I)BTA]$_n$ complex on the iron surface and inhibit the cathodic partial reaction, which is the rate determining step of the corrosion reaction.

In 1987, Singh group studied the effect of metallic cations (Cu$^{2+}$, Hg$^{2+}$, Ce$^{4+}$) on the corrosion rate of steel in 2N H$_2$SO$_4$, containing urea and alkylthio urea. They found that the dissolution of steel in acid is greatly reduced by urea or thiourea in combination with metal cations due to co-adsorption. At higher concentrations of metal cations, the corrosion rate increased due to the cathodic reduction of metal cations to metal, while lower concentrations decreased the
corrosion rate due to decatalyzing the hydrogen evolution reaction. Anoshchenko, Drazic, and Vorkapic also proposed a similar mechanism in their studies. In 1995, Singh et al.\textsuperscript{253} published a study on the role of metal cations (\(\text{Cu}^{2+}\), \(\text{As}^{3+}\), \(\text{Sb}^{3+}\), \(\text{Sn}^{2+}\)) in improving the inhibition efficiency of hexamine on steel in hydrochloric acid solution. They have performed weight loss, electrochemical polarization, and zeta potential measurements to understand the mechanism of action of the metal cations and hexamine. Metal cations form an anionic complex with the chloride ions in the acid solution and replace the absorbed chloride ions from the metal-electrolyte interface which increases the affinity towards the interface and helps the protonized hexamine to absorb strongly at the interface. That results in the increase in the inhibitive performance of hexamine. In 2017, Ali et al.\textsuperscript{254} has studied the corrosion inhibition ability of the fruiting bodies of Melia azedarach Linn extract (FB-MAL) and its synergistic effect with nickel ions (\(\text{Ni}^{2+}\)) on carbon steel in HCl. They found that FB-MAL can adsorb onto the metal surface either by neutral or protonated form. It can adsorb via electrostatic or by donor-acceptor interactions. When \(\text{Ni}^{2+}\) is present it can form \(\text{Ni}^{2+}\text{FB-MAL}\) complex and that leads to a greater surface coverage and thereby greater inhibition efficiency. More details about synergism between metal cations and organic corrosion inhibitors are summarized in a comprehensive review by Umoren et al. in 2017.\textsuperscript{255}

(ii) Discrete coordinating compounds

There are many studies have been done on the use of organic compounds to protect metals from aggressive environments. They form a protective film on the metal surface by adsorption or

\[
\begin{align*}
\text{(H}_3\text{C)}_2\text{N} & \quad \text{C} \quad \text{S} \quad \text{M} \quad \text{S} \quad \text{C} \quad \text{N(CH}_3)_2 \\
\text{(H}_3\text{C)}_2\text{N} & \quad \text{C} \quad \text{S} \\
\text{M} & \quad \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)} \text{ and Sn(II)}
\end{align*}
\]

\textbf{Figure 1.21.} Coordination complexes of TMDTO with Fe(II), Co(II), Ni(II), and Sn(II).
bridging with other solution components. Organic molecules containing oxygen, nitrogen, or sulfur are more effective. Coordination compounds, which form from organic donor ligands and metal ions are another class of compounds for corrosion inhibition. But there are limited studies done on coordination compounds for corrosion inhibition. As early as 1996, Rangelov and Mircheva studied\textsuperscript{256} the use of metal complexes of tetramethyldithio-oxamide (TMDTO) on the rate of steel corrosion in acid (Figure 1.21). It is well known that organic corrosion inhibitors prevent corrosion by absorption of their molecule on the metal surface. However, TMDTO behaves differently compared to other organic inhibitors, probably due to its ability to form metal complexes. Coordination complexes of TMDTO with Fe(II), Co(II), Ni(II), and Sn(II), have shown significant corrosion inhibition even at very low concentrations compared to uncomplexed TMDTO. They have proposed that increased corrosion inhibition of the complexes due to lower water solubility, higher molecular weight, and more planar S-C-C-S skeleton of the complexes than uncoordinated TMDTO. In 1997, Ita et. al.\textsuperscript{257} has studied steel corrosion inhibition by pyridoxal (PHC), 4-methylthiosemicarbazide (4MTS), pyridoxal- (4-methylthiosemicarbazone) (P4TS), and its Zn(II)-pyridoxal- (4-methylthiosemicarbazone) (ZnP4TS) complex. They have performed weight loss and hydrogen evolution measurements and have learned that ZnP4TS exhibit a higher inhibition efficiency than PHC, 4MTS, and P4TS. The inhibition efficiency increased with increase in inhibitor concentration, increase in molecular weight of the inhibitor, and decrease in temperature. From the average activation energies of all the inhibitors, they were able to confirm that inhibitors inhibit the corrosion reaction by physical adsorption. This observation agrees with the studies of Talati, Modi,\textsuperscript{258} and Barrow\textsuperscript{259}. Since physical adsorption is proposed, multilayer protective coverage is expected on the entire mild steel, which increases the inhibition efficiency. In 2005, Babic´-Samardzija group\textsuperscript{206} published a study on corrosion
inhibition of iron in aerated 0.1 M HClO₄ solution using four macrocyclic cobalt(III) complexes of the general formula [Co³⁺(Rdtc)cyclam](ClO₄)₂, where cyclam and Rdtc- refer to 1,4,8,11-tetraazacyclotetradecane and morpholine-, thiomorpholine-, piperazine-, N-methylpiperazine-dithiocarbamates, respectively. From potentiodynamic polarization (dc) technique and electrochemical impedance spectroscopy (ac) studies, they observed that four cobalt complexes show better inhibition than related amino-ligands. Complexes show higher inhibition efficiency due to the stabilizing chelate effect of the additional Rdtc- ligand and conformational flexibility of the folded cyclam plane. The inhibition mechanism has been studied using molecular modeling and surface coverage calculations. They proposed that cobalt complexes interact on the metal surface with the >NCS₂ delocalized part of the molecule. Unshared electrons on O-, S- or N-atoms transfer electrons to d-orbitals of the iron and form coordinate bonds. The strength of these bonds and corrosion inhibition efficiency increase with the decreasing electronegativity of O-atom > N-atom > S-atom. Hammouti et. al.²⁶⁰ published in 2007 a use of macrocyclic ruthenium–ligand complex [Ru(Mc)]₂PF₆ on the corrosion of steel in 2 M H₃PO₄ acid (Figure 1.22). The results obtained from the weight loss, electrochemical impedance spectroscopy, and potentiodynamic

Figure 1.22. Macrocyclic ruthenium–ligand complex [Ru(Mc)]₂PF₆.
polarization studies showed that inhibitor is a cathodic type and inhibitor efficiency increased with the inhibitor concentration. According to their studies, adsorption of the [Ru(Mc)]2PF6 onto the steel is exothermic and adsorption can be physical or chemical. In 2017, Lin et al. presented inhibitory effect of macrocyclic porphyrin palladium(II) complex on steel corrosion in NaCl solution. Weight loss, electrochemical methods, and surface wettability studies showed that this complex inhibit steel corrosion by forming a water-repellant layer on the surface.

In 2009, Abdel-Gaber et al.261 did an electrochemical study on the effect of Schiff base N,N’-bis (salicylaldehyde)-1,3-diaminopropane (Salpr) and its corresponding cobalt complex [Co(Salpr)] on the corrosion of steel in sulfuric acid. The stability of the [Co(Salpr)] complex in acid solution was confirmed by spectrophotometry measurements. Adsorption studies revealed that the [Co(Salpr)] complex absorbed onto the steel via free adsorption centers in the molecule and due to the bulky nature of the complex it covers more of the steel surface, so that complex inhibits more compared to the Schiff base. In 2011, Singh group262 reported corrosion inhibition studies on Schiff base cobalt(II), nickel(II), copper(II), and zinc(II) complexes with 2-acetylthiophene benzoylhydrazone (Hatbh). They have performed EIS experiments and obtained order of efficiencies as [Co(atbh)2] > [Ni(atbh)2(H2O)2] > [Zn(atbh)2] > Hatbh > [Cu(atbh)2]. [Co(atbh)2] complex showed superior inhibition due to the formation of a complex film. Because of the less negative standard electrode potential of Co(II) compared to Fe(II), it could be reduced to Co, but Hatbh can stabilize the Co(II), therefore it prevents Co(II)/Co reduction on the mild steel surface. A similar observation was observed for [Ni(atbh)2(H2O)2] complex but due to nonplanar structure, inhibition was less compared to [Co(atbh)2]. [Zn(atbh)2] complex formed insoluble Zn(II) compound on the surface with iron oxide and hydroxide, which was responsible for the decrease in further deterioration of the metal. [Cu(atbh)2] complex showed the least
inhibition due to the reduction of the Cu on the surface, which resulted in galvanic coupling. It might also be due to the distorted square planar geometry. Negatively charged ligands like Hatbh, can stabilize higher oxidation states, but in this case, more positive standard electrode potential of Cu(II)/Cu (+0.34 V SCE) compared to Fe(II)/Fe (-0.44 V SCE), led to reduction of Cu(II) on the surface. The ligand adsorbs onto the metal surface through an unpaired electron on the heteroatoms and the π electrons on the aromatic ring. All the complexes except [Cu(atbh)₂] showed higher inhibition compared to the ligand (Hatbh) due to their larger size and molecular planarity. In 2013 Singh et al. reported another corrosion inhibition study on series of Schiff base metal complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with o-hydroxyacetophenone-2-thiophenoyl hydrazone (Hhath). In this study, they mainly focused on the effect of inhibitor concentration, immersion time, and temperature on the corrosion inhibition efficiency. They observed that inhibitor efficiency increases with increasing inhibitor concentration due to larger surface coverage and optimal inhibition after 12 hours of immersion, which suggests the formation of a persistent film on the metal surface. When temperature was increased, they found that efficiency decreases due to desorption of the protective film formed on the metal surface. In this study all the metal complexes showed better inhibition than the ligand. In 2015, Keles group did a comparative

![Schiff base cobalt complex (CoPTM).](image)
study on the corrosion inhibition of carbon steel in HCl by Schiff base imine ligand (PTM) and its cobalt complex (CoPTM) (Figure 1.23) using potentiodynamic polarization curves (Tafel), electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDS) techniques. From these techniques, they observed that CoPTM complex and PTM ligand inhibit corrosion, and inhibition efficiency depends on concentration, temperature, and immersion time. From standard free energy adsorption calculations, they proposed that adsorption of the organic PTM ligand and CoPTM complex onto the metal surface is not purely chemical or physical. Inhibitor molecules adsorbed onto the steel surface via electrostatic interactions, donor-acceptor interactions, and coordinate type bonds. Electrons on the aromatic ring, unshared electron pairs on the heteroatoms, and the double bond in the imine group are involved in making bonds with the metal surface. CoPTM showed greater inhibition efficiency than the PTM ligand due to more planar shape that enables additional interactions by the delocalized electrons from the three aromatic rings and imine group of the complex. Furthermore, in 2015 according to a study done by El-Lateef265 corrosion inhibition increases with large size and high molecular weight. In 2016, Khamis et. al.266 explored the use of

Figure 1.24. Schiff base metal complexes (Cr and Co).
two new eco-friendly Schiff base metal complexes (Cr and Co) (Figure 1.24) for corrosion inhibition on steel in H\textsubscript{2}SO\textsubscript{4} acid solution. They performed electrochemical and quantum chemical studies and their results stated that both inhibitors act as mix type inhibitors and inhibition efficiency increase with the increase in concentration. Both complexes physically adsorbed onto the metal surface and interactions arose between free electron pairs of heteroatoms, π electrons of multiple bonds, and vacant d-orbitals of Fe. In addition, Schiff base ligands can be protonated in acidic solutions, so that positively charged Schiff base molecules can be adsorbed onto the negatively charged metal surface via electrostatic interactions. Furthermore, the protonated complexes can be adsorbed onto the cathodic sites and can reduce the rate of the hydrogen evolution reaction, which helps corrosion inhibition. In the same year, Nassar et al.\textsuperscript{267} studied binuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes with a Schiff base ligand for corrosion inhibition on mild steel in HCl. Weight loss, potentiodynamic polarization, and scanning optical microscopy techniques were used to study the inhibition efficiency of the inhibitors. They suggested that these complexes adsorbed onto the metal surface via methoxy groups and chlorine atoms in a complex and form a heteropolynuclear complex with the d-orbital of the ferrous ion (Figure 1.25). These heteronuclear complexes are much more stable than complexes resulting from the free ligand, and also due to the desorption of the organic ligand in the acidic medium free ligands showed lower anticorrosion activity. As recent as in 2019, the El-Lateef group\textsuperscript{268} has reported Schiff base sulfonated salicylidene thiadiazole Co(II) and Ni(II) complexes as sustainable corrosion inhibitors in HCl. From electrochemical and surface analysis methods they observed that compounds act as mixed-type inhibitors and adsorption obeyed the isotherm model of Langmuir. Co(II) complex displayed higher inhibition efficiency and similar results have been reported in previous literature.\textsuperscript{262-263}
There are very few studies that have been done on the anticorrosive behavior of metal acetylacetonate complexes. In 2003, Harms et al.\textsuperscript{269} reported Fe (III) acetylacetonate and Fe (II) acetylacetonates show corrosion inhibition on mild steel when immersed in phosphate containing solution by forming Fe(II) phosphate and Fe(III) phosphate. In 2009, Mahdavian et. al.\textsuperscript{270} explored the use of Co(acac)\textsubscript{2}, Cu(acac)\textsubscript{2}, Mn(acac)\textsubscript{2} and Zn(acac)\textsubscript{2} complexes as corrosion inhibitors for mild steel. They observed that Co, Zn, Mn(II) acetylacetonate complexes inhibit steel corrosion. But the Cu(II) acetylacetonate complex did not show any inhibitive action, which could be due to reduction of Cu(II) and formation of Cu islands on the steel surface, which leads to an increase in the effective electrode surface area accompanied by galvanic coupling. From SEM-EDX results, they proposed that Zn(acac)\textsubscript{2} forms a stable anionic complex [Fe–O–Zn(acac)\textsubscript{2}]\textsuperscript{−} on the surface, while interaction of Mn(acac)\textsubscript{2} and Co(acac)\textsubscript{2} with the steel surface is probably due to physical adsorption. The same researchers also reported another acetylacetonate study in 2011.\textsuperscript{271} In that study they compared the inhibitive effect of zinc acetate, zinc acetylacetonate, and zinc gluconate on the mild steel immersed in 3.5% NaCl solution. EIS results revealed that all three complexes inhibit steel corrosion, but zinc gluconate showed superior inhibition. Superior inhibition of the
zinc gluconate complex can be due to the formation of insoluble corrosion product on the mild steel.

In 2009, Massoud et al.\textsuperscript{272} studied anticorrosive activity of two silver(I) pyrazino complexes on mild steel. Electrochemical studies showed that both complexes can inhibit steel corrosion in nitric acid. Gibb’s free energy calculations indicated both complexes chemically absorb on the surface of mild steel. In 2015, Zheng et al.\textsuperscript{273} reported the corrosion inhibition effect of phenanthroline (Phen) and its cobalt complex (CoPhen) on the corrosion of carbon steel in sulfuric acid solution. From the experimental studies, they observed that CoPhen complex showed higher inhibition efficiency compared to Phen. The three nitrogen heterocyclic rings of the CoPhen complex contribute to more adsorption sites for the interaction with the metal surface. Furthermore, due to the presence of Cl\textsuperscript{-} ions in the CoPhen structure, CoPhen can form electrostatic interactions with metal. In the acidic medium, the metal surface can be positively charged, so that Cl\textsuperscript{-} ions can adsorb onto the surface and facilitate adsorption of positively charged complexes. This is the only study reported on phenanthroline complexes as corrosion inhibitors.

In 2015, Verani group\textsuperscript{5} reported on Langmuir-Blodgett(LB) films of phenolate-rich metallosurfactants that behave as surface pretreatment coatings for corrosion inhibition on iron.

![ complexes studied by our group (a) redox-innocent 3d\textsuperscript{10} zinc(II) and (b) 3d\textsuperscript{10} gallium(III) complexes (c) redox-active 3d\textsuperscript{5} iron(III) complex. ]
surfaces, and it showed that the complex with a redox-innocent 3d\textsuperscript{10} zinc(II) metal center (Figure 1.26a) has a higher inhibition efficiency as compared to the complex with a redox-active 3d\textsuperscript{5} iron(III) metal center (Figure 1.26c). These metallosurfactants contain a hydrophilic (polar) head group and a hydrophobic (non-polar) tail group and will bind to the metal surface with the polar head group while its tail extends into the air. This orientation will enhance the surface hydrophobicity which is important for corrosion inhibition. To the best of my knowledge, this is the first study that used Langmuir-Blodgett(LB) films for corrosion inhibition. Results from this study suggested that, redox-innocent metallosurfactants are more beneficial for corrosion inhibition. Therefore, recently we studied redox-innocent 3d\textsuperscript{10} gallium(III) complex (Figure 1.26b) for corrosion inhibition on iron and aluminum and compared with previously studied redox-innocent 3d\textsuperscript{10} zinc(II) complex. This study was performed based on the hypothesis that redox-innocent metallosurfactants can hinder electron transport by widening the Fermi/LUMO gap (Figure 1.27). More details about these studies are in Chapters 5 and 6.

1.7.2. Corrosion Inhibition of Aluminum Surfaces

(i) Discrete coordinating compounds

There are not many studies on coordination compounds as corrosion inhibitors for aluminum surfaces. In 2010, Aytac\textsuperscript{274} studied Cu(II), Ni(II), and Co(II) complexes of –Br and –OCH\textsubscript{2}CH\textsubscript{3}
substituted Schiff bases as corrosion inhibitors in HCl. Corrosion inhibition efficiencies were studied using potentiodynamic polarization, electrochemical impedance spectroscopy, and linear polarization methods. The order of the inhibition efficiencies were greatly affected by the molecular geometry and size of the complex which changes with the metal center. Due to the square-planar geometry of the Ni(APH-OCH₂CH₃) complex, it showed the greatest inhibition efficiency. Ni(II) complex showed strong adsorption compared to other complexes due to the more planer orientation that allows more oxygen, nitrogen, and π electrons to interact with the metal surface. All the complexes showed higher inhibition efficiencies compared to the free ligand. That can be explained on the basis of chelation theory. During complexation, partial sharing of the positive charge of the metal ion with donor groups and ligand orbital sharing increase the delocalization of p electrons, which is important for chemisorption of the complex onto the surface. El-Ghamry et al. discussed use of L-histidine Schiff base cobalt(II), nickel(II), and copper(II) complexes as corrosion inhibitors on aluminum in H₂SO₄. The weight loss method was used to investigate the inhibition effect of these complexes and they found that inhibition efficiency increases with increasing temperature and inhibitor concentration. Activation parameters of the corrosion inhibition were calculated, and results reflected a chemical adsorption process which suggests coordinate type bonds between the inhibitor and the metal surface. Recently, Sarkar et al. studied corrosion inhibition properties of cobalt stearate thin films on aluminum surfaces. Films were deposited via an electrodeposition method. Honeycomb-like micro-nano structure and low surface energy of cobalt stearate make the film more water repellent. They found that the molar ratio of inorganic cobalt salt (Co(NO₃)₂) and organic stearic acid (SA) plays an important role while forming the film. From electrochemical impedance spectroscopy studies they observed
excellent anticorrosion properties of the film and it indicated that films can hinder Cl\(^-\) ion penetrating through the film.\(^72\)

Due to the lack of coordination complexes-based corrosion protection coatings, we investigate the use of Langmuir-Blodgett(LB) films of redox-innocent metallosurfactants as surface pretreatment coatings on iron and aluminum surfaces.

1.8. Hypotheses
My research is based on two complementary hypotheses, as follows.

- The rectification study is based on the hypothesis that the use of redox-active metallosurfactants can promote electron transport and orderly physisorbed LB monolayers can act as a directional conductor or diode.
- The corrosion inhibition study is based on the hypothesis that the use of redox-innocent metallosurfactants can hinder electron transport and orderly physisorbed LB films can act as a barrier against environmental influences.

1.9. Research Statement and Objectives

Rectifiers play an important role in molecular electronics, they govern the directional flow of electrical current and are used to transform alternating current into direct current. We build redox-active metallosurfactants with the aim to understand the mechanisms of rectification to reach higher current efficiency. In this research, our focus was put on new bimetallic iron(III), oxovanadium(IV), and chromium(III) complexes. Rectification is attained when the Fermi energies of the electrodes match with the energy of the singly occupied molecular orbital (SOMO) /lowest unoccupied molecular orbital (LUMO) or Highest Occupied Molecular Orbital (HOMO) of the metallosurfactant.
Corrosion is the deterioration of a metal that occurs due to a chemical or electrochemical reaction of the metal with its surrounding environment. The principal objective of the corrosion inhibition study was to evaluate how efficiently LB films of redox-innocent zinc(II) and gallium(III) metallosurfactants can inhibit iron and aluminum corrosion under acidic and basic conditions. Corrosion inhibition is attained when the Fermi energies of the electrodes are mismatched with the energy of the SOMO/LUMO or HOMO of the metallosurfactant.

The specific objectives of my research are as follows,

- **Objective # 1: Modulation of Frontier Molecular Orbitals in a Bicompartmental [N₄O₆] Iron(III) Hydrophobe for Thin Film Formation and Current Rectification.**

  The primary objective of this study is to synthesize and characterize a homobimetallic iron(III) hydrophobe and study its film formation ability, then fabricate nanoscale semiconductor devices to study current rectification ability. In this study, we hypothesize that the use of a bimetallic [Fe^{III}]₂ system could lead to some degree of electronic coupling of the metal centers and will facilitate SOMO-based electron transfer. We also hypothesize that having more than one H₅Fe^{III} center may “amplify” the number of electrons being transferred by the molecule and is expected to enhance the rectification behavior of our assembly. Results are discussed in Chapter 3.

- **Objective # 2: Investigation of Structural, Electronic, and Redox Behavior of Amphiphilic [N₂O₂], [N₂O₃] Chromium(III) and Oxovanadium(IV) Complexes for Current Rectification.**

  This research objective focuses on the development of new chromium(III) and oxovanadium(IV) metallosurfactants with [N₂O₂] and [N₂O₃] donor sets for use in molecular rectifiers. The ligand consists of hydrophobic tert-butyl head groups, phenylene
diamine spacer, and hydrophilic methoxy ethane chains which enhance the film formation ability at the air/water interface.\textsuperscript{276} We hypothesize that by having higher oxidation states with earlier 3d metals we can increase the energy of the HOMOs to be close to the Fermi level and it may lead to a mechanism based on the oxidation of the metallosurfactants. Results are discussed in Chapter 4.

- **Objective # 3: A Molecular Approach for Inhibition of Aluminum Pitting based on Films of [N$_2$O$_2$] Zinc(II) and [N$_2$O$_3$] Gallium(III) Metallosurfactants.**
  The principal objective of this study is to evaluate how efficiently Langmuir-Blodgett films of salophen-like zinc and gallium metallosurfactants can mitigate iron and aluminum corrosion under acidic and basic conditions. In this study, we hypothesize by using complexes with redox-innocent metal ions, we can hinder electron transfer and orderly physisorbed Langmuir-Blodgett film can act as a barrier against environmental influences. Results are discussed in Chapter 5.

- **Objective # 4: Electrochemical Quantification of Corrosion Inhibition on Iron Surfaces with [N$_2$O$_3$] Gallium(III) and [N$_2$O$_2$] Zinc(II) Metallosurfactants.**
  The main objective of this study is to quantify electrochemically the viability of gallium(III)- and zinc(II)-containing metallosurfactants as inhibitors for iron corrosion in saline and acidic media. We evaluate their charge transfer suppression and then focus on potentiodynamic polarization and impedance spectroscopy studies, including detailed SEM data to interrogate their metal dissolution/oxygen reduction rate inhibition abilities. Results are discussed in Chapter 6.
CHAPTER 2: MATERIALS, METHODS, AND INSTRUMENTATION

2.1. Materials

Throughout this research program, various ligands and metal complexes were synthesized and characterized. All the starting materials and solvents were purchased from commercial sources such as Alfa Aesar, Sigma-Aldrich, Fisher Scientific and Oakwood Chemicals and used without further purification. For air-sensitive reactions, anhydrous solvents were used. Solid substrates (quartz, mica, gold, iron and aluminum), which were used to deposit Langmuir-Blodgett films, were purchased from GOODfellow, SPI supplies and Ted Pella, Inc.

2.2. Methods and Instrumentation

Multistep synthetic procedures were used to synthesize complexes that we discuss in each chapter. Air- and moisture-sensitive synthetic steps were carried out using standard schlenk line technique and glovebox. The synthesized organic ligands and metal complexes were characterized using several techniques such as proton nuclear magnetic resonance spectroscopy (¹H-NMR), electrospray ionization mass spectrometry (ESI-MS), CHN elemental analysis, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction for metal complexes when possible. Among them ¹H-NMR was used to identify the number of protons in different chemical environments which helps to identify the structure of the organic ligand. FTIR spectroscopy is employed to identify functional groups present in the organic ligand. ESI-MS is also a very important characterization technique which is used to identify the molecular ion peak and confirm the identity of the organic ligand or the metal complex, whereas CHN elemental analysis and X-ray diffraction studies confirm the purity of the complex and the crystal structure. Cyclic Voltammetry and UV-visible spectroscopy were used to study the electronic and redox properties of the organic ligands and complexes. The electronic nature of the oxidized or reduced species was studied using electron
paramagnetic resonance (EPR) spectroscopy and spectroelectrochemistry methods. Langmuir-Blodgett technique (LB), Brewster angle microscopy (BAM), atomic force microscopy (AFM), and infrared reflection absorption spectroscopy (IRRAS) were used to study film formation ability of the complexes and composition of the deposited films. Finally, conductivity and corrosion properties of the deposited films were investigated using current-voltage (I-V) measurements, scanning electron microscopy (SEM), potentiodynamic polarization and impedance spectroscopy studies. Detailed descriptions of the above-mentioned techniques are given below.

2.2.1. Proton Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1$H-NMR spectroscopy can be described as an analytical chemistry technique that is used to determine the purity of an organic ligand as well as its chemical structure. NMR spectra can be interpreted using several factors, such as chemical shifts, spin multiplicity, coupling constants and integration. $^2^7^7$ A typical $^1$H-NMR plot is usually measured as chemical shift in ppm (x-axis) versus signal intensity (y-axis). The chemical shifts of the peaks represent the environment of the protons and their intensities help to find the number of protons. $^2^7^8$ $^1$H-NMR spectra of synthesized ligands were recorded using Varian FT-NMR Mercury 400 MHz or 500 MHz spectrometers using CDCl$_3$ as the solvent at room temperature.

2.2.2. Mass Spectrometry

Mass spectrometry is an analytical technique that is used to measure the mass-to-charge ratio of ions, which helps to elucidate the structure of a molecule. In this research, molar masses of ligand precursors, ligands and metal complexes were obtained using electrospray ionization mass spectrometry (ESI-MS). A mass spectrometer consists of an ion source, a mass analyzer and a detector. Before the analysis, a sample preparation was done using HPLC-grade organic solvents such as methanol and acetonitrile. During the mass analyzing process, the first molecule is
introduced into an ionization source and the molecules are first ionized to positive and negative charges with fragmented or unfragmented molecules. Then, the charged species travel through the mass analyzer and arrive at the detector depending on the mass/charge (m/z) ratio of the charged species. The computer displays spectra based on relative abundance and the m/z ratio of the charged species. Most of the spectra were taken in positive mode with the molecular ion peak being the most prominent peak. ESI-mass spectra were obtained using Shimadzu LC-8040 Triple Quad, water micromass ZQLC/MS and micromass LCT Premier XE (TOF) mass spectrophotometers.

2.2.3. UV-visible Spectroscopy

UV-visible spectroscopy is an analytical technique that is used to characterize organic ligands and complexes. The electrons from the molecules will absorb near-ultraviolet (180-390 nm) or visible (390-780 nm) radiation and travel from ground state to energetically high excited states. The spectrum is typically represented as molar absorption coefficient (ε in L mol⁻¹ cm⁻¹) versus wavelength (λ in nm). The molar absorption coefficient can be calculated using Beer-Lambert law: ε = A/(C*l), in which ε is the molar absorptivity constant, A is the absorption, C is the concentration of the solution and l is the path length of the cell which is typically 10 mm. The probability of electronic transitions of these organic ligands and complexes depends on the spin selection and Laporte selection rules. The spin selection rule states that the electron spin should not change while promoting electrons, whereas the Laporte selection rule states that if the molecule is centrosymmetric, promotions within the same sub-level will be forbidden. In general, ligands show only intra-ligand charge transitions (ILCT) which are spin and Laporte allowed with ε values of 20,000-60,000 M⁻¹ cm⁻¹. Metal complexes show mainly four types of transitions. They are intraligand charge transfer (ILCT), metal-to-ligand charge transfer (MLCT), ligand to-metal charge
transfer (LMCT) and d-d transitions. ILCT and MLCT transitions show ε values of 5000-20,000 M\(^{-1}\) cm\(^{-1}\) and d-d which are Laporte and spin forbidden shows the lowest intense bands with ε values of 50-1000 M\(^{-1}\) cm\(^{-1}\).\textsuperscript{282-283}

Molecular ordering of the LB films of metal complexes were characterized using a UV-visible spectrophotometer. Mainly, there are two types of aggregation patterns which can be seen during the formation of films, namely H- and J- type aggregates. The H-aggregates display a hypsochromic shift and J-aggregates display a bathochromic shift in the UV-visible spectra when compared to the solution spectra.\textsuperscript{284-286} UV-visible spectra of films and solutions were obtained using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer or a Varian Cary 50 spectrophotometer at room temperature using a quartz cell.

2.2.4. Elemental Analysis

Elemental analysis provides detailed information about the purity of the synthesized ligands and complexes using percentages of carbon, nitrogen, and hydrogen in a sample. First, about 2-3 mg of the sample is introduced into the instrument and it undergoes complete combustion in the presence of V\(_2\)O\(_5\). This will result in oxidation of carbon, hydrogen and nitrogen to carbon dioxide (CO\(_2\)), water (H\(_2\)O) and nitrous oxide (N\(_2\)O), respectively. Then, this gaseous mixture is separated using a gas chromatographic system and the amount of each gas generated is analyzed. This analysis helps to determine elemental percentages of each sample and finally the empirical formula of the sample can be predicted.\textsuperscript{287} Elemental analysis for my samples was carried out in an Exeter analytical CHN analyzer by Midwest Microlab in Indianapolis, Indiana.
2.2.5. X-ray Crystallography

X-ray crystallography is a powerful technique that helps to determine the structure and the molecular geometry, while providing important information about bond lengths and bond angles of the complex. There are different techniques to grow crystals, in this thesis crystals were grown using slow evaporation. X-ray quality crystals were then observed under the microscope and good quality single crystals were isolated and mounted on a mitogen loop. Then the loop was mounted on a Bruker X8 APEX-II kappa geometry diffractometer which contains Mo radiation source and the sample was illuminated with X-ray radiation to obtain a diffraction pattern. Diffracted patterns were collected using a Bruker CCD (charge coupled device). Then the diffraction pattern was interpreted using Bragg’s law \( n\lambda = 2dsin\theta \) where \( \lambda \) is the wavelength of the incident X-ray, \( n \) is an integer, \( d \) is the distance between the planes of the crystal lattice and \( \theta \) is the scattering angle. SHELX, COSMO, APEX II, SAINT and OLEX2 programs were used to collect and solve the crystal structures. All the crystal structures in this thesis was collected and solved by former members of the Verani group, Dr. Habib Baydoun and Dr. Kenneth Kpogo.

2.2.6. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy is a useful analytical technique which is used to characterize inorganic and organic compounds. IR radiation is used in this technique and functional groups are identified based on the vibrational frequencies. A molecule is exposed to electromagnetic radiation in the frequency range of 400-4000 cm\(^{-1}\), and some frequencies will be absorbed by the functional groups and some will be transmitted through, which will give rise to the spectrum of \( \%\text{transmittance} \) \textit{vs.} wavelength. C=O, C=N, C=C, C-H, N-H, O-H and C-O are examples of some of the special functional groups that can be identified using this technique.
Furthermore, ClO$_4^-$, PF$_6^-$ and BF$_4^-$ counter ions also can be detected. Infrared spectra were recorded using KBr pellets on a Bruker Tensor 27 FTIR spectrophotometer.

2.2.7. Cyclic Voltammetry

Cyclic voltammetry (CV) is a characterization technique that is used to study the redox behavior of ligands and complexes.$^{296-298}$ In this thesis, cyclic voltammetry experiments were performed using a BAS 50W potentiostat, with glassy carbon working electrode, Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Before the experiment, ligands and complexes were dissolved in acetonitrile or dichloromethane with a supporting electrolyte (tetrabutyl ammonium hexafluorophosphate, TBAPF$_6$). Experiments were performed at room temperature under inert conditions. Ferrocene was used as an internal standard and added at the end of the experiment. In a cyclic voltammogram, the x-axis represents the applied potential (E), while the y-axis is the resulting current (i) passed. Reversibility of redox processes was measured in two different ways: (i) determining the difference between anodic and cathodic peak potentials ($\Delta E$) (ii) determining the ratio of anodic peak current ($i_{pa}$) and the cathodic peak current ($i_{pc}$), ideally $\Delta E = 59$ mV and $i_{pa}/i_{pc} = 1.0$ of a reversible process.$^{299}$

2.2.8. Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) is a technique used to study molecules with unpaired electrons. By using this technique, we can get information about spin states and coordination environment around the metal center. The EPR is analogous to nuclear magnetic resonance (NMR) spectroscopy, but EPR measures the electron spin instead of nuclear spin. An unpaired electron can have two spin states, $m_s = \pm 1/2$, which are degenerate in the absence of magnetic field. In the presence of a magnetic field, the two spin states will split apart. This energy difference is caused by the zeeman effect. Lower energy states occur when the magnetic moment
of the electron aligns with the magnetic field while higher energy state occur when the magnetic moment aligns against the magnetic field. Energy difference between two spin states can be calculated using the Equation 2.1, where \( g \) is the proportionality factor (or g-factor), \( \mu_B \) is the Bohr magneton and \( B_0 \) is the magnetic field.\(^{300-301}\)

\[
\Delta E = g\mu_B B_0 \quad \text{(Equation 2.1)}
\]

During the experiment, magnitude of the microwave radiation is kept fixed, while changing the magnetic field. When the magnetic field changes, \( \Delta E \) also changes according to Equation 2.1. At a certain point, \( \Delta E \) matches with the microwave radiation, electrons in the sample absorb that energy and a signal is generated. These signals were recorded as the first derivative plot of the signal as opposed to the applied magnetic field. In addition to the magnetic field, unpaired electrons are also sensitive to the surrounding environment. Interactions between unpaired electrons and surrounding nuclei are called hyperfine interactions. Hyperfine interactions can provide useful information about the sample, including the number of atoms and identity, as well as the distance from the unpaired electrons.\(^{302}\)

EPR experiments for this thesis were conducted by Dr. Jens Niklas and Dr. Oleg Poluektov at Argon National Laboratory (ANL) by using ELEXSYS E580 EPR spectrometer from Bruker Biospin (Rheinstetten, Germany).

2.2.9. Langmuir Blodgett (LB) Isothermal Compression

Langmuir-Blodgett (LB) technique is a film deposition technique that is used to obtain organized molecular assemblies. LB method is an inexpensive process and it can control orientation and placement of molecules. In this method, first a monolayer is organized on liquid subphase (mostly water) and then it is transferred onto a solid surface to form a thin film with a thickness of a constituent molecule. Multilayered films can be obtained by repeating this process.
When molecules are on the air/water interface, it is called Pockels-Langmuir monolayer and after it is transferred onto a solid surface, it is termed Langmuir-Blodgett film.

The LB experiments were performed using an automated KSV 2000 mini trough at 23 ± 0.5 °C. Barnstead NANOpure water, with a resistivity value of 18.2 MΩ•cm⁻¹, was used as the subphase solution. To carry out this technique, constituent molecules should be amphiphilic (Figure 2.1). So, when a molecule reaches the air/water interface, the hydrophilic head interacts with water, while the hydrophobic tail group points towards the air. Because of this behavior, molecules will only form a monolayer on the air/water interface. The LB setup consists of a mini trough to fill the water, two moveable barriers to skim the surface of the water in order to control the surface area of the monolayer, a thermocouple to observe the temperature on the subphase and a Wilhelmy plate (paper plates of 20 mm × 10 mm) balance to measure the surface pressure. There is a special well in the mini trough to carry out dipping experiments. In order to form a LB film,
first the compound is dissolved in a volatile solvent such as chloroform and spread over the subphase. Then after 20 minutes of waiting time, we start to compress the two moveable barriers, then the molecules on the subphase will transfer from gaseous 2D phase to an expanded 2D phase, and finally to a condensed 2D phase. This will result in an isothermal compression curve (graph between average molecular area (Å$^2$) versus surface pressure (mN/m)) (Figure 2.2). The experiment was performed at $23 \pm 0.5 \, ^\circ$C. Using the isothermal compression curve, we can get important information about the orientation of the molecule, critical area per molecule ($A_c$), collapse pressure ($\pi_c$) and if the molecules undergo any phase transitions. Films can be collapsed in two different ways: constant pressure and constant area collapse.$^{304-305}$ That also can be determined using isothermal compression curve. Most homogeneous films are formed in the steepest part of the isothermal compression curve.

By using this technique, films can be deposited onto almost all substrates. In this thesis, films were deposited on glass, mica, gold, quartz, aluminum and iron. Orientation of the molecular films depend on the hydrophobic and hydrophilic nature of the substrates. If the substrate is hydrophilic, the hydrophilic head of the molecule will interact with the substrate and the hydrophobic tail will point outwards. If the substrate is hydrophobic, the hydrophobic tail will interact with the substrate. There are three types of dipping methods, namely X-, Y- and Z-type. Among them, Y-type is the most common deposition method, which uses both up and downward strokes to transfer films onto solid substrates.$^{306}$ To determine the surface coverage, transfer ratio can be calculated [Transfer Ratio (TR) = Area covered on the substrate/Area lost from the Langmuir film].$^{32}$ If the transfer ratio is close to unity, that indicates complete surface coverage from the LB film.
2.2.10. Brewster Angle Microscopy (BAM)

Brewster angle microscopy is used to observe thin films on liquid surfaces and is mostly used with LB experiments. BAM has three components mainly: laser source, an analyzer and a CCD camera. The Laser source and CCD camera are aimed towards the liquid surface at the liquid’s Brewster angle. At this angle, light completely transmits without any reflection. The air/water interface shows a Brewster angle of 53°. When the Langmuir film is on the subphase, some of the light is reflected enabling us to determine characteristic features of the film. By using BAM images, we can observe Newton ring formation, domain formation, defects and collapse on the film. Collapse can be observed as an array of Newton rings. For this thesis, Langmuir films were observed using a KSV-Optrel 300 Brewster angle microscope with a He/Ne laser (10 mW, 632.8 nm) and a CCD detector.

2.2.11. Infrared Reflection Absorption Spectroscopy (IRRAS)

Infrared Reflection Absorption Spectroscopy (IRRAS) is an optical technique that is used to characterize thin films deposited onto solid substrates. It provides structural information on thin films. Also, IRRAS can be used to determine defects and packing topologies of the thin films. IRRA spectrophotometer consists of an IR light source, mid-infrared range (MIR) polarizer, photoelectric modulator and a detector as shown in Figure 2.3.

![Figure 2.3. A schematic representation of IRRA spectrophotometer.](image)
IR light source generates unpolarized light, then it passes through the polarizer and converts to p- and s-polarized light. If the polarization radiation is parallel to the plane of radiation, it is called p-polarized and if the polarization radiation is perpendicular to the plane of radiation, it is s-polarized light. Then the polarized light incident on the thin film at an angle ranging from 13 to 85°. The light reflected by the thin film is collected in the MCT detector and provides vibrational information about the sample. In order to minimize the noise and generate high quality spectra, the MCT detector is cooled with liquid nitrogen. In this thesis, prior to IRRAS measurements, about 50-60 layers of LB films of the metal complexes were deposited on pre-cleaned glass substrates and dried in a desiccator over a week to remove any water. After purging the sample chamber with liquid nitrogen, sample deposited glass substrate was placed inside the sample chamber with the help of a sample holder. IRRAS data were collected by varying the incident angle by using p- and s-polarized light. The same procedure was repeated with the blank sample. Finally, IRRA spectrum of the compound generated by deriving the sample spectrum from the blank spectrum. All experiments were performed using a Bruker Tensor 27 infrared spectrophotometer equipped with an A 513/Q variable-angle accessory.

2.2.12. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a very high-resolution scanning probe microscope used to study the morphology, thickness, surface roughness and texture of thin films. AFM consists of a cantilever with a tip that can scan the sample surface and provide a data map about it. AFM normally uses three imaging modes namely contact, non-contact and tapping modes. In this thesis, surface morphology of the mono and multilayer LB films on mica and quartz were analyzed by using Dimension 3100 AFM (VEECO) and thickness of the films was obtained using silicon tapping tips (nanoscience Instruments, VistaProbes T300). Nanoscope Software from Digital
Instruments (Version 5.12) was used to study the images obtained. The AFM studies were completed in collaboration with Prof. Guangzhao Mao and her student Dr. Lingxiao Xie from the Department of Chemical Engineering and Materials Science at Wayne State University.

2.2.13. Device Fabrication and Current-Voltage (I/V) Characterization

One of the main objectives of this research was to develop redox active metallosurfactants that can be used in the molecular electronics field. Nanoscale devices were fabricated using metallosurfactants and current-voltage measurements were taken. In literature, electronic properties of organic and inorganic materials were studied using metal|molecule|metal assemblies. For this thesis, metal|molecule|metal assemblies were built by sandwiching LB monolayers between two gold electrodes. Prior to device fabrication, suitable surface pressure to deposit LB monolayers was identified by using AFM. The LB monolayers were deposited on gold coated mica substrates and desiccated for about five days to remove any moisture. Then a copper TEM grid was placed on top of the gold substrate before introducing the top gold electrode by using shadow masking method with an EffaCoater gold sputter. One assembly consists of 16 individual Au|LB1|Au devices. Figure 2.4 represents general assembly layout. Assemblies were dried for one day prior to current-voltage measurements (I-V). I-V curves were obtained for each device by applying a bias voltage. The current–voltage measurements for

Figure 2.4. A schematic representation of Au|LB-Monolayer|Au.
the devices were obtained using a Keithley 4200 semiconductor parameter analyzer and a Signatone S-1160.

2.2.14. Broken Symmetry Density Functional Theory (BS-DFT)

Broken symmetry DFT calculations were performed for homobimetallic iron(III) complex, in order to confirm the strength of the magnetic interactions involving the two $^{HS}3d^5$ iron(III) ions. Calculations were done using the Gaussian 09 software package. These calculations were performed using the B3LYP/6-311G functional/basis set combination, an unabridged X-ray based structural model and a simplified geometry-optimized model for which all tert-butyl groups were replaced with H atoms. Broken symmetry DFT calculations were done in collaboration with Prof. Sebastian A. Stoian from the Department of Chemistry at University of Idaho.

2.2.15. Ferroxylic Staining

Another objective of this thesis was to study the corrosion mitigation ability of metal complexes on iron substrates. Corrosion is an electrochemical process which consists of oxidation and reduction reactions. As corrosion takes place, metal releases electrons (oxidation) while the corroding solution gains those electrons (reduction). Iron surfaces can undergo corrosion in acidic and saline media. The effect of LB-films of on iron substrates for corrosion protection can be investigated by placing 99.5% iron substrate (10 × 25 mm) in a Petri dish and covering with warm agar containing two indicators. Upon cooling, the agar forms a semi-solid gel. An acid-base indicator phenolphthalein, and $K_3[Fe^{III}(CN)_6]$ were used to identify the location of the anode and the cathode in the corrosion process. Phenolphthalein is colorless in an acidic or a neutral medium, but it turns pink in the presence of OH$^-$ ions. (Equations 2.2-2.3)

\[
O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad \text{Equation 2.2}
\]

\[
H_2In(aq) + OH^-(aq) \rightarrow In^{2+}(aq) + H_2O(l) \quad \text{Pink} \quad \text{Equation 2.3}
\]
Potassium ferricyanide $K_3[Fe^{III}(CN)_6]$ was used to detect the formation of $Fe^{2+}$ ions during the corrosion process. Ferricyanide ions react with $Fe^{2+}$ ions to form a prussian blue complex which represents the anode (Equations 2.4-2.5). Experiments were performed in both acidic and basic media with a bare iron substrate, covering half of the iron substrates with LB films over a course of one week.$^{314-315}$

\[
Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad \text{Equation 2.4}
\]

\[
3Fe^{2+}_{(aq)} + 2Fe(CN)_6^{3-}_{(aq)} \rightarrow Fe_3[Fe(CN)_6]_2^{2+}(s) \quad \text{Blue} \quad \text{Equation 2.5}
\]

2.2.16. Weight Loss Measurement

Weight loss measurement is one of the simplest and most widely recognized techniques used to measure the corrosion inhibition efficiency of inhibitors. For this technique no special equipment is needed other than an accurate balance. During the corrosion, mass loss is an important parameter that can be used determine the extent of corrosion. This method is slower than electrochemical techniques, but several samples can be examined simultaneously. The experiment was performed by measuring the weight of the sample before and after immersion in the corrosive medium for a specific duration of time. Corrosion rate can be determined using Equation 2.6.

\[
\text{Corrosion rate (R) = } K(W_1-W_2)/A(t_1-t_2)\rho \quad \text{(Equation 2.6)}
\]

Where, $W_1$ and $W_2$ are initial and final weight (g), $K$ is a constant, $A$ is exposed surface area, $\rho$ is the density, $t_1$ and $t_2$ are starting and ending times.

2.2.17. Electrochemical Corrosion Testing

Electrochemical methods are considered as by far the most suitable methods to monitor corrosion. Since corrosion is an electrochemical process, electrochemical measurements can provide more efficient and reliable information about corrosion. In this thesis, we have used
potentiodynamic polarization and electrochemical impedance spectroscopy measurements to quantify the corrosion mitigation ability of the metallosurfactants. \textsuperscript{313, 315}

2.2.17.1. Potentiodynamic Polarization Studies

Potentiodynamic polarization experiments provide information on the corrosion potential and current density, and were performed using a three-electrode setup, where iron and aluminum substrates were used as the working electrodes, a Pt wire as the auxiliary electrode and Ag/AgCl as the reference electrode. Before the experiment substrates were immersed in 3.5% NaCl and in 0.01M H\textsubscript{2}SO\textsubscript{4} for 30 min. To study the changes that occur on the substrate/solution interface, potentiodynamic polarization curves (Tafel plots) were obtained while applying a potential between -0.25 V and 0.25 V vs open circuit potential with a scan rate of 10 mV/s. Tafel plots were generated directly from the Butler-Volmer equation (Equation 2.7).\textsuperscript{316}

\[ I = I_{\text{corr}} \left( e^{\frac{2.303(E - E_{\text{corr}})}{\beta_a}} - e^{-\frac{2.303(E - E_{\text{corr}})}{\beta_c}} \right) \]  \textbf{(Equation 2.7)}

I - Measured current from the cell in amperes

I\textsubscript{corr} - Corrosion current in amperes

E - Electrode potential in volts

E\textsubscript{corr} - Corrosion potential in volts

\beta_a - Anodic \beta Tafel constant in volts/decade

\beta_c - Cathodic \beta Tafel constant in volts/decade

Butler-Volmer equation represents both anodic and cathodic reactions. This equation is generated by assuming rates of both the anodic and cathodic reactions are controlled by the kinetics of the electron-transfer reaction at the metal surface.
In this thesis, Tafel plots were obtained for bare unprotected and complex coated substrates. In both saline and acidic media corrosion currents ($i_{corr}$) and corrosion potentials ($E_{corr}$) were obtained by extrapolating the linear parts of the anodic and cathodic curves to their intersection. (Figure 2.5). Also, anodic $\beta$ Tafel constant ($\beta_a$) and cathodic $\beta$ Tafel constant ($\beta_c$) were attained by cathodic and anodic slopes of the Tafel plot. Inhibition efficiencies (IE%) were calculated using Equation 2.8.\(^\text{317}\)

$$\text{% Inhibition efficiency} = (i_{corr} - i'_{corr} / i_{corr}) \times 100 \text{ (Equation 2.8)}$$

In which $i_{corr}$ and $i'_{corr}$ are the corrosion current values of the bare substrates and LB-film coated substrates, respectively. Potentiodynamic polarization studies were performed by using a CHI650E potentiostat. A detailed description of potentiodynamic polarization experiments is given in Chapter 6.
Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) technique was used to further investigate the corrosion resistance properties of the metallosurfactants. Electrochemical impedance is measured by applying an AC potential and then measuring the current through the cell. When a sinusoidal excitation potential is applied, resultant a sinusoidal AC current (Figure 2.6).

The excitation potential, expressed as a function of time (Equation 2.9),

\[ E_t = E_0 \sin(\omega t) \quad \text{(Equation 2.9)} \]

where \( E_t \) is the potential at time \( t \), \( E_0 \) is the amplitude of the signal and \( \omega \) is the radial frequency.

The response signal (Equation 2.10),

\[ I_t = I_0 \sin(\omega t + \Phi) \quad \text{(Equation 2.10)} \]

where \( I_t \) is the potential at time \( t \), \( I_0 \) is the amplitude of the signal, and \( \Phi \) is the phase shift.

The impedance of the system (Equation 2.11).

\[ Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \Phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \Phi)} \quad \text{(Equation 2.11)} \]

The impedance is therefore expressed in terms of a magnitude, \( Z_0 \), and a phase shift, \( \Phi \).

Figure 2.6. Sinusoidal excitation signal and current response.
In this thesis, all the samples were immersed in the 3.5% (w/v) NaCl and 0.01M H₂SO₄ solution for 30 minutes to achieve the equilibrium before the measurements. EIS data were collected at the open circuit potential in 3.5% (w/v) NaCl and 0.01M H₂SO₄ at 25°C using an electrochemical workstation (CHI 650E, CH Instruments). A carbon sheet (AvCarb MGL190, FuelCellStore, USA) and a Ag/AgCl electrode were used as the counter electrode and the reference electrode. The frequency range was set from 100 kHz to 1 Hz with an excitation amplitude of ± 5 mV. Data were collected at 10 points per decade. ZView 2.1 software was used to analyze and fit the data to the equivalent circuit shown in the **Figure 2.7**. R\text{sol} represents the solution resistance between the metal substrate and the reference electrode. R\text{ct} is the charge transfer resistance to the corrosion reaction at the metal substrate/solution interface. C\text{dl} stands for the capacitance of the double layer of the sample, which normally behaves as a constant phase element rather than a pure capacitor. Results from the electric circuit represented by a "Nyquist Plot." The expression for

![Figure 2.7. Equivalent circuit used for modelling the EIS data.](image)

![Figure 2.8. A schematic representation of the Nyquist Plot.](image)
impedance (Z) is composed of a real and an imaginary part. So, the x-axis represents the real part of impedance and the y-axis represents the imaginary part. In the Nyquist plot low frequency data are on the right side and higher frequencies are on the left side of the plot. Charge transfer resistance ($R_{ct}$) and solution resistance ($R_{sol}$) can be obtained from the plot as shown in Figure 2.8. Impedance spectroscopy studies were performed in collaboration with Dr. Long Luo in the Chemistry Department of Wayne State University. Chathuranga C. Hewa-Rahinduwage performed the experiments. A detailed description of electrochemical impedance spectroscopy is given in Chapter 6.
CHAPTER 3; MODULATION OF FRONTIER MOLECULAR ORBITALS IN A BICOMPARTMENTAL [N\textsubscript{4}O\textsubscript{6}] IRON(III) HYDROPHOBE FOR THIN FILM FORMATION AND CURRENT RECTIFICATION


3.1, Introduction

Solid state rectifier diodes, similar to check valves for liquids, allow unidirectional flow of current in electronic circuitry. Aviram & Ratner proposed that this process may be scaled further down to molecular devices based on an electrode|molecule|electrode architecture\textsuperscript{19} where suitable molecules are expected to display distinct donor (D) and acceptor (A) moieties that show moderate coupling via a bridge (b). These molecules usually display a neutral ground state [D-b-A] and a charge-separated [D\textsuperscript{+}-b-A\textsuperscript{-}] excited state of higher but accessible energy.\textsuperscript{19, 33, 43, 319} Additionally some zwitterionic rectifiers display a [D\textsuperscript{+}-b-A\textsuperscript{-}] ground state.\textsuperscript{33, 319} Rectification takes place if the respective energies of the frontier highest occupied and lowest unoccupied molecular orbitals (MOs) are energetically close to the Fermi levels of the electrodes.\textsuperscript{69} Traditionally, these systems have been synthesized using purely organic molecules.\textsuperscript{32, 34, 63, 320-323} Nonetheless, rectifiers based on coordination complexes, particularly with ferrocene, porphyrin and terpyridine moieties, are also attracting interest.\textsuperscript{64, 66-67, 324-329} Recent efforts spearheaded by our group have expanded considerably the vocabulary of molecular rectification by using arguments of ligand field theory to obtain high-spin HS\textsuperscript{3d\textsuperscript{5}} iron(III)-containing phenolate-rich surfactants of low symmetry described as [Fe\textsuperscript{III}(L\textsuperscript{N2O3})].\textsuperscript{68-69} When the rectifying activity of such species was compared to that of equivalent [Cu\textsuperscript{II}(L\textsuperscript{N2O2})Cl] surfactants with a 3d\textsuperscript{9}
configuration where the $3(d_{x^2-y^2})^1$ MO shows inaccessible energy, an insulating behavior was observed. This enabled us to conclude that rectification proceeds via the singly-occupied molecular orbitals (SOMOs) of the metal via an asymmetric mechanism.\textsuperscript{35, 38, 40}

Therefore, the spatial and energetic modulation of the SOMO orbitals is an essential step towards the design of diode-like molecules with rectifying properties.\textsuperscript{69} Because our rectifiers display five-coordination, rectification must be attained with either low molecular symmetry or local orbital distortion provided by the different N and O donor sets.

Building on our interest in the modulation of the frontier orbitals, we hypothesize that the use of a bimetallic Fe\textsuperscript{III}$_2$ system may allow for inference on the role played by low molecular symmetry and orbital distortion. The overall molecule displays a low idealized $C_{2v}$ symmetry where both metal ions show comparable orbital distortion. Furthermore, such a molecule could lead to some degree of electronic coupling of the metal centers and therefore facilitate SOMO-based electron transfer expected to enhance the rectification behavior of our assembly. As such, we synthesized the new homobimetallic iron(III) complex [Fe\textsuperscript{III}$_2$(L\textsuperscript{N4O6})] (1) (Scheme 3.1) which is based on the new bicompartamental

\textbf{Scheme 3.1.} Homobimetallic iron(III) complex [Fe\textsuperscript{III}$_2$(L\textsuperscript{N4O6})] (1).
ligand $H_6L^{N4O6}$ in which two $N_2O_3$ binding cavities are connected via a tetraamino bridge. Because of the quasi-planar nature of the complex and the presence of eighteen tertiary butyl groups, this species behaves as a hydrophobe able to form Langmuir-Blodgett films needed for device fabrication.

3.2. Experimental Section

3.2.1. Synthetic Procedure

The Ligand $H_6L^{N4O6}$. The ligand $H_6L^{N4O6}$ was synthesized by the addition of 0.28 g of 1,2,4,5-benzenetetramine tetrahydrochloride (1.0 mmol) on to 1.52 g of 2,4-di-tert-butyl-6-(chloromethyl)phenol (6.0 mmol) and 2.1 mL of triethylamine (15 mmol) in dichloromethane. The resulting solution was heated under reflux for 24 h to complete the imine conversion. The reaction mixture was allowed to cool down to room temperature before being washed with brine solution. The organic layer was then dried over anhydrous sodium sulfate and rota-evaporated as a pale yellow powder. Yield: 1.0 g, 70 %). $^1H$ NMR, ppm (CDCl$_3$, 400 MHZ): δ 8.35 (s, 2H), δ 7.50- 8.36 (m, 14H), δ 4.10 (m, 8H), δ 3.88 (d, 2H), δ 1.07-1.44 (m, 54H). ESI (m/z) = 1449.1 for $[L + H]^+$.

The Metal Complex $[Fe^{III}_2(L^{N4O6})]$ (1). $[Fe^{III}_2(L^{N4O6})]$ was synthesized by dissolving 290 mg of $L^{N4O6}$ (0.2 mmol) and 65 mg of sodium methoxide (1.2 mmol) in 20 mL of a 1:1 methanol:dichloromethane solution. To this solution 108 mg of FeCl$_3$·6H$_2$O (0.4 mmol) dissolved in 5 mL of methanol were added dropwise. The resulting solution turned brown and was stirred for 3 h at 50 °C. The solution was subsequently filtered and X-ray quality crystals were obtained via slow evaporation from the mother liquor. Yield: 0.20 g (65 %). ESI-MS (m/z+; CH$_3$OH) = 1550.8939, 100 % for $[C_{96}H_{132}N_4O_6Fe_2 + H]^+$. Anal. Calc. for $C_{96}H_{132}N_4O_6Fe_2$: 74.40; H: 8.59; N: 3.62; Found: C: 74.19; H: 8.94; N: 3.60.
3.2.2. X-ray Structural Characterization

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**Table 3.1.** Crystal data and structure refinement for [Fe₃(ŁN₄O₆)] (1).

Diffraction data were measured on a Bruker X8 APEX-II kappa geometry diffractometer with Mo radiation and a graphite monochromator. Frames were collected at 100K with the detector at 40 mm and 0.3 degrees between each frame and were recorded for 50 s. APEX-II³³⁰ and SHELX²⁹⁰ software were used for data collection and refinement of models. Crystals of [Fe₃(ŁN₄O₆)] appeared as dark rhomboids and yielded a total of
160,610 reflections, from which 21,982 were unique ($R_{int} = 0.0664$). Hydrogen atoms were placed at calculated positions. The solvate regions did not refine reasonably. The PLATON programme SQUEEZE$^{331}$ was utilized to account for the solvate electrons.

3.2.3. UV-visible Spectroelectrochemistry

Spectroelectrochemical data was taken at room temperature using an optically transparent thin layer-cell, composed of a sandwich of two glass slides equipped with a U-shaped flat platinum working electrode that extended to the outside for electrical contact. The inner sides of the slides were coated with indium-tin oxide (ITO) (8-2 Ω/sq). A second platinum wire was used as a counter electrode and a pseudo Ag/AgCl wire served as the reference electrode. The $[\text{Fe}^{III} \text{II}(\text{L}^{\text{N4O6}})] \ (1)$ species was dissolved in dichloromethane and purged with argon before being introduced into the cell through capillary interaction. Potentials of -1.35 and -1.70 $V_{\text{Fe/Fe}^+}$ were applied to the cell for measurement of the reductive processes. The selected potentials assured that the respective reductions to $[\text{Fe}^{III} \text{Fe}^{II}(\text{L}^{\text{N4O6}})]$ and $[\text{Fe}^{II} \text{II}(\text{L}^{\text{N4O6}})]$ occurred. These potentials were controlled using a BAS 50W potentiometer coupled to a Varian Cary 50 apparatus.

3.2.4. Electron Paramagnetic Resonance (EPR)

Continuous wave (cw) X-band (9 - 10 GHz) EPR experiments of $[\text{Fe}^{III} \text{II}(\text{L}^{\text{N4O6}})] \ (1)$ were carried out with an ELEXSYS II E500 EPR spectrometer from Bruker Biospin (Rheinstetten, Germany) equipped with a $\text{TE}_{102}$ rectangular EPR resonator (Bruker ER 4102ST) and a helium gas-flow cryostat (ICE Oxford, UK). An intelligent temperature controller (ITC503) from Oxford Instruments, UK, was also used. Measurements on frozen solutions were done at cryogenic temperature ($T = 30 \text{ K}$). Data processing was done using Xepr (Bruker BioSpin) and Matlab 7.11.2 (The MathWorks, Inc., Natick) environments.
3.2.5. Broken Symmetry Density Functional Theory (BS-DFT)

Calculations were performed using the Gaussian 09 software package. These calculations employed the B3LYP/6-311G functional/basis set combination, an unabridged X-ray based structural model, and a simplified geometry-optimized model for which all tert-butyl groups were replaced with H atoms. For the later models, geometry optimized structures were obtained for both the broken symmetry (BS) and the ferromagnetic (F) states. Geometry optimizations and single point, self-consistent field (SCF) calculations and were done using typical convergence criteria. The theoretical exchange coupling constants $J$ were appraised by comparing the predicted SCF energies of the BS and F states. The initial electronic points of the starting SCF calculations were obtained using the default guess option for the F configuration and the fragment option of the guess keyword for the BS states. For the homodinuclear [Fe$^{III}_2$] complex the F state had an $S_T = 5$ configuration. The BS state corresponds to a $S_T = 0$ configuration for which 5α, spin-up, electrons are localized on one iron site and 5β, spin-down, electrons were localized on the other iron site. The value of the exchange coupling constant was obtained using the expression $J = 2(E_F - E_{BS})/25$ where the $E_{BS}$ and $E_F$ are the SCF energies obtained for the respective states. For the [Cu$^{II}$Fe$^{III}$] dimer the BS corresponds to a $S_T = 2$ and the F state $S_T = 3$ configuration. In this case, the coupling constant was obtained using the $J = 2(E_F - E_{BS})/5$ expression. Charge and spin distributions were assessed based on the Mulliken atomic spin densities and charges.


The pressure vs. area ($\Pi$-A) isotherms of [Fe$^{III}_2$(L$^{N4O6}_4$)] (1) were carried out using an automated KSV Minitrough (now Biolin, Espoo, Finland) at 22.8 ± 0.5 °C. Ultra-pure
water with a resistivity of 17.5-18 MΩ.cm⁻¹ was obtained from a Barnstead NANOpure system and used in all experiments. Impurities present at the surface of the freshly poured aqueous subphase were removed by vacuum after the compression of the barriers. Spreading solutions were prepared in spectra grade chloroform. A known quantity of Fe^{III}_2(L^{N4O6}) \text{(1)} was dissolved in chloroform and 30 µL of a 1.0 mg/mL solution were spread over the water subphase. The system was allowed to equilibrate for approximately 20 min before monolayer compression. The Π vs. A isotherms were obtained at a compression rate of 10 mm.min⁻¹. The Wilhelmy plate method (paper plates, 20 × 10 mm) was used to measure the pressure.\textsuperscript{334}

3.2.7. Brewster Angle Microscopy (BAM)

A KSV-Optrel BAM 300 equipped with a HeNe laser (10mW, 632.8 nm) and a CCD detector was used in all micrographs of [Fe^{III}_2(L^{N4O6}) \text{(1)}]. The compression rate was 10 mm/min, the field of view was 800 x 600 microns, and the lateral resolution was about 2-4 µm.

3.2.8. Infrared Reflection Absorption Spectroscopy (IRRAS)

Infrared reflection absorption spectroscopy of the LB films of [Fe^{III}_2(L^{N4O6}) \text{(1)}] was carried out on a Bruker Tensor 27 infrared spectrophotometer outfitted with an A 513/Q variable-angle accessory, using s-polarization and an incidence angle of 30°. A 5-minute scanning time was used to obtain the IRRAS spectrum. The static contact angle of the modified substrates was determined at room temperature on a KSV CAM 200 goniometer equipped with a CCD camera.
3.2.9. Atomic Force Microscopy (AFM)

Monolayers of LB films of [Fe\textsuperscript{III}\textsubscript{2}(L\textsuperscript{N4O6})] (1) deposited at 17, 20, 25, and 30 mN.m\textsuperscript{-1} were probed in a Dimension 3100 AFM (VEECO) in the tapping mode in ambient air. The height, amplitude, and phase images were obtained using silicon tapping tips (nanoScience Instruments, VistaProbes T300) with resonance frequency of 300 kHz and a nominal tip radius less than 10 nm. The scan rate used was 0.5–2 Hz. Height images have been plane-fit in the fast scan direction with no additional filtering operation. Film thickness was determined by blade-scratching the film to expose the substrate, and then measuring the step height between the substrate and film surface at five different locations using the sectional height analysis.

3.2.10. Fabrication of Au|LB1|Au Devices and Measurement of I-V Curves

Device fabrication used SPI supplied Au-coated mica substrates covered with LB films of [Fe\textsuperscript{III}\textsubscript{2}(L\textsuperscript{N4O6})] (1) at 25 mN/m. The top Au-electrode was coated on an EffaCoater gold sputter using the shadow masking method. The current–voltage (I-V) characteristics of the devices were measured using a Keithley 4200 semiconductor parameter analyzer coupled to a Signatone S-1160 Probe Station at ambient conditions.

3.3. Results and Discussion
3.3.1. Synthesis and Structural Characterizations

Scheme 3.2. Synthesis of H\textsubscript{6}L\textsuperscript{N2O6} and [Fe\textsuperscript{III}\textsubscript{2}(L\textsuperscript{N4O6})] (1).
The new ligand $\text{H}_6\text{L}^{\text{N4O6}}$ was synthesized by the nucleophilic substitution reaction of 1,2,4,5-benzene tetramine tetrahydrochloride with six equivalents of 2,4-di-tert-butyl-6-(chloro methyl)phenol in presence of excess triethylamine (Scheme 3.2).

The metal complex $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}})]$ (1) was prepared by the treatment of $\text{H}_6\text{L}^{\text{N4O6}}$ with $\text{FeCl}_3.6\text{H}_2\text{O}$ in methanol, using $\text{NaOCH}_3$ as base to deprotonate the phenol groups into coordinating phenolates. The Fourier-Transform infrared (FTIR) spectrum of the complex showed a distinct C=N stretch at 1579 cm$^{-1}$. Along with the absence of N-H peaks, this indicates that the two secondary amine groups were oxidized to the imine form during the complexation process. This behavior has been observed during complexation in similar tris phenolate ligand environments under aerobic conditions and was studied in detail elsewhere.$^{335,336}$ The high-resolution mass spectrum of the compound showed a peak cluster at 1550.8939, which corresponds to $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}}) + \text{H}^+]^+$. The elemental analysis supported the proposed structural assignment.

**Figure 3.1.** The crystal structure of $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}})]$ (1) (CCDC 1842912) Hydrogen atoms and t-butyl groups have been removed for clarity, ellipsoids are drawn at 50 % probability. Selected bond lengths for Fe$_2$L: Fe(1)-O(1) = 1.903(4), Fe(1)-O(2) = 1.828(4), Fe(1)-O(3) = 1.862(4), Fe(1)-N(1) = 2.220(4), Fe(1)-N(2) = 2.112(5), Fe(2)-O(4) = 1.885(3), Fe(2)-O(5) = 1.860(3), Fe(2)-O(6) = 1.836(3), Fe(2)-N(3) = 2.137(4), Fe(2)-N(4) = 2.234(3), N(2)-C(86) = 1.284(9), N(3)-C(9) = 1.331(10).
X-ray quality crystals were grown from the parent solution via slow evaporation of dichloromethane (DCM) and methanol (Figure 3.1). The unit cell contains a single molecule of (1), in which two binding cavities are separated by a tetraaminobenzene bridge that imposes an Fe-Fe distance of 8.26 Å. Moreover, short N(2)-C(86) and N(3)-C(9) bond lengths confirm the complete conversion of the ligand amines into imines in excellent agreement with the FTIR spectrum. Interestingly, the two imine nitrogen atoms are cis to one another with respect to the bridge. Finally, as desired for rectification, the iron centers are in a five-coordinate geometry. Each of those ions display a $\tau$ value$^{337}$ of 0.69 and 0.74 associated with a distorted trigonal bipyramidal geometry.

### 3.3.2. Redox and Electronic Behavior

Cyclic voltammetry of [Fe$^{\text{III}}$(L$^{\text{N4O6}}$)$_2$] (1) revealed rich electrochemical response consisting of three two-electron oxidation processes at $0.57 \ V_{\text{Fc+/Fc}}$ ($\Delta E_p = 0.12 \ V$, $|I_{\text{pa}}/I_{\text{pc}}| = 2.0$), $0.79 \ V_{\text{Fc+/Fc}}$ ($\Delta E_p = 0.17 \ V$, $|I_{\text{pa}}/I_{\text{pc}}| = 0.142$), and $1.17 \ V_{\text{Fc+/Fc}}$, attributed to conversions from phenolate to phenoxy radical. This behavior is expected for

![Figure 3.2](image-url). The CV of [Fe$^{\text{III}}$(L$^{\text{N4O6}}$)$_2$] (1mM) in DCM. TBAPF$_6$ supporting electrolyte, glassy carbon (WE), Ag/AgCl (RE), Pt wire (AE). Ferrocene is used as an internal standard. Resting potential -0.5 $V_{\text{Fc+/Fc}}$. 
environments with structurally equivalent moieties. Furthermore, two one-electron reduction processes observed at -1.27 $V_{Fc+/Fc}$ ($\Delta E_p = 0.11$ V, $|I_{pa}/I_{pc}| = 0.68$) and -1.44 $V_{Fc+/Fc}$ ($\Delta E_p = 0.11$ V, $|I_{pa}/I_{pc}| = 1.01$) were attributed to the sequential reduction $[\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}] \rightarrow [\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}] \rightarrow [\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}]$, or (1) to (1') to (1'') (Figure 3.2).

We considered the possibility of ligand-centered reductions described as $[\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}L] \rightarrow [\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}L] \rightarrow [\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}L^\bullet]$, or (1) to (1') to (1'•). However, while this is the case for quinonoid chloranilates and tetraazalenes, the tetrasubstituted benzene ligands pioneered by Collins and Journaux only show radical formation at considerably lower negative potentials. Because the ligand $H_6L^1$ is structurally similar to tetrasubstituted benzene ligands, and because ligand reduction in the similar $[\text{Ga}^{\text{III}}_2(L^{N4O6})]$ (2) appears at 1.79 $V_{Fc+/Fc}$ (Figure 3.3) we consider both reductions as metal-based. The EPR data, discussed later, support this argument. Therefore the sequential $[\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}] \rightarrow [\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}]$ reduction could suggest some degree of coexistence of intermediate mixed valence.

![Figure 3.3. Comparative electrochemistry for $[\text{Fe}^{\text{III}}_2(L^{N4O6})]$ (1) and $[\text{Ga}^{\text{III}}_2(L^{N4O6})]$ (2). Conditions: Dichloromethane, glassy carbon; Ag/AgCl; Pt wire; TBAPF$_6$; Scan rate: 100 mV/s, Ferrocene as internal standard.]}
[Fe$^{III}$Fe$^{II}$] species with weak electronic coupling between the two centers. This is likely due to variations of the local $\tau$ value associated with dissimilar ligand fields when in solution. This weak coupling can be measured using the separation of 164 mV (Figure 3.4) between the metal-centered redox processes in terms of comproportionation constant $K_c$ given in Equation 3.1.

\[
K_c = \frac{[\text{Fe}^{III} - \text{Fe}^{II}]^2}{[\text{Fe}^{III} - \text{Fe}^{III}][\text{Fe}^{II} - \text{Fe}^{II}]} = \exp^{\frac{\Delta E_{1/2} F}{RT}} \text{ (Equation 3.1)}
\]

Where $\Delta E_{1/2}$ is the separation between the first and second waves, as measured in millivolts, $F$ is the Faraday constant, $R$ is the universal gas constant and $T$ is the temperature in Kelvin. This leads to $K_c \approx 10^3$, expected in a Robin-Day class II complex. Hence, the two metal centers are weakly coupled allowing the feasibility of an $[\text{Fe}^{III}\text{Fe}^{II}] \leftrightarrow [\text{Fe}^{II}\text{Fe}^{III}]$ equilibrium. This coupling suggests that intramolecular electron transfer relevant for rectification can take place, and is in good agreement with a weak antiferromagnetic coupling of $J \approx 3 \text{ cm}^{-1}$ experimentally observed by SQUID magnetization and EPR methods in a heterodinuclear $[\text{Cu}^{II}\text{Fe}^{III}]$ species. In order to confirm the strength of the magnetic interactions involving the two $^{\text{HS}3d^5}$ iron(III) ions present in (1) we have performed a series of measurements:

**Figure 3.4.** Measurement of $\Delta E_{1/2}$ for calculation of the comproportionation constant.
of broken symmetry DFT calculations. The exchange coupling constant (in the $\hat{H} = J\hat{S}_1 \cdot \hat{S}_2$ notation) was obtained using the B3LYP/6-311G functional/basis set combination for both the unabridged X-ray structure and for a simplified and geometry-optimized computational model. As expected, these calculations predicted a weak antiferromagnetic coupling characterized by $J = 0.83 \text{ cm}^{-1}$ for the geometry optimized X-ray structure. A comparable value of 0.65 \text{ cm}^{-1} was found for the original and non-optimized structure. To assess the validity of these calculations we have calculated the exchange coupling constant for the [Cu$^{II}$Fe$^{III}$] heterodinuclear complex, previously experimentally characterized. In this case we obtained $J = 2.01 \text{ cm}^{-1}$ (1.78 for the non optimized structure), thus in good agreement with the experimental value.

The electronic spectrum of [Fe$^{III}$_2(L$^{N4O6}$)] (1) taken in the UV-visible region (Figure 3.5) reveals three distinct absorption bands; the first appears at 285 nm ($\varepsilon = 29,700 \text{ L mol}^{-1} \text{ cm}^{-1}$) and is associated with a $\pi-\pi^*$ intraligand charge transfer, while absorption peaks at 320 nm ($\varepsilon = 25,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 434 nm ($\varepsilon = 13,600 \text{ L mol}^{-1} \text{ cm}^{-1}$) are respectively

![Figure 3.5. UV-visible spectrum of the [Fe$^{III}$_2(L$^{N4O6}$)] in dichloromethane.](image)
attributed to N-imine-to-iron and phenolate-to-iron ligand to metal charge transfers (LMCT). The latter transition is mainly attributed to in-plane and out-of-plane $p\pi_{\text{phenolate}} \rightarrow d\sigma^*_{\text{Fe}}$ and $p\pi_{\text{phenolate}} \rightarrow d\pi^*_{\text{Fe}}$ transitions.\(^{335}\)

Spectroelectrochemistry of (1) following the first reduction process at an applied potential of \(-1.35\ V_{\text{Fc}+/\text{Fc}}\) revealed a featureless decrease in absorption intensity in the range of 350 to 550 nm (Figure 3.6a). This decrease in intensity is consistent with a one-electron metal-based reduction of (1) to a mixed valent product $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{L}^{\text{N4O6}})]$. The formation of $\text{Fe}^{\text{II}}$ would partially extinguish the LMCT transitions from taking place due to occupation of a low-lying metal-based SOMO thus explaining the decrease in intensity in the CT region. On the other hand, spectroelectrochemistry following the second reduction at an applied potential of \(-1.70\ V_{\text{Fc}+/\text{Fc}}\) revealed two consecutive processes, as shown in Figure
3.6b. The first detailed in Figure 3.6c is similar to that obtained for the one-electron reduction product (Figure 3.6a), which suggests an initial conversion from (1) to [Fe$^{III}$Fe$^{II}$(L$^{N4O6}$)]. The second (Figure 3.6d) consists of a decrease in the absorption bands at 350 and 500 nm, as well as an increase in the absorption band at 450 nm. These changes were also accompanied by the formation of isosbestic points at 404, 484, and 630 nm. The decline in absorption at 350 and 500 nm is attributed to a decrease in the LMCT bands, while the increase at 450 is consistent with the formation of a new phenolate-to-imine intraligand CT band.$^{346}$

Figure 3.7 compares the EPR data for the equivalent monometallic species [Fe$^{III}$L$^{N2O3}$]$^{335}$ in spectrum (a) with that of the bimetallic [Fe$^{III}_2$(L$^{N4O6}$)] (1) in spectrum (b). While spectrum (a) shows a distinctive signal around 1500 G with $g = 4.3$ diagnostic of a

![EPR spectra](image)

**Figure 3.7**: EPR spectra of (a) [Fe$^{III}$(L$^{N2O3}$)], (b) [Fe$^{III}_2$(L$^{N4O6}$)], and (c) [Fe$^{III}$Fe$^{II}$(L$^{N4O6}$)] with some demetallation in DCM.
five-coordinate $^{HS}3d^5$ species in a largely anisotropic ligand field, the bimetallic species is EPR silent, as indicative of antiferromagnetic coupling among the two $^{HS}3d^5$ centers with $S = 5/2 – 5/2 = 0$. This assignment is based on the observation and detailed study of a similar heterodinuclear [Cu$^{II}$Fe$^{III}$] species, where even couplings of very weak magnitude suffice for the signal to disappear. A weak magnetic coupling is in good agreement with the weak electronic coupling described above. A one-electron reduction of (1) leads to the formation of an [Fe$^{III}$Fe$^{II}$] species, as seen in spectrum (c). This species is expected to be predominantly described by an $S = 1/2$ signal at $g \approx 2$ around 3350 G, and resulting from the antiferromagnetic coupling between $^{HS}3d^5$Fe$^{III}$ ($S = 5/2$) and $^{HS}3d^6$Fe$^{II}$ ($S = 4/2$). Indeed, this is the major component of the spectrum. Additionally, a smaller signal at $g \approx 4.3$ appears to be associated with a spin 5/2 attributed to the presence of monometallated [Fe$^{III}$($L^{N4O6}$)]. Because this signal was not present in the EPR of (1), we assume that a reduction of the parent species into its [Fe$^{III}$Fe$^{II}$] equivalent prompts some demetallation of the more labile 3d$^6$ Fe$^{II}$ ion, as recently observed by Brand et al. Attempts at both simultaneous and sequential two-electron bulk electrolysis to attain the fully reduced [Fe$^{II}$Fe$^{II}$] species resulted in slow and sluggish processes that ultimately led to the decomposition of (1).

### 3.3.3. Analysis of Feasibility of Rectification

Directional electron transfer, or rectification, can only take place if there is an energy match between the Fermi levels ($E_F$) of the gold electrode and the frontier orbitals of the rectifying molecule. The energies associated with the frontier orbitals for [Fe$^{III}$_2($L^{N4O6}$)] (1) can be assessed with the data provided by the electrochemical measurement of reduction and oxidation potentials. These energies can be calculated considering $V_a = 4.7$ eV + $E_{1/2}^{red}$
(vs. SCE), and $V_i = 4.7 \text{ eV} + 1.7E_{1/2}^{\text{ox}}$ (vs. SCE), where $V_a$ and $V_i$ are a good approximation to the equivalent first electron affinity and first ionization energy respectively. While gold has an $E_F$ value of -5.1 eV below vacuum, the first metal-based singly occupied MO has a $V_a$ of -3.8 eV which is 1.3 eV above the gold electrode Fermi levels. Conversely, the energy of the highest occupied MO is -6.4 eV, which is 1.3 eV below the Fermi levels of the gold electrode. The match between the Fermi and SOMO energy levels is similar to other systems where rectification has been observed experimentally and therefore, leads us to conclude that molecular rectification will take place.

3.3.4. Interfacial Behavior

Complementary to the necessary electronic behavior, appropriate interfacial behavior must be attained to enable the construction of devices capable of current rectification. For $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}})]$ (1), some caution is needed because the system deviates from the expected amphiphilic behavior. The presence of tert-butyl-substituted phenolate

![BAM images](image1.png)

**Figure 3.8.** (a) Selected BAM images (b) Compression isotherm for $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}})]$ (1).
groups, and the absence of well-defined polar headgroups or alkoxy chains renders a primarily hydrophobic nature. Nonetheless, this hydrophobic nature, aligned with the previously discussed redox behavior, makes (1) a good candidate for formation of redox-responsive Langmuir-Blodgett (LB) monolayer films on solid. Indeed, the isothermal compression curve obtained for (1) shown in Figure 3.8a suggests that the complex can form homogenous Pockels-Langmuir (PL) films at the air/water interface. The absence of phase transitions, along with collapse at 32 mN/m are in good agreement with a constant pressure mechanism. Furthermore, the collapse, as observed by Brewster angle microscopy (BAM), is marked by sporadic ridges and Newton circles attributed to multilayer granule formation from ejection of matter due to localized oscillations. This behavior is similar to other flat hydrophobes investigated by our group. BAM images

Figure 3.9. Mass spectrum for [Fe$^{III}_2$(L$^{N4O6}$)] (1). Left: in bulk mass spectrum with experimental (bars) and simulated (line) isotopic distribution. Right: Mass spectrum from [Fe$^{III}_2$(L$^{N4O6}$)] (1) recovered (scraped) from LB films. Both spectra show the same distinctive envelope, confirming that the deposited species has retained its molecular identity.
support the formation of a homogenous PL film between 10 and 30 mN m\(^{-1}\), whereas the formation of Newton rings above 30 mN m\(^{-1}\), are indicative of collapse (Figure 3.8b). The average limiting area per molecule is close to 185 Å\(^2\)/molecule.

The identity of the deposited hydrophobes was verified by electrospray ionization mass spectrometry (ESI-MS) and infrared reflection absorption spectrum (IRRAS). ESI-MS confirmed that the bulk \([\text{Fe}^{III}_2(\text{L}^{N=O6})]\) (1) prior to deposition, and that scraped off of LB films deposited as multilayers on glass substrates present the same isotopic envelopes and m/z values (Figure 3.9). IRRAS uses s-polarized light at an angle of incidence of 40° and is compared to the IR spectrum of the bulk sample in Figure 3.10. Equivalent peak patterns were observed for both the IRRAS of the LB film and the bulk samples, showing prominent peaks due to aromatic C=C stretching and CH\(_3\)/CH\(_2\) deformation bands at 1610-1360 cm\(^{-1}\). A stretching vibration at 1580 cm\(^{-1}\) confirms the presence of C=N groups associated with the imine ligand, which remains intact after film deposition.\(^{35}\) Symmetric and antisymmetric stretching vibrations of CH\(_2\) groups were observed in bulk and in the LB film between 2850 cm\(^{-1}\) to 2920 cm\(^{-1}\). The most prominent asymmetric CH\(_3\) vibrations in
the bulk sample appear at 1955 cm\(^{-1}\) and are shifted to 1962 cm\(^{-1}\) in the LB film. Shifting of the wavenumbers is associated with a well packed film.\(^{35,67}\) In IRRAS the C-H stretching region bands are pointing downwards while fingerprint region peaks are pointing upwards. This detection of positive (upward) and negative (downward) bands is explained by means of surface selection rules: a monolayer deposited on dielectric substrates displays positive bands for vibrations with perpendicular transition dipole moment, whereas negative bands will be observed for vibrations with parallel transition dipole moments.\(^{356-357}\)

Atomic force microscopy (AFM) images were taken for LB monolayers deposited on mica substrates at the four different surface pressures of 17, 20, 25 and 30 mN/m. The transfer ratio was kept near unity during the deposition of the monolayers. Films deposited at lower surface pressures show higher pinhole defects and films deposited at higher surface pressures shows higher surface aggregation, while films deposited at 25 mN/m show ordered and defect-free film formation (Figure 3.11). Therefore, films deposited around that region were selected for device fabrication. Blade-scratching\(^68\) was used to determine the monolayer thickness of the LB films deposited on quartz substrates. One to nine layers were deposited, and films were scratched. The depth of the scratch was determined using tapping mode and a linear relationship between the thickness and the number of layers.

**Figure 3.11.** (a) AFM images of monolayers of [Fe\(^{III}\)_2(L\(^{N4O6}\))] (1) deposited on mica substrates at different surface pressures for complex.
indicated the average thickness of ca. 33 to 35 Å per monolayer. The results, including AFM height images, 2D and 3D view, sectional analysis, and a plot of thickness (nm) vs. number of layers from monolayer to 9 layers.

Figure 3.12. AFM height images of the 9-layer deposited film on quartz substrate for [Fe\textsuperscript{III}_{2}(L\textsuperscript{N4O6})] : (a) 2D view, (b) 3D view, (c) sectional analysis, (d) plot between the thickness (nm) vs. number of layers from monolayer to 9 layers.

Using data from the X-ray structure, the molecule can be approximately described as a cylinder of radius \( r \approx 8 \text{ Å} \) and height \( h \approx 17 \text{ Å} \).

Figure 3.13. Approximate model for calculation of molecular area. The molecule is considered as roughly cylindrical with a radius \( r \approx 8 \text{ Å} \) and height \( h \approx 17 \text{ Å} \), thus yielding a sectional area \( 2r \times h \approx 272 \text{ Å}^2 \).
Å, thus yielding a sectional area $2r \times h \approx 272 \text{ Å}^2$ (Figure 3.13) This area is larger than the experimental average limiting area per molecule of ca. 185 Å$^2$, obtained from isothermal compression. The discrepancy suggests that each molecule shows a certain degree of overlap, yielding buckled or intercalated monolayers. This is also evidenced by transfer ratios between 1.1 and 1.3, thus slightly larger than expected (Table 3.2).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Transfer ratio</th>
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</thead>
<tbody>
<tr>
<td>Monolayer 1</td>
<td>1.262</td>
</tr>
<tr>
<td>Monolayer 2</td>
<td>1.161</td>
</tr>
<tr>
<td>Monolayer 3</td>
<td>1.109</td>
</tr>
<tr>
<td>Monolayer 4</td>
<td>1.072</td>
</tr>
<tr>
<td>Monolayer 5</td>
<td>1.133</td>
</tr>
</tbody>
</table>

Table 3.2. Transfer ratios in five independent assemblies.

3.3.5. Rectification Behavior

The fabrication of Au|LB1|Au devices was necessary in order to test the rectification behavior of $[\text{Fe}^{\text{III}}_2(\text{L}^{\text{N4O6}})]$ (1). A PL monolayer was transferred from the air/water interface as an LB film onto a pre-cleaned gold substrate. The top gold electrode was gently deposited via gold sputtering using the shadow masking method on an Effa-Coater gold sputter. This method has yielded good results with our systems and has been described in detail elsewhere.\textsuperscript{35, 68} Five assemblies each containing 16 individual Au|LB1|Au devices were constructed, enabling current-voltage measurements of each device. About 6-8 devices per assembly were short-circuited due to defects on the monolayer. Rectification behavior was observed as asymmetric I-V curves with a sharp negative response and negligible positive response. The rectification ratio ($RR = |I_{\text{at } -V_0}|/I$
at $+V_o$), an important parameter that characterizes the rectification behavior of a device, varied from 2.6 to 9.8 between -2.0 and 2.0 V and between 4.5 and 15.5 between -4.0 and 4.0 V, as shown in Figure 3.14 and Figures 3.15. Retention of the rectification ratio was indicated by reversing the drain and the source contacts, which led the reversed current response expected for a diode-like molecule. Increased symmetry of the I-V curves was observed upon repeated measurements. This behavior has been observed for similar iron phenolate complexes and is attributed to reorientation of molecules to minimize dipole moment. Compared to other species in similar five-coordinate environments, the behavior of the Au|LB1|Au assembly is similar to that of monometallic HSFeIII species in Au|LB|Au assemblies: Species [FeIII(LN2O3)] showed RR values from 4.5 to 12 at ±2 V and from 3 to 37 at ±4 V, whereas [FeIII(LN2O2)Cl] showed RR ranging from 4 to 29 at ±2 V and from 2 to 31 at ±4 V, thus comparable to the previous example. The latter species was also probed using EGaIn/Ga2O3|LB|Au assemblies and yielded RR values of 3 and 12 at ±0.7 V and between 50 and 200 at ±1.0 V, with fast conversion to a sigmoidal curve after a few full scans. Using a similar EGaIn/Ga2O3|LB|Au assembly, a new species, [FeIII(L8)(OMe)2]

![Figure 3.14. I-V measurements for [FeIII2(LN4O6)] (1).](image)
in which the ligand contains a pyridine and a phenolate, a maximum $RR$ of 300 was observed between ±1 V. While the asymmetry of this species confirms the feasibility of rectification, a desired enhancement of the rectification ratio remains elusive. This is likely associated with the

**Figure 3.15.** I-V measurements for $[\text{Fe}^{\text{III}}_2(L_{\text{N4O6}})]$ (1) in five independent assemblies.
observed large average area per molecule that suggests limited film uniformity, where only certain molecules may contact the electrodes directly.

### 3.4. Conclusions

In conclusion, we have successfully developed and studied an unprecedented bimetallic iron(III) hydrophobe described as \([\text{Fe}^{\text{III}}_2(\text{L}_{4\text{O}6})]\) (1). The studies included synthesis, redox, spectroscopic and magnetic characterization, along with DFT calculations to simulate magnetic couplings. The CV of (1) suggests that the two metal centers are weakly coupled. This unique hydrophobe forms Pockels-Langmuir monolayers at the air-water interface showing a moderate collapse pressure of 32 mN/m. The associated Langmuir-Blodgett films were deposited onto glass substrates and films were investigated using IR-reflection/absorbance spectroscopy; the features of the film correlate well with those of the bulk IR spectrum of \([\text{Fe}^{\text{III}}_2(\text{L}_{4\text{O}6})]\) indicating that the identity of the compound remains unchanged after deposition. Although some degree of overlap among the molecules was observed, assemblies were built in which LB monolayers sandwiched between two gold electrodes. Rectification of current was observed by asymmetric I-V curves. Based on previous arguments on the modulation of the frontier orbitals, we proposed that bimetallic systems may allow for inference on the role played by low molecular symmetry and orbital distortion. Considering the evidence for electronic coupling of the metal centers and facilitated SOMO-based electron transfer, the use of a \(C_{2v}\) molecule has clearly enabled current rectification. However, the large area measured per molecule observed by isothermal compression and by the scratching test suggests that only certain molecules display direct contact with the electrodes, thus precluding assessment of rectification enhancement. Ligand changes will be necessary in order to improve the amphiphilic
behavior of such bimetallic species, and enable better film packing required for such assessment. These modifications are currently being pursued in our laboratories.
CHAPTER 4: INVESTIGATION OF STRUCTURAL, ELECTRONIC, AND REDOX BEHAVIOR OF AMPHIPHILIC \([\text{N}_2\text{O}_3], [\text{N}_2\text{O}_2]\) CHROMIUM(III), AND OXOVANADIIUM(IV) COMPLEXES FOR CURRENT RECTIFICATION

4.1. Introduction

Rectifiers are devices that allow the unidirectional flow of current, placing them among the key components in electronic circuitry. Metzger proposed that rectification can occur due to the formation of Schottky barriers or asymmetric/unimolecular electron transport through the frontier orbitals of the molecule.\(^{32-34, 43, 45, 63}\) The Schottky rectification mechanism can be excluded due to the use of symmetrical electrodes (Au electrodes) and Langmuir-Blodgett films that are physisorbed onto surfaces.\(^{26, 28, 30, 358}\) Accordingly, the placement of frontier orbitals (HOMO/LUMO/SOMO) of a molecule with respect to the electrode Fermi levels plays a significant role in determining between the unimolecular and asymmetric mechanisms.\(^{35, 68-69, 359}\)

Unimolecular rectification is attained when the highest occupied HOMO and lowest (or singly) occupied MOs are closer to one another, while asymmetric rectification is attained when the lowest unoccupied or singly occupied MOs are energetically comparable with the electrode Fermi level. However, Baranger and Whitesides have proposed that HOMO alone can carry the electron transport process.\(^{39-40}\)

In 2013, we demonstrated that molecular rectification could occur using an \([\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_3)]\) complex with low symmetry. In that report, we showed that the phenolate moieties act as electron donors, while the Fe(III) acts as the electron acceptor. Also, we observed rectification in few other surfactants containing a five-coordinate high-spin Fe\(^{\text{III}}\) ion (3d\(^5\), \(S = 5/2\)) when the closest metal-based SOMOs (\(d_{xx} + d_{yz}\)) are within 1eV from the Fermi level of the electrodes.\(^{68}\) In one of the studies, we compared the rectifying behavior of an \([\text{Fe}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}]\) complex to an insulating \([\text{Cu}^{\text{II}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}]\) complex and showed that rectification proceeds \textit{via} the SOMOs of iron and
therefore likely proceeds via the asymmetric mechanism. This mechanism is based on the momentary reduction of the metal.

Aiming at the development of electronic materials that can operate at the molecular level, we focused on the use of 3d\(^3\) chromium(III)-containing and 3d\(^1\) oxovanadium(IV)-containing complexes based on the hypothesis that by having high oxidation states with earlier 3d metals, we can increase the energy of the HOMOs, to be close to the Fermi level and it may lead to a mechanism based on the oxidation of the metallosurfactants. As such, in this chapter, we investigate the structural, electronic, redox, and rectification behavior of amphiphilic \([\text{N}_2\text{O}_2]\) chromium(III) \([\text{Cr}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}]\) (1), \([\text{N}_2\text{O}_3]\) chromium(III) \([\text{Cr}^{\text{III}}(\text{L}^\text{N}_2\text{O}_3)](2)\), and \([\text{N}_2\text{O}_2]\) oxovanadium(IV) \([(\text{V=O})^{\text{IV}}\text{L}^\text{N}_2\text{O}_2]\) (3) complexes (Scheme 4.1).

**Scheme 4.1.** The metallosurfactants \([\text{Cr}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}]\) (1), \([\text{Cr}^{\text{III}}(\text{L}^\text{N}_2\text{O}_3)](2)\), and \([(\text{V=O})^{\text{IV}}\text{L}^\text{N}_2\text{O}_2]\) (3).

4.2, Experimental Section

4.2.1. Synthesis and Characterizations

The metal complex \([\text{Cr}^{\text{III}}(\text{L}^\text{N}_2\text{O}_2)\text{Cl}]\) (1). Complex 1 was synthesized by treating an anhydrous tetrahydrofuran solution of \([\text{H}_2\text{L}^\text{N}_2\text{O}_2]\)(L\(^1\)) (0.1 g, 0.145 mmol) with anhydrous \(\text{CrCl}_2\) (0.0213 g, 0.174 mmol). The resulting dark brown solution was stirred under argon for about 18 hours and then in the air for an additional 6 hours. The reaction mixture was then diluted with diethyl ether and washed with aqueous saturated NH\(_4\)Cl (3×150 ml) and brine solution (3×150 ml). The organic
phase was dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting product was recrystallized in methanol: dichloromethane (3:1) solution to yield dark brown crystals. Yield: 80.1 %. ESI (m/z$^+$) in CH$_3$OH= 802.42 for [C$_{44}$H$_{66}$N$_2$O$_8$Cr]$^+$. Anal. Calc. for [C$_{43}$H$_{64}$ClCrN$_2$O$_8$]: C, 62.65; H, 7.82; N, 3.40% Found: C, 62.87; H, 8.02; N, 3.34%. IR (KBr, cm$^{-1}$) 2851-2920 (vC-H), 1610 (vC=C, aromatic), 1509 (vC=C, aromatic) 1588 (vC=N), 1263 (vC-O-C), 1121 (vC-O-C).

The metal complex [Cr$^{III}$L$_2$(N$_2$O$_3$)] (2). Complex 2 was synthesized using the same method as complex 1. [H$_3$L$_2$(N$_2$O$_3$)](L$^2$) (0.6g, 0.658 mmol), anhydrous CrCl$_2$ (0.097 g, 0.790 mmol). Yield=74.8 %. ESI (m/z$^+$) in CH$_3$OH=992.78 [C$_{58}$H$_{87}$CrN$_2$O$_8$ + H]$^+$. Anal. Calc. for [C$_{58}$H$_{87}$CrN$_2$O$_8$]: C, 70.20; H, 8.84; N, 2.82%. Found C, 69.96; H, 8.64; N, 2.89% IR (KBr, cm$^{-1}$) 2840-2970 (vC-H), 1605 (vC=C, aromatic), 1508 (vC=C, aromatic) 1260 (vC-O-C), 1119 (vC-O-C).

The metal complex [(V=O)$^{IV}$L$_2$(N$_2$O$_2$)] (3). A solution containing [H$_2$L$_2$(N$_2$O$_2$)] (0.6g, 0.870 mmol) in methanol (15 ml) was treated with methanolic vanadyl acetylacetonate (0.276 g, 1.04 mmol). The reaction mixture was refluxed with stirring for about 4 hours. Then the solvent was evaporated to 1/5 value and was kept in the refrigerator for one week. Then it was washed after one week with n-hexane, and the solvent was evaporated, and greenish crystals were obtained. Yield= 63.2%, ESI (m/z$^+$) in CH$_3$OH=754.27 [C$_{42}$H$_{58}$VN$_2$O$_7$ + H]$^+$. Anal. Calc. for [C$_{42}$H$_{58}$N$_2$O$_7$V]: C, 66.92; H,7.76; N, 3.72 %. Found: C, 67.08; H, 7.74; N, 3.82%. IR (KBr, cm$^{-1}$) 2850-2970 (vC-H), 1608 (vC=C, aromatic), 1507 (vC=C, aromatic), 1590 (vC=N), 1253 (vC-O-C), 1112 (vC-O-C).
4.2.2. X-ray Structural Characterization

Diffraction data for [Cr$^{III}$($L^N$O$_2$)Cl](1) and [Cr$^{III}$($L^N$O$_3$)](2) without the methoxy-substituted analogue were measured on a Bruker X8 APEX-II$^{60}$ kappa geometry diffractometer with Mo radiation and a graphite monochromator. A suitable dark brown colored crystal of [Cr$^{III}$($L^N$O$_2$)Cl](1) was selected and mounted on the diffractometer. Frames were collected at 100.1 K with the detector at 40 mm and 0.3 degrees between each frame and were recorded for 15 sec. A total 42,448 reflections were collected, with 4162 independent reflections ($R_{int} = 0.0482$). Using Olex2$^{361}$, the structure was solved with the olex2.solve$^{362}$ structure solution program using Charge Flipping and refined with the XL$^{363}$ refinement package using Least Squares minimization. Hydrogen atoms were placed in calculated positions. The asymmetric unit contained one complex coordinated to water, and methanol molecules axially, one uncoordinated methanol solvate and a chloride counter ion.

Single crystals of [Cr$^{III}$($L^N$O$_3$)](2) without the methoxy-substituted analogue were metallic brown. A suitable crystal was selected and mounted on the Bruker APEX-II CCD diffractometer. The crystal was kept at 100.1 K during data collection. In all, 16244 reflections were measured, out of which 6522 reflections were unique [$R_{int} = 0.0621$]. Using Olex2$^{361}$, the structure was solved with the olex2.solve$^{362}$ structure solution program using Charge Flipping and refined with the XL$^{363}$ refinement package using Least Squares minimization. Hydrogen atoms were placed in calculated positions. The asymmetric unit contained one complex having an axially coordinated methanol molecule, with three methanol solvates at full occupancy. The highest difference peak of 0.8 e- was in the vicinity of the disordered t-butyl group on the complex. All crystallographic parameters are shown in Table 4.1.
Isothermal compression curves were obtained for complexes 1, 2, and 3 using a KSV 2000 mini trough at 23 °C with Barnstead NANOpure water as the liquid subphase (18.2 MΩ cm⁻¹). Impurities present at the surface of the subphase were removed by suction after barrier compression. 1 mg/mL chloroform solutions were prepared, and 35 µL of the solution was introduced on the subphase from each complex. This was allowed to stand for about 20 minutes, and isothermal compression curves were obtained at a compression rate of 10 mm/min. The pressure was measured using the Wilhelmy plate method.

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### Important Crystallographic Parameters

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<th>Parameter</th>
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<td>Triclinic, P-1</td>
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</tr>
<tr>
<td>c (Å)</td>
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</tr>
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<td>γ (°)</td>
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<tr>
<td>R_w(F) (%)</td>
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<td>19.49</td>
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</table>

**Table 4.1.** Important crystallographic parameters

### 4.2.3. Isothermal Compression

Isothermal compression curves were obtained for complexes 1, 2, and 3 using a KSV 2000 mini trough at 23 °C with Barnstead NANOpure water as the liquid subphase (18.2 MΩ cm⁻¹). Impurities present at the surface of the subphase were removed by suction after barrier compression. 1 mg/mL chloroform solutions were prepared, and 35 µL of the solution was introduced on the subphase from each complex. This was allowed to stand for about 20 minutes, and isothermal compression curves were obtained at a compression rate of 10 mm/min. The pressure was measured using the Wilhelmy plate method.
4.2.4. Infrared Reflection Absorption Spectroscopy (IRRAS)

Bruker Tensor 27 infrared spectrophotometer outfitted with an A 513/Q variable-angle accessory was used to perform the Infrared reflection absorption spectroscopy of the LB films. Five minutes of scanning time was used for each IRRAS spectra.

4.2.5. Atomic Force Microscopy (AFM)

Monolayers of LB films of 1, 2, and 3 were deposited on mica substrates and probed in a Dimension 3100 AFM (VEECO) in the tapping mode in ambient air.

4.2.6. Fabrication of Au|LB|Au Devices and Measurement of I–V Curves

SPI supplied Au-coated mica substrates were used to deposit monolayers of complexes 1, 2, and 3. To make devices, the top Au-electrode was introduced using the shadow masking method using EffaCoater gold sputter. The current-voltage (I–V) measurements of the devices were taken using a Keithley 4200 semiconductor parameter analyzer coupled to a Signatone S-1160 Probe Station at ambient conditions.

4.3. Results and Discussion

4.3.1. Synthesis and Structural Characterizations

The ligands [H2L(N2O2)(L1)] and [H3L(N2O3)(L2)] were synthesized according to previously published procedures. Complexes [CrIII(L(N2O2)Cl)] (1) and [CrIII(L(N2O3))] (2) were obtained by treating one equiv. of L1 and L2 ligands with CrCl2 in anhydrous tetrahydrofuran solution under inert conditions and then exposed to air. The ligand L1 was treated with VO(acac)2 in methanol to obtain the [(V=O)L(N2O2)](3) complex. Detailed descriptions of the synthetic procedures are available in the experimental section. The FTIR spectra for 1, 2, and 3 showed symmetric and asymmetric C-H stretching vibrations in the range of 2840-2970 cm⁻¹. Complexes 1 and 3 showed a prominent peak at 1588 cm⁻¹ for C=N stretching vibrations, while complex 2 did not show any
peak around that region. This suggests that complex 2 maintains its amine character, whereas complexes 1 and 3 convert to imine during synthesis. This behavior is similar to other trisphenolate complexes synthesized under inert conditions.\textsuperscript{68, 313, 366} ESI-mass spectrometry showed a peak at m/z = 802.13 for 1, m/z = 992.78 for 2 and m/z = 754.01 for 3. Elemental analysis for 1, 2, and 3 showed a good correlation between experimental and theoretical values.

X-ray quality brown single crystals were obtained for [Cr\textsuperscript{III}(\text{L}^2O_2)Cl] (1) complex from a dichloromethane and methanol solvent mixture (1:1) (Figure. 4.1a). The crystal structure reveals a six-coordinate geometry: the [Cr\textsuperscript{III}(\text{L}^2O_2)Cl] center is coordinated to two imine nitrogen atoms, two phenolate oxygen atoms, one axial water, and one axial methanol. Nitrogen and oxygen donors in the ligand framework are trans to each other, with Cr-O and Cr-N average bond lengths being 1.902 Å and 2.004 Å, respectively. These distances are comparable to data reported for salophen-based chromium(III) complexes.\textsuperscript{367} Attempts to grow X-ray quality single crystals for the methoxy-substituted analogue of complexes 2 and 3 were unsuccessful. However, structural information was obtained for [Cr\textsuperscript{III}(\text{L}^2O_2)Cl] (2) complex without the methoxy-substituted analogue.

![Figure 4.1](image-url)

**Figure. 4.1** The crystal structures of (a) [Cr\textsuperscript{III}(\text{L}^2O_2)Cl] (1) and (b) trisphenolate chromium(III) complex without the methoxy-substituted analogue.
analogue of the respective ligand (Figure. 4.1b). The X-ray crystal structure features a hexa-
coordinated complex with one methanol in the axial position. The chromium (III) center is
coordinated to two amine nitrogen atoms and three phenolate oxygen atoms. The three phenolate
oxygen-chromium bond lengths are comparable. The Cr-N1, Cr-N2 bond lengths are 2.106 Å and
2.057 Å, respectively. The obtained Cr-O and Cr-N bond lengths are consistent with reported
literature values.

4.4. Electronic Behavior

The UV-visible spectra of ligands (L¹, L²) and complexes (1, 2, and 3) were taken in
dichloromethane solution (Figure. 4.2). The ligand L¹ showed two absorption bands at 281 nm
(ε = 19933 L mol⁻¹ cm⁻¹), and 359 nm (ε = 18227 L mol⁻¹ cm⁻¹) while L² showed one absorption
band at 283 nm (ε = 13100 L mol⁻¹ cm⁻¹) and a shoulder band at 300 nm (ε = 7714 L mol⁻¹ cm⁻¹).
These bands can be attributed to π → π* transitions. The spectrum of complex 1 was dominated
by intense absorptions at 309 nm (ε = 12260 L mol⁻¹ cm⁻¹), 356 nm (ε = 12650 L mol⁻¹ cm⁻¹), 508
nm (ε = 6840 L mol⁻¹ cm⁻¹), and a low intensity shoulder at around 559 nm (ε < 500 L mol⁻¹ cm⁻¹).
The 508 nm band, which was absent in the spectrum of free ligand, was attributed to a ligand-
to-metal charge transfer (LMCT) band. Another variance observed in the electronic spectra of
complex 1, compared to that of the free ligand L¹ was the appearance of the 559 nm shoulder band,
which can be assigned to the d-d transitions of the chromium ion. The characteristically lower
molar absorptivity, ε, is due to Laporte forbidden transitions. Complex 2 was dominated by an
intense absorption at 290 nm (ε = 13563 L mol⁻¹ cm⁻¹), a shoulder peak ca. 355 nm (ε = 5743 L
mol⁻¹ cm⁻¹), a peak at 500 nm (ε = 3208 L mol⁻¹ cm⁻¹), and a low intensity shoulder peak at 555
nm (ε <500 L mol⁻¹ cm⁻¹). The band at 500 nm which is absent in the spectrum of the free ligand
L² can be reasonably attributed as LMCT transitions. The shoulder band around 550 nm can be attributed to the d-d transitions of the chromium ion. The UV-visible spectrum of the complex 3 displayed intense absorptions at 255 nm (\(\varepsilon = 35563 \text{ L mol}^{-1} \text{ cm}^{-1}\)), 325 nm (\(\varepsilon = 17962 \text{ L mol}^{-1} \text{ cm}^{-1}\)), 429 nm (\(\varepsilon = 22603 \text{ L mol}^{-1} \text{ cm}^{-1}\)), shoulder peak around 474 nm (\(\varepsilon = 11952 \text{ L mol}^{-1} \text{ cm}^{-1}\)), and a low intensity band at 540 nm (\(\varepsilon < 500 \text{ L mol}^{-1} \text{ cm}^{-1}\)). Unlike in the spectrum of the free ligand, an intense band at 429 nm with a shoulder band ca. 474 nm appears in the spectrum of [(V=O)⁴L¹]Cl, due to ligand to metal charge transfer transitions. In addition, the [(V=O)⁴L¹]Cl(3) complex displays a weak, broad band around 545 nm due to d-d transitions.

4.4.1. Redox Behavior

Cyclic voltammetry for complexes 1, 2, and 3 were performed in \(1.0 \times 10^{-3} \text{ mol L}^{-1}\) dichloromethane solution using TBAPF₆ as the supporting electrolyte (Figure 4.3). Complex 1 showed two quasi-reversible ligand-based oxidation processes at 0.31 \(\text{V}_{\text{Fc}+/\text{Fc}}\) (\(\Delta E_p=0.10 \text{ V},|I_{\text{pa}}/I_{\text{pc}}| = 1.4\)) and 0.85 \(\text{V}_{\text{Fc}+/\text{Fc}}\) (\(\Delta E_p=0.17 \text{ V}\)) and one irreversible metal-based reduction process at extreme
negative potentials. This metal-based reduction can only be seen when the ligand stabilizes the Cr(II) state. Complex 2 showed three quasi-reversible oxidation processes at 0.15 V<sub>Fc+/Fc</sub> (ΔE<sub>p</sub>=0.09 V, |I<sub>pa</sub>/I<sub>pc</sub>| = 2.3), 0.52 V<sub>Fc+/Fc</sub> (ΔE<sub>p</sub>= 0.10 V), and 0.84 V<sub>Fc+/Fc</sub> (ΔE<sub>p</sub>=0.10 V) that can be attributed to ligand base oxidations. Complex 2 does not show any metal-based reduction process. Complex 3 showed a quasi-reversible process at 1.08 V<sub>Fc+/Fc</sub> (ΔE<sub>p</sub>= 0.12 V), which can be ascribed to a ligand-centered, phenolate/phenoxyl redox couple. The V<sup>IV</sup>/V<sup>V</sup> oxidation is quasi-reversible in nature and observed at 0.08 V<sub>Fc+/Fc</sub> (ΔE<sub>p</sub>=0.17 V, |I<sub>pa</sub>/I<sub>pc</sub>| = 1.9) and

**Figure. 4.3.** Cyclic voltammograms for 1, 2, and 3; TBAPF₆ supporting electrolyte, glassy carbon (WE), Ag/AgCl (RE), Pt wire (AE). Potentials vs. the Fc⁺/Fc couple.
an irreversible reduction process was observed at -1880 \( \text{V}_{\text{Fc/Fc}^+} \), that can be attributed to \( \text{V}^{IV}/\text{V}^{III} \) reduction.\(^{371}\) Large separations between cathodic and anodic peaks can be attributed to protonation of the oxoligand after reduction of the oxovanadium(IV) complex.\(^{372}\)

### 4.4.2. Interfacial Behavior

To build nanoscale rectification devices using LB films, the properties of the films have to be evaluated. Isothermal compression and Brewster Angle Microscopy (BAM) were used to assess the collapse pressure of the monolayer and the film topology. During compression, intermolecular interactions start to appear at the air-water interface, at about 88, 120, and 80 Å\(^2\) molecule\(^{-1}\) for complexes 1, 2, and 3, respectively. Further compression leads to the formation of a homogeneous film as observed by BAM images. No phase transitions were observed for complexes 1 and 3, but complex 2 showed a phase transition at around 28-38 mN/m region. Complexes 1, 2, and 3 showed a collapse pressure of ca. 45, 50, and 40 mN/m, respectively. All three complexes showed a constant pressure collapse,\(^{304}\) followed by Ries mechanism (Figure 4.4).\(^{373}\)

**Figure. 4.4.** (a) Isothermal compression curves for 1, 3 and selected BAM micrographs (b) Isothermal compression curve for 2 and selected BAM micrographs.
In order to evaluate the retention of the molecular composition after film deposition, LB films deposited glass substrates were characterized by using UV-visible spectra and infrared reflection absorption spectra (IRRAS). About 70-80 layers of LB-films were deposited, keeping the transfer ratio close to unity using Y-type dipping method.\textsuperscript{374} UV-visible spectra of LB films of complexes 1 and 2 correlate well with the solution spectra of each complex (\textbf{Figure 4.5}). But when compared to the solution spectra, some absorption bands have been weakened and some bands shifted due to possible rearrangements and conformational changes of the molecules during the film deposition.\textsuperscript{375} UV-visible spectrum of LB films of complex 2 displayed a new shoulder band at around 415 nm, which can be due to phenolate-to-azomethine charge transfer associated with the amine/imine conversion when forming the LB film. The IRRA spectra predict the composition and the ordering of the molecules after film deposition. For all three complexes, bulk and the LB film spectra showed peaks that are due to aromatic C=C stretching between 1610 and 1500 cm\textsuperscript{-1} and angular CH\textsubscript{2} and CH\textsubscript{3} deformations between 1359 and 1500 cm\textsuperscript{-1}. IRRAS of the complexes 1 (\textbf{Figure 4.6a}) and 3 (\textbf{Figure 4.6c}) showed C=N stretching vibrations around 1585 cm\textsuperscript{-1} and it

![](image.png)

\textbf{Figure. 4.5.} UV-visible spectra of LB multilayer (50-60 layers) films of (a) complex 1 and (b) complex 2 in comparison to their solution spectra.
correlates well with the bulk IR spectrum. The bulk IR spectrum of complex 2 does not show any peak around that region, but IRRAS of the LB film showed a peak around 1590 cm$^{-1}$, which can

**Figure. 4.6.** Full IRRAS spectra for complexes (a) 1(b) 2, and (c) 3 in comparison with their bulk IR spectra.
be assigned to C=N stretching vibrations (Figure 4.6b). It further validates the intraligand amine/imine conversion. For complex 3, bulk showed a characteristic peak around 977 cm⁻¹, that can be assigned for V=O vibrations (Figure 4.7). But we did not see that in the IRRAS spectrum. Therefore, to further confirm the chemical composition of the complex 3, after the film deposition mass spectrum of the film was taken by dissolving the film in methanol. The mass spectrum showed a peak at m/z = 754.27, which is the mass of the complex with the V=O bond (Figure 4.8).

The morphology of the LB monolayers were studied using AFM technique. AFM measurements were taken for LB-monolayers deposited at surface pressures of 15, 20, 25, and 35 mN m⁻¹ for 1, 10, 15, 25, and 45 mN m⁻¹ for 2 and 15, 20, 27 and 35 mN m⁻¹ for 3 (Figure 4.9). When depositing the monolayers, the transfer ratio was kept near unity. Monolayers of 1, 2, and 3 deposited at lower surface pressures show higher pinhole defects, and monolayers at higher surface pressures show rougher surfaces due to surface aggregation, while films deposited around 25 mN m⁻¹ for complexes 1, 2, and 20 mN m⁻¹ for complex 3 shows smooth film formation. Therefore, for 1 and 2, devices were fabricated using monolayers deposited at 25 mN m⁻¹ and for 3 at 20 mN m⁻¹.

![Figure 4.7. Bulk IR spectrum of complex 3.](image)
Figure 4.8. Mass spectrum of the LB film of the complex 3.

Figure 4.9. AFM images of monolayer films deposited on mica substrates at different surface pressures for complexes 1 (a)-(d), 2 (e)-(h), and 3 (i)-(l).
4.4.3. Rectification Behavior

In order to study the rectification behavior of the films of complexes 1, 2, and 3, Au|LB|Au devices were fabricated. Monolayers of the complexes were deposited on precleaned gold substrates. The monolayers deposited gold substrates were then dried in a desiccator for five days. The top gold electrode was introduced using the shadow masking method with an Effa-Coater gold sputter. Three assemblies were fabricated from complexes 1, 2, and 3, and each assembly consists of 16 individual devices. Current-voltage (I-V) characteristics were measured in each device using a Keithley 4200 semiconductor parameter analyzer and a Signatone S-1160 Probe Station at ambient conditions. Among them, about 5-6 devices per assembly were short-circuited, likely due to monolayer defects. Asymmetric I-V curves were observed for all three complexes with a

![Graphs showing I-V characteristics of complexes 1, 2, and 3.](image)

**Figure 4.10.** I-V characteristics of complex 1 (a) from -2 to +2 V; (b) from -3 to +3 V; (c) from -4 to +4 V; (d) from -5 to +5 V; (e, f) from -6 to 6V.
negligible positive response and a sharp positive response (Figure 4.10-4.12). The rectification behavior of the devices was studied using the rectification ratio ($RR = |I_{at-V_{o}}/I_{at+V_{o}}|$). The higher the rectification ratio, the more precise the control of current. For all three complexes
rectification ratio ranges from 3.08 to 17.22 between -2 to +2V. This observation is similar to what we observed for five-coordinate iron(III) complexes reported earlier.35, 68, 72

4.4.4. Analysis of Feasibility of Rectification

Rectification or unidirectional electron transport can be attained when the energy of the Fermi levels \( E_F \) of the gold electrode match with the energies of the frontier orbitals of the rectifying molecule. Energies correlated with the frontier orbitals can be calculated from redox potentials obtained from cyclic voltammetry. To calculate the first lowest unoccupied molecular orbital (LUMO) energy associated with the first reduction process, Equation 4.1 can be used.

\[
V_a = 4.7 \text{ eV} + E_{\text{red} \frac{1}{2}} \text{(SCE)} \quad \text{Equation 4.1}
\]

To calculate the first highest occupied molecular orbital (HOMO) energy associated with the oxidation process, Equation 4.2 can be used,

\[
V_i = 4.7 \text{ eV} + (1.7) E_{\text{ox} \frac{1}{2}} \text{(SCE)} \quad \text{Equation 4.2}
\]

where \( V_a \) and \( V_i \) are a good resemblance to the equivalent first electron affinity and first ionization energy, respectively. The \( E_{\text{red} \frac{1}{2}} \) and \( E_{\text{ox} \frac{1}{2}} \) are half-wave potentials of first reduction and first oxidation versus standard calomel electrode (SCE). However, according to our previous studies,35, 72 due to the presence of partially filled d-orbitals of the metal complexes, singly occupied molecular orbitals (SOMOs) can act as LUMOs. Therefore, after applying the above two equations, HOMO and SOMO energies were calculated for all three complexes. The calculated HOMO energies were -6.0, -5.7, and -5.6 eV for complexes 1, 2, and 3, respectively, and SOMO energies were -3.3 for 1 and -3.2 eV for 3. According to calculations, HOMO energies of complexes 1, 2, and 3 lie 0.9, 0.6, and 0.5 eV below the gold Fermi energy level and SOMO
energies of complexes 1 and 3 lie 1.8 and 1.9 eV above the Fermi level, respectively (Figure 4.13). Previous findings of iron(III) complexes with similar ligand environments have shown that energetically favorable SOMO energies with 1.0 eV difference to gold Fermi energy can transport electrons and act as rectifiers, following an asymmetric mechanism, without any HOMO involvement. However, Baranger and Whitesides have proposed that the HOMO alone can carry the electron transport process. Therefore, results suggest that for all three complexes electron transport can happen efficiently via the HOMO energy levels without any SOMO involvement. This explains the observed current rectification for all three complexes.

To further understand the electron transport mechanism of these rectifiers, we performed DFT calculations for complexes 1 and 2. According to DFT calculations, the ligands of both
complexes 1 and 2 are getting oxidized during the electron transport process. For complex 1, the oxidation locus is phenylene moiety, while for complex 2 the oxidation locus is one of the phenolate rings. We compared the orbital energies of ligand-based and metal-based SOMO in the oxidized molecule and found that ligand-based SOMO is lower in energy than the metal-based SOMO. These results are consistent with the previous studies. Thus, it is viable to propose the following electron transport mechanism,

\[ \text{Au}_1|\text{L-}^\text{Cr}^{III}|\text{Au}_2 \rightarrow \text{Au}_1|\text{L}^+|^\text{Cr}^{III}|\text{Au}_2 \rightarrow \text{Au}_1^+|\text{L-}^\text{Cr}^{III}|\text{Au}_2^{(+)} \]

In our devices, \( \text{Au}_1 \) is the gold substrate and \( \text{Au}_2 \) is the top cold gold electrode. According to a previous study with a similar ligand environment and similar conditions, we have learned that SOMO is closer to the \( \text{Au}_2 \) electrode. Considering molecular asymmetry HOMO should be closer to the \( \text{Au}_1 \) electrode. When we apply a negative bias, the Fermi energy of the top gold electrode (\( \text{Au}_2 \) in the right) increases and the HOMO energy increases with it. Therefore, when

![Figure 4.14](image)

**Figure 4.14.** Proposed electron transport model for complex 1. Complex 2 also will follow a similar mechanism.
a negative bias is applied as the model described in Figure 4.14, electron transport can happen from the HOMO to Au₁ and then Au₂ to HOMO.

### 4.5. Conclusions

In conclusion, amphiphilic [N₂O₂], [N₂O₃] chromium(III)(1, 2), and [N₂O₂] oxovanadium(IV)(3) complexes were successfully synthesized and structurally characterized as precursors for molecular rectification. X-ray crystallography data revealed that both 1 and 2 complexes are hexa-coordinated with distorted octahedral geometry. X-ray structures of oxovanadium complexes with similar ligand environments showed distorted square-pyramidal geometry around vanadium(IV) center. All three complexes showed amphiphilic properties and homogeneous film formation ability with collapse pressures of ca. 45, 50, and 40 mN/m for 1, 2, and 3, respectively. IRRAS UV-visible spectroscopy data revealed that molecular structures of all three complexes remain intact at the air/water interface. Rectification was observed for well-ordered LB monolayers of all three complexes by asymmetric I-V curves. Theoretical calculations performed using redox potentials of 1, 2, and 3 suggested that HOMO energies are energetically comparable with gold electrode Fermi energy compared to SOMO energies. Furthermore, DFT calculations revealed that HOMOs are ligand-centered for complexes 1 and 2. Results from both DFT and theoretical calculations suggest that rectification takes place through HOMOs, which results in oxidation of the metallosuractants first.
CHAPTER 5: A MOLECULAR APPROACH FOR INHIBITION OF ALUMINUM PITTING BASED ON FILMS OF [N₂O₂] ZINC(II) AND [N₂O₃] GALLIUM(III) METALLOSURFACTANTS


5.1. Introduction

Aluminum is a light, malleable, moldable, and non-magnetic metal that resists atmospheric corrosion, and displays electrical and thermal conductivity. These attributes enable wide use in automotive, aerospace, and naval industries. Although the metal is the third most abundant element in the crust (80,700 ppm), isolation from bauxite has a high environmental cost and generates an estimated 13 tons of CO₂ per ton of Al, along with a toxic solid waste known as red mud. As such, conservation efforts are necessary at all levels and include recycling and corrosion inhibition.

Unlike iron, in which adventitious oxygen and water leads to formation of Fe(OH)₃ and Fe₂O₃, the mechanisms of Al corrosion are more complex and less understood. Nonetheless, the action of pitting corrosion leads to pernicious structural failures in car frames, airplane fuselages, and ship hulls, and demands immediate attention. With an electronic configuration given by [Ne] 3s² 3p¹, the metal has a standard potential of −1.7 Vₜₚₜₜ associated with the loss of the 3s² and 3p¹ electrons during the process given by Al(₆) ⇌ Al³⁺ + 3e⁻. Pitting is initiated in neutral media by the presence of chloride and other anions that physisorb at the positively charged surface of the Al₂O₃ passivation layer. The Cl⁻ anions penetrate through nanometer-sized cracks or migrate via oxygen vacancies reaching the Al₂O₃ | Al⁰ interface, quickly converting Al⁰ into AlCl₃, and then the anionic tetrahedral complex [AlIIICl₄]⁻. This
soluble anion reacts with water forming aluminum hydroxide, given by \([\text{Al}^{III}\text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{[Al}^{III}(\text{OH})_3] + 3\text{H}^+ + 4\text{Cl}^-}\). The *propagation* phase yields localized blisters of acidic pH that eventually erupt and expose the corrosion pit.\(^{119}\) The corrosion rate decreases over time, but perforation may occur, and chromium-based coatings have been commonly used.\(^{129,389}\) However, concerns with the environmental impact of hexavalent chromium generated by these coatings impose steep restrictions to their use.\(^{129}\) In searching for potential alternatives, we hypothesize that the presence of an ordered Langmuir-Blodgett (LB) multilayer of molecular metallosurfactants would act as a hydrophobic barrier that decreases access of water, dissolved chlorides, and electrons to the \(\text{Al}_2\text{O}_3\) layer. In this paper we probe the LB films of a bisphenolate zinc(II) complex \([\text{Zn}^{II}(\text{L}^{N2O2})\text{H}_2\text{O}] (1)\) and a bulkier trisphenolate gallium(III) complex \([\text{Ga}^{III}(\text{L}^{N2O3})]\) (2) (Scheme 5.1) as inhibitors for pit corrosion when physisorbed onto 99.0% aluminum substrates. The presence of hydrophobic *tert*-butyl groups installed to the phenolate groups along with hydrophilic alkoxy chains installed to the phenylenediamine bridge renders these species amphiphilic, enabling the formation of ordered molecular films. The presence of redox-inactive 3d\(^{10}\) ions like \(\text{Zn}^{II}\) or \(\text{Ga}^{III}\) confers added structural resistance to the organic framework limiting mobility of adventitious
chlorides, and increases the energies of the ligand-based lowest unoccupied MOs (LUMOs), thus precluding electron transfer through the film.

5.2. Experimental Section

5.2.1. Synthetic Procedure

The ligands [H$_2$L$_{N2O2}$], [H$_3$L$_{N2O3}$], and the metallosurfactant [Zn$_{II}$L$_{N2O2}$H$_2$O] (1) were obtained as described.$^{5, 68}$

The metallosurfactant [Ga$_{III}$L$_{N2O3}$] (2): This product was obtained by treatment of the ligand (0.301 g, 0.330 mmol in anhydrous methanol and dichloromethane (15 mL : 5 mL)) with anhydrous GaCl$_3$ (0.058 g, 0.330 mmol) in presence of anhydrous NaOCH$_3$ (0.054 g, 0.990 mmol). The resulting solution was warmed at 50 °C for 30 minutes, and stirred for 2 h at ambient temperature. The solvent was completely removed, the crude product was dissolved in 20 mL dichloromethane, and filtered through celite. Finally, the solvent was removed to allow precipitation of a yellow microcrystalline powder. Yield: 68%. Anal. Calc. for [C$_{57}$H$_{83}$GaN$_2$O$_7$.2H$_2$O]: C, 67.51; H, 8.65; N, 2.76%. Found: C, 67.53; H, 8.49; N, 2.83%. IR (KBR, cm$^{-1}$) 3190 (ν$_{N-H}$), 2869-2964 (ν$_{C-H}$), 1607 (ν$_{C=C}$, aromatic), 1512 (ν$_{C=C}$, aromatic), 1269 (ν$_{C-O-C}$), 1130 (ν$_{C-O-C}$). $^1$H-NMR, ppm (CDCl$_3$, 400 MHz): δ 1.28 (s, 18H$_{tBu}$), 1.62 (s, 18H$_{tBu}$), 1.07 (s, 9H$_{tBu}$), 1.48 (s, 9H$_{tBu}$), 3.44 (s, 3H$_{OCH_3}$), 3.52 (s, 3H$_{OCH_3}$), 3.76 (t, 2H$_{OCH_2}$), 3.85 (t, 2H$_{OCH_2}$), 3.99 (s, 1H$_{CH_2}$), 4.01 (s, 1H$_{CH_2}$), 4.17 (m, 4H$_{OCH_2}$), 4.31 (t, 2H$_{OCH_2}$), 4.52 (s, 2H$_{CH_2}$), 6.41 (s, 1H$_{ph}$), 6.79 (s, 2H$_{ph}$), 6.90 (s, 1H$_{ph}$), 6.98 (s, 2H$_{ph}$), 7.04 (s, 1H$_{ph}$), 7.17 (s, 1H$_{ph}$).

5.2.2. Isothermal Compression

Curves were measured using a KSV 2000 minitrough with Barnstead NANOpure water as the liquid subphase at a temperature of 23 °C. Impurities on the surface of the subphase were removed by vacuum suction. A 31 µL of 1.0 mg/mL chloroform solution of the metallosurfactant
was introduced on the subphase and allowed to stand for 20 minutes before compression. Surface pressure vs average molecular area isotherms were obtained at a compression rate of 10 mm/min. The Wilhelmy plate method was used to measure the surface pressure. Films were deposited onto a glass substrate at 40 mN/m and the transfer ratio was kept near unity. LB film characterization was done using IRRAS and UV-visible spectrum of the film. The IRRAS spectrum was measured using a Bruker Tensor 27 infrared spectrometer with a Pike A 513/Q variable-angle accessory. UV-visible spectrum of the LB film was taken using a SHIMADZU UV-3600 spectrophotometer. The static contact angles of the films deposited on aluminum substrates were determined by KSV CAM 200 goniometer equipped with a CCD camera at room temperature.

5.2.3. Thickness Measurements

LB films of complexes 1 and 2 were deposited on thermal oxide wafers (300 nm SiO2 layer on Si) and their thickness was measured using a scanning electron microscope. Thickness measurements were taken at nine different cross-sectional areas and the thickness is reported as an average of all measurements. Measurements were taken using a JSM-7600 FE scanning electron microscope.

5.2.4. Electron Passivation Studies

Performed using the BAS 50W potentiostat with three electrode-cells. LB films were deposited on Au electrodes and used as working electrodes. Cyclic voltammograms were performed for LB films deposited at different surface pressures and different numbers of layers.

5.2.5. Surface Analysis

Performed by using 99.0% pure, 0.20 mm thick aluminum foil which was precleaned by ethanol, then with ultrapure water and air dried. Scanning electron micrograph images were taken using a JSM-7600 FE scanning electron microscope.
5.2.6. Potentiodynamic polarization studies

Potentiodynamic polarization measurements were performed using a CHI 650E electrochemical workstation. A three-electrode setup consisted of an aluminum foil with a surface area of 0.5 cm² as the working electrode, a Pt wire as the auxiliary electrode and Ag/AgCl/saturated KCl as the reference electrode. 3.5% NaCl (w/v) solution was prepared from ultrapure water. All experiments were conducted at 25°C. Tafel curves were obtained by scanning the electrode potential between -0.25 V and 0.25 V vs. open circuit potential with a scan rate of 10 mV/s.

5.2.7. Electrochemical Impedance Spectroscopy Measurements

All EIS data were collected at the open circuit potential in 3.5% (w/v) NaCl at 25°C using an electrochemical workstation (CHI 650E, CH Instruments). A carbon sheet (AvCarb MGL190, FuelCellStore, USA) and an Ag/AgCl electrode were used as the counter electrode and the reference electrode. The frequency range was set from 100 kHz to 1 Hz with an excitation amplitude of ± 5 mV. Data were collected at 10 points per decade. All the samples were immersed in the NaCl solution for 30 minutes to achieve the equilibrium before the measurements.

5.3. Results and Discussion

5.3.1. Synthesis and Structural Characterizations

The ligands H₂L²⁻¹, H₃L²⁻¹, and the ZnII species 1 were synthesized as previously described.⁵ The GaIII species 2 was obtained by treating one equiv. of the ligand H₃L²⁻¹ with one equiv. of GaCl₃ in presence of three equiv. of NaOCH₃ in a MeOH:CH₂Cl₂ mixture under inert conditions (Scheme 5.2). The associated mass spectrum showed a peak at m/z = 977.55 attributed to [GaIII⁺L²⁻¹+H+]⁺ in MeOH and elemental analysis is in excellent agreement with the calculated
The FTIR and UV/Vis spectroscopies confirm the amine character of the species, as expected for complexes synthesized under anaerobic conditions.\textsuperscript{68}

### 5.3.2. Redox and Electronic Behavior

Cyclic voltammograms (CV) of 1 and 2 were performed in $1.0 \times 10^{-3}$ mol L$^{-1}$ CH$_2$Cl$_2$ solution using TBAPF$_6$ as supporting electrolyte. Potentials were recorded versus the Fc$^+$/Fc couple. The CV of 1 was recorded previously\textsuperscript{5} and displays well-behaved oxidation processes at 0.22 V$_{Fc/Fc^+}$ ($\Delta E_p = 0.78$ V, $|I_{pa}/I_{pc}| = 0.9$) and at 0.56 V$_{Fc/Fc^+}$ ($\Delta E_p = 0.16$ V, $|I_{pa}/I_{pc}| = 1.2$). Species 2 showed similar features at 0.43 and 0.77 V$_{Fc/Fc^+}$ ($\Delta E_p = 0.10$ and 0.22 V, respectively, Figure 5.1). These

![Figure 5.1](Image)

**Figure 5.1.** Cyclic voltammogram for [Ga$^{III}$L$^{\text{N2O3}}$]$^\text{(2)}$ (1 mM) in DCM. TBAPF$_6$, glassy carbon (WE), Pt wire (AE), Ag/AgCl (RE). Ferrocene is used as an internal standard. Scan rate: 100 mV/s.
processes are attributed to phenolate-to-phenoxy radical conversion\textsuperscript{390-391} with no metal-based reduction observed. The first oxidation is a quasi-reversible 1e\textsuperscript{-} process, while the second is an irreversible 2e\textsuperscript{-} process, as described in other gallium(III) species in similar environments.\textsuperscript{22}

The UV-visible spectra of ligand and complex were taken in dichloromethane. The ligand \([\text{H}_3\text{L}^\text{N}^2\text{O}_3]\) showed an intense band at 281 nm (\(\varepsilon, \sim 12909 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\)) and a shoulder band at \(\sim 304 \text{ nm (}\varepsilon, \sim 7607 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\)) respectively. The \([\text{Ga}^\text{III}(\text{L}^\text{N}^2\text{O}_3)]\) complex exhibited only an intense band at 288 nm (\(\varepsilon= 12805 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\)) that can be attributed to intraligand \(\pi-\pi^*\) charge transfer transitions. \([\text{Ga}^\text{III}(\text{L}^\text{N}^2\text{O}_3)]\) complex has filled d-orbitals, therefore the gallium complex does not show any ligand to metal charge transfer transitions (Figure 5.2).

### 5.3.3. Interfacial Behavior

In order to inhibit corrosion, metallosurfactants must be deposited and physisorbed onto the metal substrate. Langmuir-Blodgett films were deposited using isothermal compression and the behavior of species 1 and 2 at the air/water interface was assessed by surface pressure (\(\Pi, \text{ mN/m}^{-1}\)) vs. average area per molecule (\(A, \text{ Å}^2/\text{molecule}\)) plots and Brewster angle microscopy (BAM). Compression isotherms were performed in a minitrough with movable barriers triggering 2D...
activities at the air/water interface that lead to the formation of Langmuir-Pockels films. The assessment of mono or multilayers, collapse pressures \( (\pi_c) \), and the area at the collapse of the monolayer \( (A_c) \) can be extrapolated. When the barriers are compressed, the tension \( (\gamma) \) of the amphiphile-containing air/water interface decreases as compared to that of the air/water interface only \( (\gamma_0 = 72 \text{ mN·m}^{-1} \text{ at } 23 \, ^\circ\text{C}) \), following an increase in \( \Pi = \gamma_0 - \gamma \). When compression is concomitant to BAM, polarized light passes throughout media with different refractive indexes at the air/water interface revealing agglomerates and domains, as well as film homogeneity in their absence. The behavior of 1 has been described\(^5\) and shows an interaction area of 60 Å\(^2\) molecule\(^{-1}\) with collapse pressure at 45 mN/m. The isotherm and BAM for the Ga\(^{III}\)-containing 2 are shown in Figure 5.3. This species displays interaction in a vapor-like phase at ca.117 Å\(^2\) molecule\(^{-1}\) (Figure 5.3a). Between 10 and 27 mN/m a homogeneous liquid-expanded phase is observed, as supported by lack of BAM activity. Phase rearrangement was observed between 28 and 37 mN/m, likely leading to a condensed phase between 38 and 45 mN/m. Above 42 mN/m the formation of multiple ring-shaped events\(^392\) associated with multilayer granules resulting from the ejection of \( \Pi \), \( (\pi_c) \), and the area at the collapse of the monolayer \( (A_c) \) can be extrapolated. When the barriers are compressed, the tension \( (\gamma) \) of the amphiphile-containing air/water interface decreases as compared to that of the air/water interface only \( (\gamma_0 = 72 \text{ mN·m}^{-1} \text{ at } 23 \, ^\circ\text{C}) \), following an increase in \( \Pi = \gamma_0 - \gamma \). When compression is concomitant to BAM, polarized light passes throughout media with different refractive indexes at the air/water interface revealing agglomerates and domains, as well as film homogeneity in their absence. The behavior of 1 has been described\(^5\) and shows an interaction area of 60 Å\(^2\) molecule\(^{-1}\) with collapse pressure at 45 mN/m. The isotherm and BAM for the Ga\(^{III}\)-containing 2 are shown in Figure 5.3. This species displays interaction in a vapor-like phase at ca.117 Å\(^2\) molecule\(^{-1}\) (Figure 5.3a). Between 10 and 27 mN/m a homogeneous liquid-expanded phase is observed, as supported by lack of BAM activity. Phase rearrangement was observed between 28 and 37 mN/m, likely leading to a condensed phase between 38 and 45 mN/m. Above 42 mN/m the formation of multiple ring-shaped events\(^392\) associated with multilayer granules resulting from the ejection of
matter from the compressed monolayer start to be noticeable and account for the thermodynamic instability and ultimate collapse of the film at ca. 48 mN/m (Figure 5.3b). Collapse follows a Ries constant pressure mechanism. These air/water Langmuir-Pockels films were later transferred onto air/solid interfaces at different surface pressures yielding Langmuir-Blodgett films.

The composition, topology, and defects of the LB films were investigated by infrared reflection absorption spectroscopy (IRRAS). A total of 50 layers of LB-films were deposited keeping the transfer ratio close to unity and using a Y-type dipping method. Data was collected using $p$-polarized light at respective angles of incidence of 20° and 40° for 1 and 2. While the results for 1 were previously discussed, 2 displayed asymmetric and symmetric C-H stretching vibrations at ca. 2860-2960 cm$^{-1}$. The slight shift in the asymmetric C-H stretching vibrations in LB film compared to bulk correlates well with previous studies. In the fingerprint region, bands around 1350-1610 cm$^{-1}$ are assigned to aromatic C=C stretching vibrations and CH$_n$ deformation bands. A new band at 1592 cm$^{-1}$ and absent in the bulk IR spectrum was assigned to C=N stretching associated with amine-to-imine conversion at the air/water interface. This is a

![Figure 5.4. IRRAS spectra of LB films of 2 compared to their bulk IR spectra.](image-url)
Another feature in the IRRAS spectrum is that C-H stretching peaks are pointing upwards (positive) while other peaks are pointing downward (negative). This can be explained by the surface selection rules which states that positive bands are for vibrations with perpendicular transition dipole moments, and negative bands are for vibrations with parallel transition dipole moments. This inversion is due to the formation of anisotropic films with high molecular order. (Figure 5.4). UV-visible spectrum of the LB film was taken using 60-layer deposited glass substrate. UV-visible spectrum of LB film does not correlate well with the solution spectrum of \([\text{Ga}^{III}L_{N2O3}]\) (2). The two new absorption bands were observed at around 352 and 456 nm while the band around 288 nm remain similar to the solution spectrum. According to the previous studies, changes in the UV-visible spectrum of the LB film is due to oxidation of the amine nitrogen to azomethine moiety at the air water interface (Figure 5.5).

Static contact angle measurements were taken to evaluate the characteristic of the 99.0% aluminum substrates and infer the orientation of the molecules in the film. Species 1 and 2 showed respective contact angles of 92.55° and 90.97°, which when compared to the bare aluminum
substrate at 86.47°, confirms enhancement of surface hydrophobicity. This indicates that the tert-butyl rich portions of both metallosurfactants point outwards. This observation is similar to other structurally related metal/phenolate systems.\textsuperscript{17,18}

5.3.4. Charge Transfer Suppression by Metallosurfactants

Pitting is particularly pronounced in Al | metal junctions\textsuperscript{396} and in order to optimize charge transfer suppression, films containing an increasing number of LB layers were probed by CV experiments with $1.0 \times 10^{-3}$ M $K_3[Fe^{III}(CN)_6]$ in 0.1 M KCl aqueous solution at room temperature. The idea is to investigate how many layers are necessary to completely avoid electron transfer from an electrode to a good acceptor such as an Fe\textsuperscript{III} complex in a redox process given by $[Fe^{III}(CN)_6]^{3-} + e^- \rightarrow [Fe^{II}(CN)_6]^{4+}$. A standard electrochemical cell was used, in which LB films of 1 and 2 were deposited on Au plates acting as working electrodes with Ag/AgCl and Pt wire acting respectively as the reference and auxiliary electrodes. For Zn\textsuperscript{II}-containing 1, optimal charge

![Figure 5.6](image-url)

**Figure 5.6.** (a) CVs for the passivation of Au electrode with LB monolayers of 2 at different surface presures, (b) CVs for passivation of Au electrode with different LB layers of 2, at 40 mN/m. CVs were performed in $1.0 \times 10^{-3}$ M $K_3[Fe^{III}(CN)_6]$ in 0.1 M KCl aqueous solution at room temperature and scan rate of 100 mV/s.
transfer suppression was attained with a maximum residual current of 0.002 mA on films containing 11 layers deposited at 33 mN/m.\textsuperscript{5} Monolayers of 2 were probed at three different surface pressures (20, 30, and 40 mN/m) and optimal charge transfer suppression was observed at 40 mN/m. (Figure 5.6a). Because this surface pressure precedes the point in which ring-shaped events appear (42 mN/m) the formation of condensed monolayers is assumed. Therefore, this surface pressure was selected for additional depositions. Maximum charge transfer suppression was attained with a residual current of 0.006 mA (Figure 5.6b). The ligands H\textsubscript{2}L\textsuperscript{N2O2} and H\textsubscript{3}L\textsuperscript{N2O3} showed larger residual currents at 0.025 mA and 0.024 mA, respectively, therefore in a tenfold increase (Figure 5.7). The results suggest that the use of metallated surfactants lead to enhanced charge suppression compared to their respective ligands. These results seem to confirm that redox-inactive 3d\textsuperscript{10} ions increase the energy of the ligand-based LUMOs precluding electron transfer through the film. Furthermore, surfactant 1 shows superior charge transfer suppression, possibly due to packing and film thickness. In order to investigate this aspect, the thickness of the films for 1 and 2 was determined by scanning electron microscopy (SEM).

**Figure 5.7.** Cyclic voltammograms obtained for the passivation of gold electrode using 13 layers of LB films of complex 2 and the ligand H\textsubscript{3}L\textsuperscript{N2O3}. Scan rate: 100 mV s\textsuperscript{-1}. CVs were performed in 1.0 × 10\textsuperscript{-3} M K\textsubscript{3}[Fe\textsuperscript{III}(CN)\textsubscript{6}] in 0.1 M KCl aqueous solution at room temperature.
5.3.10. Film Thickness and Surface Analysis

Eleven layers of metallosurfactant 1 and thirteen layers of 2 were deposited on silicon thermal oxide wafers and the thickness of the cross section was measured. The average thickness for 11 layers of the Zn\textsuperscript{II}-containing 1 was 14.0 nm, whereas 13 layers of the Ga\textsuperscript{III}-containing 2 yielded 13.2 nm (Figure 5.8). The film of [Zn\textsuperscript{II}(L\textsuperscript{N2O2})\textsubscript{2}H\textsubscript{2}O] (1) showed a larger thickness compared to that of [Ga\textsuperscript{III}(L\textsuperscript{N2O3})] (2) suggesting that the bulky trisphenolate ligand tilts while forming the film. This observation is in good agreement with the results of a recent \textit{in situ} spectroelectrochemical study on the orientation changes of a monolayer film of an Fe\textsuperscript{III}-containing metallosurfactant with the same ligand deposited on a Au electrode.\textsuperscript{347} Metallosurfactant 1, based on a bisphenolate ligand, seems to form a well-ordered film.

SEM images were recorded to evaluate the extent of pitting corrosion on aluminum substrates immersed in 3.5% NaCl solutions for different time periods. This environment simulates that found in seawater, and pitting was observed as conical or hemispherical shaped cavities with white gelatinous aluminum hydroxide at the rim of the pits. After being immersed in saline medium for 5 days, the unprotected bare aluminum substrate showed considerably more pithole defects

Figure 5.8. Selected SEM images of the cross section of the 11 layers of complex 1 and 13 layers of complex 2.
compared to those aluminum substrates protected by the deposition of molecular LB films (Figures 5.9). However, substrates protected with films of the unmetallated ligands displayed more pitting than those substrates protected by Zn$^{II}$- and Ga$^{III}$-containing metallosurfactants. After 10 days of immersion, the protected aluminum substrates showed dramatically less corrosion than the unprotected aluminum substrates (Figures 5.10).
**Figure 5.9.** SEM images of Al substrates: blank, 11 layers of $\text{H}_2\text{L}^\text{N2O2}$, complex 1 and 13 layers of $\text{H}_3\text{L}^\text{N2O3}$, complex 2 before and after 5 days immersed in 3.5% NaCl solution.

**Figure 5.10.** SEM images of Al substrates: blank, 11-layer LB film of 1 and 13-layer LB film of 2 before and after 10 days immersed in 3.5% NaCl solution.
5.3.5. Electrochemical Corrosion Analysis

To study the corrosion resistance properties of the LB films, potentiodynamic polarization experiments were performed by employing a three-electrode cell with the sample as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl as the reference electrode. By extrapolating the linear parts of the anodic and cathodic curves to their intersection, we can obtain the corrosion potential ($E_{corr}$) and the corrosion current ($i_{corr}$). Inhibition efficiency can be calculated from the measured $i_{corr}$ values based on Equation 5.1:397

$$\% \text{ Inhibition efficiency} = \left( \frac{i_{corr} - i'_{corr}}{i_{corr}} \right) \times 100 \quad (\text{Equation 5.1})$$

In which, $i_{corr}$ and $i'_{corr}$ are the corrosion current values of the bare aluminum and LB-film coated aluminum, respectively. Both samples and blank were immersed in 3.5% NaCl for 30 min at room temperature before potentiodynamic polarization studies. The corrosion potentials of (i) bare substrate, (ii) Ga$^{III}$-containing 2, and (iii) Zn$^{II}$-containing 1 were −0.825 V, −0.789 V and −0.764

![Figure 5.11](image-url)  

**Figure 5.11.** Potentiodynamic polarization curves after 30 min exposure to 3.5% NaCl. A scan rate of 10 mV s$^{-1}$ was used for the experiment performed in 3.5% NaCl solution.
V, respectively. In saline medium, corrosion current for bare aluminum substrate was 9.929 µA/cm². The [Zn^{II}(L_{N2O2})H_2O] (1) surfactant displayed a corrosion current of 2.248 µA/cm², associated with the inhibition efficiency of 77%, while the [Ga^{III}(L_{N2O3})] (2) surfactant exhibited a corrosion current of 3.766 µA/cm² with an inhibition efficiency of 62%. Increase in the corrosion potential and decrease in the corrosion current density of the substrates protected by the molecular films are evidence for the corrosion inhibition efficiency of 1 and 2. The Zn^{II}-containing species 1 showed higher inhibition efficiency compared to the Ga^{III}-containing 2 (Figure 5.11).

The corrosion resistance properties of metallosurfactants 1 and 2 were further investigated by electrochemical impedance spectroscopy (EIS). All data were collected at the open circuit potential in 3.5% NaCl. Figure 5.12a shows the Nyquist plots for the bare aluminum and the samples with different coatings (including 1, 2, H_2L_{N2O2}, and H_3L_{N2O3}). ZView 2.1 software was used to analyze and fit the data to the equivalent circuit shown in Figure 5.12b. R_s represents the

![Figure 5.12](image)

**Figure 5.12.** (a) Overlay of Nyquist plots for the blank aluminum and the aluminum substrates with different coatings. EIS experiments were performed in 3.5% NaCl solution. (b) Equivalent circuit used for modelling the EIS data.
solution resistance between aluminum foil and the reference electrode. $R_{ct}$ is the charge transfer resistance to the corrosion reaction at the metal/solution interface. $C_{dl}$ stands for the capacitance of the double layer of the sample, which normally behaves as a constant phase element rather than a pure capacitor. The results of the EIS modeling are summarized in Table 5.1. A higher $R_{ct}$ value indicates a higher resistance to the corrosion. Both aluminum substrates coated with 1 and 2 show significantly larger $R_{ct}$ than the bare, unprotected substrate (144 and 113 kΩ.cm$^2$ vs 28 kΩ.cm$^2$, respectively). Because aluminum substrates coated with the ligands $\text{H}_2\text{L}^{\text{Nzo}_2}$ and $\text{H}_3\text{L}^{\text{Nzo}_3}$ exhibited lower $R_{ct}$ compared to substrates coated with 1 and 2, the increased $R_{ct}$ values of substrates coated with metallosurfactants give evidence of the structural role of redox-inactive metal ions such as zinc and gallium in metallosurfactants for molecular films and coatings.

Table 5.1. Electrochemical parameters of Al samples obtained by fitting EIS data to the equivalent circuit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω. cm$^2$)</th>
<th>$R_{ct}$ (Ω. cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Al</td>
<td>5.67</td>
<td>28024</td>
</tr>
<tr>
<td>$<a href="1">\text{Zn}^{\text{II}}(\text{L}^{\text{Nzo}_2})\text{H}_2\text{O}</a>$</td>
<td>8.63</td>
<td>144106</td>
</tr>
<tr>
<td>$<a href="2">\text{Ga}^{\text{III}}(\text{L}^{\text{Nzo}_3})</a>$</td>
<td>7.82</td>
<td>113339</td>
</tr>
<tr>
<td>$\text{H}_2\text{L}^{\text{Nzo}_2}$</td>
<td>8.75</td>
<td>70064</td>
</tr>
<tr>
<td>$\text{H}_3\text{L}^{\text{Nzo}_3}$</td>
<td>5.54</td>
<td>53761</td>
</tr>
</tbody>
</table>

5.4. Conclusions

In conclusion, we have evaluated the behavior of two metallosurfactants, $[\text{Zn}^{\text{II}}(\text{L}^{\text{Nzo}_2})\text{H}_2\text{O}]$ (1) and $[\text{Ga}^{\text{III}}(\text{L}^{\text{Nzo}_3})]$ (2), along with their metal-free and protonated ligands as precursors for molecular films capable of inhibiting pitting corrosion on aluminum surfaces. CV experiments indicate that 11-13 LB layers suffice to passivate electron transfer much more effectively than their respective ligands. SEM images, potentiodynamic polarization studies and impedance
spectroscopy confirmed that both molecular LB films of 1 and 2 inhibit corrosive pitting, with the Zn$^{II}$ species showing superior inhibition associated with an inhibition efficiency of 77%. This high inhibition is explained by structural and electronic contributions of the 3d$^{10}$ metal ions, as well as by the thickness and order of the LB films. As such, the thicker and better ordered 1 passivates electron transfer more efficiently.

These results clearly evidence the value of molecular films based on non-redox metallosurfactants in the inhibition of pitting corrosion on aluminum surfaces. Ongoing studies involve enhancement of ligand hydrophobicity and use of covalent interactions between molecular film and the Al$_2$O$_3$ layer that covers the metal substrate.
CHAPTER 6: ELECTROCHEMICAL QUANTIFICATION OF CORROSION INHIBITION ON IRON SURFACES WITH [N\textsubscript{2}O\textsubscript{3}] GALLIUM(III) AND [N\textsubscript{2}O\textsubscript{2}] ZINC(II) METALLOSURFACTANTS


6.1. Introduction

Corrosion is the deterioration of a metal surface caused by chemical and electrochemical interaction with its surrounding environment. It is an inevitable problem confronted by almost all industries at an annual cost of $2.5 trillion, equivalent to 3.4% of the global gross domestic product.\textsuperscript{399} Aqueous iron corrosion consists of an anodic reaction which causes metal dissolution as Fe\textsuperscript{2+} ions and the cathodic reduction of H\textsuperscript{+} and O\textsubscript{2} present in the electrolyte solution. Saline and acidic media expedite iron corrosion because they facilitate and intensify electron transfer,\textsuperscript{400} leading to the formation of hydrated iron(III) oxide or Fe\textsubscript{2}O\textsubscript{3}. xH\textsubscript{2}O, the thermodynamically stable product known as rust.\textsuperscript{130, 401}

The search for corrosion prevention strategies may lead to considerable global savings,\textsuperscript{399, 402} and the use of protective coatings can be beneficial to the preservation of iron surfaces.\textsuperscript{125-126} Coatings usually consist of layered protective systems encompassing pretreatment, primer, and top coat. Relevant to this study, the pretreatment layer is directly physisorbed or chemisorbed to the metal surface and chromium(III)-based systems have been traditionally favored.\textsuperscript{127-128} Environmental concerns with hexavalent chromium impose steep restrictions to the use of chromium-based coatings.\textsuperscript{129} The discovery of new and more benign inhibitors has attracted considerable attention,\textsuperscript{226-227, 264, 380-381, 403-406} and surfactants figure among well-known molecular inhibitors.\textsuperscript{130, 133, 136-137, 158, 161, 407-411}
We recently reported on Langmuir-Blodgett (LB) films of phenolate-rich metallosurfactants \([\text{Ga}^{\text{III}}(\text{L}^{\text{N2O3}})] (1)\) and \([\text{Zn}^{\text{II}}(\text{L}^{\text{N2O2}})\text{H}_2\text{O}] (2)\) that seem to behave as a surface pretreatment for corrosion inhibition on iron\(^{412}\) and aluminum\(^{313}\) surfaces. Metallosurfactants 1 and 2 are designed to contain hydrophobic \textit{tert}-butyl groups installed to the phenolates along with hydrophilic alkoxy chains installed to a phenylenediamine bridge that enable physisorption to the metal surface. These species accommodate the redox-inert 3\textit{d}\(^{10}\) ions gallium(III) and zinc(II) (Scheme 6.1) in order to confer added structural resistance to the organic framework and increase the energies of empty ligand-based molecular orbitals (LUMOs), precluding electron transfer through the film. As a consequence these species show qualitative inhibition of the corrosive process.\(^{412, 313}\) Those studies were focused on non-electrochemical techniques based on weight loss\(^{413}\) and SEM measurements to assess corrosion inhibition on iron surfaces. Because a quantitative analyses of the inhibition abilities of these materials to prevent metal dissolution and oxygen reduction is still lacking, in this study we assess the properties of 1 by non-electrochemical methods and compare with those of 2, and then use the more sophisticated electroanalytical techniques of impedance spectroscopy and potentiodynamic polarization. This comprehensive evaluation enables a more

**Scheme 6.1.** The metallosurfactants \([\text{Ga}^{\text{III}}(\text{L}^{\text{N2O3}})] (1)\) and \([\text{Zn}^{\text{II}}(\text{L}^{\text{N2O2}})\text{H}_2\text{O}] (2)\).
complete characterization of the corrosion inhibition behavior of these species and informs about the viability and limitations of these metallosurfactants in mitigating corrosion.

6.2. Experimental Section

6.2.1. Syntheses and Film Deposition

Ga^{III}(L^{N2O3}) \) (1) and \([\text{Zn}^{II}(L^{N2O2})\text{H}_2\text{O}] \) (2) complexes were synthesized according to published procedures.\(^{313, 412}\) LB films were deposited on iron substrates using a KSV 2000 minitrough. The Langmuir-Blodgett (LB) films were deposited at the air|water interface at a surface pressure of 40 and 33 \(\text{mN/m}\) for 1 and 2, respectively, with an average transfer ratio kept near unity.

6.2.2. Charge Transfer Suppression Studies

Charge transfer suppression studies were performed using a 3-electrode setup. Gold substrates coated with 13 LB layers of 1 or 11 LB layers of 2 were used as the working electrodes, Pt wire was used as the auxiliary electrode, and Ag/AgCl as the reference electrode.

6.2.3. Qualitative Corrosion Analysis

Corrosion experiments were performed using 99.5% iron foil substrates with 0.20 mm thickness. The substrates were abraded using 600 grade emery papers, polished with 0.05 micron alumina powder, then rinsed with ethanol and ultrapure water, and air dried. For agar gel experiments, the agar sample was prepared by using 0.25 g of agar, 2% phenolphthalein, 0.1 M \(\text{K}_3[\text{Fe}^{III}(\text{CN})_6]\) and 3% \(\text{NaCl}\) or 0.01 M \(\text{H}_2\text{SO}_4\) depending on the acidic or saline corrosion. Scanning electron micrograph images were taken using a JSM -7600 FE scanning electron microscope.

6.2.4. Potentiodynamic Polarization Studies

Potentiodynamic polarization measurements were conducted using a CHI 650E electrochemical workstation. A three-electrode setup consisted of an iron foil with a surface area of 0.5 \(\text{cm}^2\) as the working electrode, Ag/AgCl/saturated KCl as the reference electrode, and a Pt wire as the auxiliary
electrode. 3.5% NaCl (w/v) and 0.01M H₂SO₄ solutions were prepared from ultrapure water. All experiments were conducted at 25°C. Tafel curves were obtained by scanning the electrode potential between -0.25 V and 0.25 V vs. open circuit potential with a scan rate of 10 mV/s. All the measurements were carried out in triplicate and the corrosion current values recorded as average ± standard deviation.

6.2.5. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy data were collected using a CHI 650E electrochemical workstation. The iron substrate was the working electrode, a fresh carbon sheet (AvCarb MGL190, FuelCellStore, USA) was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The electrolyte solution was 3.5% NaCl (w/v) or 0.01 M H₂SO₄. The initial potential of the working electrode was set at the open circuit potential. The frequency range was from 100 kHz to 0.01 Hz with an excitation amplitude of 5 mV. Data were collected at 12 points per decade of frequency. The samples were immersed in the corrosion test solutions (3.5% NaCl or 0.01 M H₂SO₄) for 30 minutes to reach equilibrium before the measurements. ZView 2.1 software was used to fit the data to an equivalent circuit. \( R_s \) represents the solution resistance between the Fe substrate and the reference electrode. \( R_{ct} \) is the charge transfer resistance at the metal/solution interface. The capacitance of the electrical double layer (\( C_{dl} \)) of the working electrode was modeled as a constant phase element.

6.2.6. UV-Visible Spectroscopy

UV-visible spectra were recorded with standard quartz cells at room temperature in 1.0x10⁻⁴ or 1.0x10⁻⁵ M wet methanol (2-3% water) solutions of 1, 2, FeCl₂•xH₂O or FeCl₃•xH₂O under aerobic conditions. A Shimadzu 3600 UV-Vis-NIR spectrophotometer operating in the range of 190 to 1600 nm was utilized. Values of \( c \) are given in M⁻¹ cm⁻¹.
6.3. Results and Discussion

6.3.1. Synthesis of the Metallosurfactants

The species $[\text{Ga}^{III}(\text{L}^{N2O3})]$ (1) and $[\text{Zn}^{II}(\text{L}^{N2O2})\text{H}_2\text{O}]$ (2) were synthesized as reported by us elsewhere. In brief, the ligand $\text{H}_3\text{L}^{N2O3}$ was obtained by treating 4,5-bis(2-methoxyethoxy)benzene-1,2-diamine with 2,4-di-tert-butyl-6-(chloromethyl) phenol in the presence of triethylamine, while $\text{H}_2\text{L}^{N2O2}$ was synthesised by treating the above mentioned diamine precursor with 3,5-di-tert-butyl-2-hydroxybenzaldehyde under an inert atmosphere in methanol under reflux. Species 1 was obtained by treatment of one equiv. of the purified $\text{H}_3\text{L}^{N2O3}$ ligand with one equiv. of $\text{GaCl}_3$, whereas 2 was synthesised by treating one equiv. of $\text{H}_2\text{L}^{N2O2}$ with one equiv. of $\text{Zn}^{II}\text{Cl}_2.6\text{H}_2\text{O}$ under refluxing conditions. Both procedures require the presence of $\text{NaOCH}_3$ to deprotonate the phenol groups into coordinating phenolates.

6.3.2. Interfacial Properties

The interfacial properties that lead to the formation of mono and multilayered LB films by $[\text{Ga}^{III}(\text{L}^{N2O3})]$ (1) and $[\text{Zn}^{II}(\text{L}^{N2O2})\text{H}_2\text{O}]$ (2) were studied using surface pressure ($\pi$, mN/m) vs. average molecular area ($A$, Å$^2$/molecule) isothermal compression and Brewster angle microscopy (BAM) at 23±1 °C. The isothermal compression curve for 1 (Figure 6.1a) at the air/water interface showed an area of intermolecular interaction at approximately 120 Å$^2$/molecule. An initially homogeneous Langmuir-Pockels (LP) film with no remarkable BAM activity was observed between 10 and 27. Compression of this liquid-expanded film was followed by phase rearrangement between 28 and 37 mN/m to yield another homogeneously looking condensed phase film between 38 to 45 mN/m. BAM data (Figure 6.1b) reveals the formation of granular
Figure 6.1. (a) Isothermal compression curve for 1 (b) Selected BAM micrographs of 1 (c) Isothermal compression curve for 2 (d) Selected BAM micrographs of 2.

Texture above 42 mN/m as the compressed monolayer becomes thermodynamically unstable and forms localized multilayer regions that lead to film collapse at ca. 47-48 mN/m following a constant pressure mechanism. Interaction for 2 starts at around 60 Å²/molecule with further compression of the LB film yielding a homogeneous film between 10 and 44 mN/m (Figure 6.1c). Although a minor change in slope is visible at ca. 30 mN/m, uneventful BAM images support the formation of a homogenous film. Like for the more obvious 1 this change is likely associated with a phase transition. An area of about 65 Å²/molecule is registered at 45 mN/m, prior to collapse: BAM images reveal the presence of arrays of Newton rings (Figure 6.1d). Langmuir-Blodgett (LB) films were deposited on glass substrates as Y-type multilayers while keeping the transfer ratio close to unity, and were studied using infrared reflection absorption spectroscopy (IRRAS) with p-polarized light at 40° and 20° incidence for 1 and 2. The films for both species displayed asymmetric and symmetric C-H stretching vibrations between 2860-2960 cm⁻¹, therefore slightly shifted from the asymmetric C-H stretching vibrations observed in bulk. Other bands observed around 1350-1610 cm⁻¹ are associated with aromatic C=C stretching vibrations and CH₃ deformation bands. Species 2 shows a band at 1592 cm⁻¹ assigned to the C=N
stretching of the imine ligand. Allied to previous IRRAS and static contact measurement studies, these results confirm that the hydrophilic ethoxymethoxy chains of species 1 and 2 interact with the iron substrate by physisorption while the t-butyl-decorated phenolates that envelop the metal centers groups point outwards. While a stronger covalent interaction would be beneficial, this molecular arrangement enhances the hydrophobicity of the surface to be protected.

6.3.3. Charge Transfer Suppression by Metallosurfactants

Cyclic voltammetry experiments were performed to determine whether LB films of 1 and 2 suppress electron transport on gold electrodes. An aqueous $1.0 \times 10^{-3}$ M $K_3[Fe^{III}(CN)_6]$ solution in 0.1 M KCl was added to a standard 3-electrode cell equipped with gold plates coated with 1-13 LB layers of 1 and 2 at room temperature. The coated gold plates were used as working electrodes, whereas Ag/AgCl and Pt wire were respectively used as the reference and auxiliary electrodes. Initially, the reversible redox wave associated with the $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4-}$ couple was observed for bare gold electrodes, but decreased significantly upon coating with a monolayer of 1 or 2. To optimize the most adequate deposition pressures that yield ordered films able to suppress charge transfer, monolayers were deposited on gold substrates at three different surface pressures, namely 20, 30, and 40 mN/m. These surface pressures are associated with respective average molecular areas of 80, 64, and 35 Å$^2$/molecule for 1 and 51, 47, and 44 Å$^2$/molecule for 2 and are related to film uniformity. Best suppression was observed in monolayers deposited at 40 mN/m for 1, while 30 mN/m worked best for 2. As the number of insulating LB layers increased, charge transfer between the $[Fe^{III/II}(CN)_6]^{3-}$ species and the electrode became less and less pronounced, being negligible after 10 layers. Near complete charge suppression was attained at 13 layers for 1, with a residual current of 0.006 mA, and at 11 layers for 2 with a current of 0.002 mA. The
stability of the deposited LB films was tested under acidic conditions by immersing each of the gold electrodes protected either by 13 layers of 1 or 11 layers of 2 in 0.01M H$_2$SO$_4$ for three, five and eight days. **Figure 6.2** shows charge transfer suppression of gold electrodes with 1. The stability of ligands H$_3$L$_{N2O3}$, H$_2$L$_{N2O2}$ was also studied in acidic solution (**Figure 6.3**). Impressively, the maximum current for both metallosurfactants only reached a maximum of 0.02 mA, while the
ligands showed higher currents of 0.05 and 0.06 mA, respectively. This result confirms that the metallosurfactants withstand the acidic environment and retain their metal centers.

6.3.4. Qualitative Corrosion Analysis

Iron corrosion is an electrochemical process that depends on the concentration of oxygen, iron(II) and iron(III) species, pH, and presence of electrolytes to trigger complex mechanisms. Under aerobic conditions, the main steps can be summarized by the semi-reactions listed in Equations 6.1-6.4:

\[
2\text{Fe}^0_{(s)} \rightarrow 2\text{Fe}^{2+}_{(aq)} + 4e^- \quad (\text{Anodic}) \quad (\text{Equation 6.1})
\]

\[
\text{O}_2_{(g)} + 2\text{H}_2\text{O}_{(l)} + 4e^- \rightarrow 4\text{OH}^-_{(aq)} \quad (\text{Cathodic}) \quad (\text{Equation 6.2})
\]

\[
\text{Fe}^{2+} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe(OH)}_{2(s)} \quad (\text{Equation 6.3})
\]

\[
\text{Fe(OH)}_{2(s)} + \text{O}_2_{(g)} \rightarrow \text{Fe}_2\text{O}_3\cdot x\text{H}_2\text{O}_{(s)} \quad (\text{Equation 6.4})
\]

The cathodic step is determinant and rates of reaction for each of the above steps increase significantly when in acidic or saline media, where electron transfer is facilitated. Materials able to inhibit corrosion must withstand such conditions and either prevent the anodic dissolution of the metal (Equation 6.1) or the cathodic reduction of oxygen (Equation 6.2). The effect of these media on 99.5% iron surfaces coated by LB films of [Ga^{III}(L^{N2O3})] (1) can be investigated by ferroxyll staining and compared to that of [Zn^{II}(L^{N2O2})H_2O] (2). Iron substrates measuring 10 × 25 mm are placed in a Petri dish filled with warm agar containing the acid-base indicator phenolphthalein, potassium ferricyanide K_3[Fe^{III}(CN)_{6}], and either 3% NaCl or 0.01 M H_2SO_4. Upon cooling, the agar forms a semi-solid gel that encases the substrate while the indicators are used to identify the corrosion processes taking place in the anode and in the cathode. Phenolphthalein, colorless in acidic and neutral media, turns pink in the presence of OH^- ions at the cathode indicating the absence of iron oxidation. Potassium ferricyanide reacts with Fe^{2+} ions...
formed during the corrosion process yielding a visible Prussian blue complex at the anode. Experiments were performed with iron substrates having half of their length covered with 13 layers of 1, whereas the other half is left bare; the substrates are exposed to both saline and acidic media over a course of one and seven days. For emphasis on the iron degradation process, experiments were also carried out in the absence of phenolphthalein (Figure 6.4 and Figure 6.5). In both experiments, no blue coloration associated with Fe$^{2+}$ generation was observed in the coated region, indicating that the film acts as a corrosion protection barrier in both acidic and saline media. This protective behavior indicates that iron oxidation and dissolution is substantially curbed, although oxygen reduction persists. Because iron(II) generation is inhibited, formation of rust, as described in Equation 6.3-6.4 is partially prevented. A similar response is observed for metallosurfactant 2.
Scanning electron micrograph (SEM) images were recorded to evaluate the formation and agglomeration of Fe$_2$O$_3$$\cdot$$x$H$_2$O$_{(s)}$, rust, on the iron substrates immersed in 0.01 M H$_2$SO$_4$ and 0.1 M NaCl solutions for 5 days. In acidic medium, the bare section of the iron substrates exhibited well-defined granular rust formation, while corrosion was inhibited in the section coated with LB films of 1. In saline medium, iron plates were degrading with the formation of an insoluble black material visually similar to magnetite-like Fe$_3$O$_4$. In saline medium, the bare section of the iron substrates showed a rougher surface compared to the coated section (Figure 6.6). Metallosurfactant 2 showed visually similar results reported elsewhere.$^{412}$

Figure 6.5. Ferroxyll staining for acidic corrosion after 1 and 7 days. Bare iron substrates on (a) and (d), substrates coated with 13 layers of 1 on (b) and (e) and substrates coated with 13 layers of 1 without phenolphthalein on (c) and (f).
6.3.5. Quantitative Corrosion Analysis

We carried out potentiodynamic polarization and electrochemical impedance spectroscopy measurements to quantify the ability of metallosurfactants \([\text{Ga}^{III}(\text{L}^{\text{N}_2\text{O}_3})]\) (1) and \([\text{Zn}^{II}(\text{L}^{\text{N}_2\text{O}_2})\text{H}_2\text{O}]\) (2) to act on metal dissolution (Equation 6.1) or on oxygen reduction (Equation 6.2). Potentiodynamic polarization experiments provide information on the corrosion potential and current density, and were performed using a three-electrode setup, where iron substrates were used as the working electrode, a Pt wire as the auxiliary electrode, and Ag/AgCl as the reference electrode. We evaluated the corrosion inhibition ability of 1 and 2 in saline and acidic solution by immersing the metallosurfactant-coated iron substrates in a 3.5% NaCl or 0.01M H\(_2\)SO\(_4\) for 30 min before the electrochemical measurement. Corrosion currents (\(i_{\text{corr}}\)) and corrosion potentials (\(E_{\text{corr}}\)) were obtained by extrapolating the small linear parts of both anodic and cathodic polarization curves known as Tafel lines to their intersection (Figure 6.7).\(^{417}\) If the displacement
leads to $E > E_{corr}$ anodic polarization for metal oxidation in $E_{corr}$ informs the inhibition activity. If greater than $85 \text{ mV}/E_{corr}$, either the cathodic or anodic steps are inhibited. For displacements smaller than $85 \text{ mV}/E_{corr}$ a mixed type inhibition takes place and both anodic and cathodic steps are affected. The Tafel slopes $\beta_a$ and $\beta_c$ inform about the anodic and cathodic polarization constants and the possible alterations of mechanisms by which corrosion takes place. Inhibition efficiencies (IE$_{pol}$%) were calculated using \textbf{Equation 6.5} \textsuperscript{317}

$$\text{IE}_{pol}\% = \left( \frac{i_{corr} - i'_{corr}}{i_{corr}} \right) \times 100 \quad (\text{Equation 6.5})$$

where $i_{corr}$ and $i'_{corr}$ are the corrosion current values of the bare and coated substrates, respectively. \textbf{Table 6.1} summarizes the data.
In saline medium there is a significant decrease in the corrosion currents for the LB-coated substrates, as compared to the bare iron substrates. The corrosion current for the bare iron reached 64±4 µA/cm², whereas the iron substrate protected with either the Ga-containing 1 or the Zn-containing 2 showed respective corrosion currents of 40±9 µA/cm² and 32±7 µA/cm² with averaged IEpol% of 38% for 1 and 50% for 2. This decrease indicates that these metallosurfactants inhibit the corrosion process. The $E_{corr}$ shifts towards less negative potentials, thus indicating that the modified surfaces are more resistant to corrosion than the bare substrates. With the metallosurfactants, the anodic curves move toward a lower current density region, while the variations of cathodic curves are not obvious. This phenomenon suggests that inhibition takes place by limiting the anodic reaction of metal dissolution (Equation 6.1). This is in good agreement

**Figure 6.8.** Potentiodynamic polarization curves for Blank, 1 and 2 (a) in 3.5% NaCl. (b) in 0.01 M H$_2$SO$_4$. Scan rate: 10 mV s$^{-1}$.

**Table 6.1.** Electroanalytic parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA/cm²)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_c$ (mV/dec)</th>
<th>Avg. IEpol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-542</td>
<td>64±4</td>
<td>128.1</td>
<td>-525.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-468</td>
<td>40±9</td>
<td>119.3</td>
<td>-426.8</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>-438</td>
<td>32±7</td>
<td>101.8</td>
<td>-437.7</td>
<td>50</td>
</tr>
<tr>
<td>Acidic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-561</td>
<td>167±9</td>
<td>92.9</td>
<td>-193.1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-559</td>
<td>145±3</td>
<td>86.8</td>
<td>-176.0</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>-556</td>
<td>137±5</td>
<td>88.7</td>
<td>-177.0</td>
<td>18</td>
</tr>
</tbody>
</table>
with the ferroxyl staining shown in Figures 6.4-6.5. The variability of the cathodic and anodic slopes ($\beta_c$ and $\beta_a$) with the presence of molecular films imply that oxygen reduction and metal dissolution were affected without modifying the mechanism of corrosion. Substrates with deposited films also showed more positive corrosion potentials of $-468$ mV$_{Ag/AgCl}$ and $-438$ mV$_{Ag/AgCl}$ for 1 and 2 than for bare iron substrates ($-542$ mV$_{Ag/AgCl}$), further confirming the inhibition efficiency of both metallosurfactants.

Similar results were found for corrosion tests in acid. The $i_{corr}$ and $E_{corr}$ of the bare iron substrates reached 167±9 $\mu$A/cm$^2$ and -561 mV$_{Ag/AgCl}$, respectively. Substrates coated with metallosurfactant 1 showed a corrosion current and corrosion potential of 145±3 $\mu$A/cm$^2$ and -559 mV$_{Ag/AgCl}$, while these two values for substrates coated with 2 are 137±5 $\mu$A/cm$^2$ and -556 mV$_{Ag/AgCl}$, respectively. Similar to the results for saline, $E_{corr}$ shifts towards less negative values associated with metal dissolution inhibition, although with a considerably lower variation. Based on these results, the average $IE_{pol}$% value for 1 was calculated at 13%, whereas that of 2 was found at 18%. These observations suggest that coated substrates show higher inhibition efficiency in the saline medium compared to the acidic medium (Figure 6.8).
Electrochemical impedance spectroscopy was used to further assess the corrosion inhibition ability of the films of metallosurfactants 1 and 2. Figure 6.9 shows the Nyquist plots of the bare iron substrates and iron substrates coated with the metallosurfactants 1 and 2 in 3.5% NaCl and in 0.01 M H₂SO₄. Charge transfer resistance (R\text{ct}) values were obtained by fitting the data to an equivalent circuit (Figure 6.10, Table 6.2). Inhibition efficiencies (IE\text{imp}%) from charge transfer resistance (R\text{ct}) was calculated using following Equation 6.6.\textsuperscript{154, 410, 419}

\[ \text{IE}_{\text{imp}}\% = \left( \frac{R_{\text{ct}} - R'_{\text{ct}}}{R'_{\text{ct}}} \right) \times 100\% \]

where \( R'_{\text{ct}} \) and \( R_{\text{ct}} \) are the charge transfer resistance of the LB-film coated substrate and the bare substrate, respectively. In 3.5% NaCl, iron substrates coated with 1 and 2 showed a notably higher \( R_{\text{ct}} \) than the observed for the bare substrate (825.7 and 802.8 \( \Omega \cdot \text{cm}^2 \) vs 703.0 \( \Omega \cdot \text{cm}^2 \), respectively). Substrates coated with 1 and 2 showed respective inhibition efficiencies of 15% and 12%. Similar measurements were performed in 0.01 M H₂SO₄. All iron substrates showed significantly smaller
R_{ct} values in H\textsubscript{2}SO\textsubscript{4} than those in 3.5\% NaCl. Nonetheless, the substrates coated with 1 and 2 still showed slighty higher R_{ct} values than bare iron, indicating some degree of corrosion inhibition.

6.3.6. Acidic Inhibition and Coordination Chemistry

All methods used in this study point out to two observations: (i) the metallosurfactants [Ga\textsuperscript{III}(L\textsubscript{N\textsuperscript{2}O\textsuperscript{3}})] (1) and [Zn\textsuperscript{II}(L\textsuperscript{N\textsuperscript{2}O\textsuperscript{2}})H\textsubscript{2}O] (2) act predominantly on the anodic reaction associated with metal dissolution (Equation 6.1), and (ii) the inhibition activity is pronounced in saline and modest in acidic media. In fact the anodic process described in Equation 6.1 is best described as:

\[ \text{Fe}^0 + 6\text{H}_2\text{O} \rightarrow [\text{Fe}^{	ext{II}}(\text{H}_2\text{O})_6]^{2+} + 2e^- \text{ (Equation 6.7)} \]

Because the rates of corrosion depend heavily on the presence of acids and electrolytes, sulfuric acid self-regenerates in presence of Fe\textsuperscript{2+} perpetuating the corrosion process that can be summarized in Equations 6.8-6.11 as follows: \[ \text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{FeSO}_4 \text{ (Equation 6.8)} \]

\[ 2\text{Fe}^{2+} + 3\text{SO}_4^{2-} \rightarrow \text{Fe}_2(\text{SO}_4)_3 \text{ (Equation 6.9)} \]

\[ 4\text{FeSO}_4 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 4\text{H}_2\text{SO}_4 \text{ (Equation 6.10)} \]

\[ 4\text{H}_2\text{SO}_4 + 4\text{Fe}^{2+} + 2\text{O}_2 \rightarrow 4\text{FeSO}_4 + 4\text{H}_2\text{O} \text{ (Equation 6.11)} \]

Therefore, in aqueous solution the salts described as FeSO\textsubscript{4} and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} are the complex octahedral species hexaaquaferrous and hexaaquaferric sulfates [Fe\textsuperscript{II}(H\textsubscript{2}O\textsubscript{6})](SO\textsubscript{4}) and [Fe\textsuperscript{III}(H\textsubscript{2}O\textsubscript{6})\textsubscript{2}](SO\textsubscript{4})\textsubscript{3}, respectively. This self-regenerating acidic environment may enable localized high-concentrations of iron sufficient to compete with the Ga\textsuperscript{3+} and Zn\textsuperscript{2+} ions coordinated to the ligands that form metallosurfactants 1 and 2. To test this possibility we have treated wet methanolic solutions of 1.0x10^{-4}M 1 and 1.0x10^{-5}M 2 with 0.25, 0.5 and 1 equivalent of FeCl\textsubscript{2} and
FeCl$_3$•6H$_2$O salts and followed the spectroscopic changes that take place (Figure 6.11, Figure 6.12). [Ga$^{III}$($L^{N2O3}$)] (1) has bands at 287 ($\varepsilon = 12,460$), 348 (1,580), 448 nm (1,470 M$^{-1}$cm$^{-1}$) and the addition of Fe$^{II}$ led to negligible changes. However, the aerobic environment and the triply negative pocket in the ligand ($L^{N2O3}$)$^3$- strongly favor Fe$^{III}$ coordination. In this case prominent changes were observed when 1 equiv. of Fe$^{III}$ was added to 1; the band at 287 nm increased its $\varepsilon$ to 16,000 and was followed by a broad and complex area with three overlapping bands at ca. 330, 350, and 370 nm of similar $\varepsilon \approx 5,000$, while the band at 448 nm doubled its intensity to 2900 M$^{-1}$cm$^{-1}$ and displayed a shoulder at ca. 460 nm. This behavior indicates the presence of multiple species. However, the more intense band at 287 nm and those at 330 and 370 nm are relevant because they coincide with the previously reported$^{68}$ spectrum for the isolated and characterized [Fe$^{III}$($L^{N2O3}$)]. The last two bands are diagnostic of phenolate-to-Fe$^{III}$ charge transfer and can be detected in solutions containing [Ga$^{III}$($L^{N2O3}$)]:Fe$^{III}$ ratios of 2:1 and 4:1, confirming that replacement of Ga by Fe ions in 1 is a relevant mechanism of deactivation and explaining the marginal inhibition provided by this species when in acidic media.

Figure 6.11. Spectral changes related to the addition of 1 equiv. FeCl$_2$•xH$_2$O and FeCl$_3$•xH$_2$O to (a) 1 and (b) 2 in methanol.
The behavior of the zinc-containing \( \text{Zn}^{\text{II}}(\text{L}^{\text{N2O2}})\text{H}_2\text{O}^2 \) is more subtle due to the large number of bands that arise from a square-planar environment. This species has bands at 251 (\( \varepsilon = 26400 \)), 304 (21700), 337 (15350), 358 (15100), 417 (25000), and 472 nm (12300 M\(^{-1}\)cm\(^{-1}\)) while its previously published \(^{35}\) analogue [Fe\(^{\text{II}}\)(L\(^{\text{N2O2}}\))Cl] shows bands at 310 (49900), 351 (40360), 395 (30520), and 447 (19210). Addition of both Fe\(^{\text{II}}\) and Fe\(^{\text{III}}\) maintain the original band positions while changing their \( \varepsilon \) values. The most dramatic change is the decrease of the band at 417 nm in presence of Fe\(^{\text{II}}\), and the increase of the bands between 300 and 400 nm in presence of Fe\(^{\text{III}}\) ions. These changes also convey that metal replacement can take place when a critical concentration of iron is attained.

Figure 6.12. Spectral changes related to the addition of FeCl\(_2\)•6H\(_2\)O to (a) Ga\(^{\text{III}}\)(L\(^{\text{N2O3}}\))\(^{-}\), to (b) [Zn\(^{\text{II}}\)(L\(^{\text{N2O2}}\))H\(_2\)O\(^2\)] and FeCl\(_2\) to (c) Zn\(^{\text{II}}\)(L\(^{\text{N2O2}}\))H\(_2\)O\(^2\)] in methanol.
6.4. Conclusions

In conclusion, both metallosurfactants [Ga\textsuperscript{III}(L\textsubscript{N2O3})] (1) and [Zn\textsuperscript{II}(L\textsubscript{N2O2})H\textsubscript{2}O] (2) show the ability to preclude electron transfer from the environment to the iron surface, and prevent to some extent the anodic reaction associated with metal dissolution. These species do not seem to influence the cathodic reaction associated with oxygen reduction nor alter the mechanisms of corrosion. The extend of the inhibition activity depends on the metallosurfactant and on the media used. Although 1 is a more efficient inhibitor than 2, both species show better activity in saline medium. Their inhibition in acidic medium is much less pronounced, possibly because self-regeneration of H\textsubscript{2}SO\textsubscript{4} builds up trivalent Fe ions in concentrations sufficient to compete with gallium(III) in 1 and zinc(II) in 2.
CHAPTER 7: CONCLUSIONS AND PERSPECTIVES

In this thesis, I have studied the new homobimetallic iron(III) hydrophobe \([\text{Fe}^{\text{III}}_2(\text{L}^{\text{N406}})]\), [N\(_2\)O\(_3\)] chromium(III) \([\text{Cr}^{\text{III}}(\text{L}^{\text{N2O3}})]\), [N\(_2\)O\(_2\)] chromium(III) \([\text{Cr}^{\text{III}}(\text{L}^{\text{N2O2}})\text{Cl}]\) and oxovanadium(IV) \([(\text{V}=\text{O})^{\text{IV}}\text{L}^{\text{N2O2}}]\) complexes for current rectification and [N\(_2\)O\(_2\)] zinc (II) \([\text{Zn}^{\text{II}}(\text{L}^{\text{N2O2}})\text{H}_2\text{O}]\), [N\(_2\)O\(_3\)] gallium(III) \([\text{Ga}^{\text{III}}(\text{L}^{\text{N2O3}})]\) complexes for corrosion inhibition (Figure 7.1). Rectification studies have shown that all four complexes can behave as rectifiers, but with two different electron transport mechanisms. From the solid-state calculations, we have learned that for the homobimetallic iron(III) hydrophobe, SOMO energies are so close to the electrode Fermi level therefore, electron transport can happen through SOMOs. In this mechanism, the metallosurfactant gets reduced first. For chromium(III) complexes, DFT and solid-state calculations suggested that HOMO energies are close to the electrode Fermi level compared to SOMOs. Therefore, electron transport can happen through HOMOs. In this mechanism, the metallosurfactant gets oxidized first. For corrosion inhibition studies, both redox-innocent gallium(III) and Zn(II) complexes showed corrosion inhibition on aluminum and iron surfaces. These observations suggest that

![Image](a). Complexes studied for rectification. (b) Complexes studied for corrosion inhibition.

Figure 7.1. (a) Complexes studied for rectification, (b) Complexes studied for corrosion inhibition.
redox-innocent metallosurfactants can hinder electron transport and can protect the metal from corrosion.

In Chapter 3, we have successfully developed and studied an unprecedented bimetallic iron(III) hydrophobe, described as [Fe$^{\text{III}}$]$_2$(L$^{\text{N4O6}}$), for current rectification. The new bicompartental ligand H$_6$L$^{\text{N4O6}}$ was able to accommodate two five-coordinate HS-Fe$^{\text{III}}$ ions which are separated by tetraaminobenzene at a close distance of ca. 8 Å. The [Fe$^{\text{III}}$]$_2$(L$^{\text{N4O6}}$) displayed a well-behaved redox properties with three, two electron ligand-centered oxidation processes and two, one electron metal-based reduction processes. Reduction processes can be attributed to [Fe$^{\text{III}}$Fe$^{\text{III}}$] → [Fe$^{\text{III}}$Fe$^{\text{II}}$] → [Fe$^{\text{II}}$Fe$^{\text{II}}$], which suggested that the two metal centers are moderately coupled and a SOMO-based electron transfer can take place. Broken symmetry DFT calculations, spectroelectrochemistry, and EPR studies confirmed this behavior. The [Fe$^{\text{III}}$]$_2$(L$^{\text{N4O6}}$) hydrophobe forms a Pockels-Langmuir film at the air-water interface, with a collapse pressure of 32 mN/m. Devices were fabricated by sandwiching LB monolayers and current-voltage (I-V) measurements were taken. The bimetallic hydrophobe [Fe$^{\text{III}}$]$_2$(L$^{\text{N4O6}}$) acts as a molecular rectifier with a rectification ratio between 2.63 and 15.52. However, the rectification ratio was not enhanced as we anticipated, due to only certain molecules present in direct contact with the electrodes.

In Chapter 4, asymmetric [N$_2$O$_3$] chromium(III) [Cr$^{\text{III}}$ (L$^{\text{N2O3}}$)], [N$_2$O$_2$] chromium(III) [Cr$^{\text{III}}$(L$^{\text{N2O2}}$)Cl] and oxovanadium(IV) [(V=O)$^{\text{IV}}$L$^{\text{N2O2}}$] complexes were synthesized and characterized successfully to investigate their potential performance as molecular current rectifiers. Film formation properties and thin film characterization were investigated by Langmuir-Blodgett(LB) isothermal compression, Brewster angle microscopy, and IR-reflection/absorption spectroscopy techniques. Au|LB-monlayer|Au nanoscale devices were fabricated for all three complexes and current-voltage characteristics were measured. Current-voltage curves of [Cr$^{\text{III}}$}
\([\text{L}_2\text{O}_3]\), \([\text{Cr}^{\text{III}}(\text{L}_2\text{O}_2)\text{Cl}]\), and \([\text{V}=\text{O}]^{\text{IV}}\text{L}_2\text{O}_2\] complexes displayed asymmetrical current responses, indicative of current rectification. DFT calculations were performed for chromium complexes and suggested that HOMO energy levels are ligand-centered. Additionally, calculations carried out using redox potentials and DFT suggested that the HOMO energy levels are accessible during the electron transfer and SOMOs are not involved. Therefore, the chromium complexes showed asymmetric current rectification.

In Chapter 5, we have tested two metallosurfactants, \([\text{Zn}^{\text{II}}(\text{L}_2\text{O}_2)\text{H}_2\text{O}]\) (1), \([\text{Ga}^{\text{III}}(\text{L}_2\text{O}_3)]\) (2), and their ligands as inhibitors for pitting on aluminum surfaces. Cyclic voltammetry experiments suggest that 11 layers of the zinc(II)-containing complex and 13 layers of the gallium(III)-containing complex can effectively passivate electron transfer as compared to their ligands. SEM images, potentiodynamic polarization, and electrochemical impedance spectroscopy studies confirmed that both LB films of zinc(II) and gallium(III) complexes inhibit aluminum corrosion and the zinc(II) complex showed superior inhibition. This observation can be explained by the thickness measurements of the LB films of zinc(II) and gallium(III) complexes. Due to the higher thickness of the \([\text{Zn}^{\text{II}}(\text{L}_2\text{O}_2)\text{H}_2\text{O}]\) (1) complex, it can passivate electron transfer more efficiently than the \([\text{Ga}^{\text{III}}(\text{L}_2\text{O}_3)]\) (2) complex.

In Chapter 6, we quantified electrochemically the effectiveness of gallium(III)- and zinc(II)-containing metallosurfactants \([\text{Ga}^{\text{III}}(\text{L}_2\text{O}_3)]\) (1) and \([\text{Zn}^{\text{II}}(\text{L}_2\text{O}_2)\text{H}_2\text{O}]\) (2) as inhibitors for iron corrosion in acidic and saline media. Agar staining and SEM images indicated qualitatively that both metallosurfactants protect the iron surface in which they are deposited, thus inhibiting corrosion. The electroanalytical techniques of potentiodynamic polarization and electrochemical impedance spectroscopy were used to quantify the corrosion inhibition ability by these LB films; they showed that the \([\text{Zn}^{\text{II}}(\text{L}_2\text{O}_2)\text{H}_2\text{O}]\) (2) species is capable of higher inhibition efficiency
than the $[\text{Ga}^{III}(\text{L}^{\text{N2O3}})]$ (1) species. This behavior is due to better packing of the layers of 2 and attributed to a flatter square planar structural configuration of the bisphenolate metal-containing site. Species 1 leads to less packed layers due to its tris-phenolate metal-binding site. Both metallosurfactants 1 and 2 act best as inhibitors in saline medium, while in acidic medium inhibition is present, but less pronounced. These results suggest that metallosurfactants based on $3d^{10}$ redox-inactive metal ions are good candidates for inhibition of corrosion on iron surfaces. Ligand design that enables more effective chemisorption and packing will guide future developments.

From these studies, we were able to understand the influence of the electron configuration of the metal on the modulation of the Fermi/SOMO and Fermi/HOMO gaps to develop molecular rectifiers and corrosion inhibitors.

To advance these research projects further, a few studies can be proposed: To develop more efficient molecular rectifiers modulation of the ligand framework can be done with various electron-donating and -withdrawing substituents to modulate the redox properties of the complex leading to accessible HOMO and LUMO/SOMO energy levels for electron transfer. To analyze this notion further, a few probable ligand designs are shown in Figure 7.2. We hypothesize by introducing electron-withdrawing iodide and chloride groups, we can bring SOMOs close to electrodes Fermi level, while by introducing electron-donating methoxy groups, we can bring

**Figure 7.2.** Proposed ligands to modulate the orbital energies.
HOMOs close to electrodes Fermi level. Narrow Fermi-SOMO and Fermi-HOMO gaps will facilitate electron transport.

![Diagram of multimetallic complex]

**Figure 7.3.** Proposed multimetallic complex \([\text{[(}M^{III}\text{L}^9\text{)}_3\text{Fe}^{II}]\), \(M^{III} = \text{Cr, Fe, Mn.}\)

In addition to the \([\text{N}_2\text{O}_2]\) and \([\text{N}_2\text{O}_3]\) monometallic complexes, multimetallic complexes can be developed to see whether we can increase the rectification ratios (Figure 7.3). This is based on the hypothesis that multimetallic complexes can increase the number of electrons transported in time by molecular area on LB films.

To develop more efficient corrosion protection films, the hydrophobicity of the molecules can be increased by introducing longer alkoxy chains (e.g., \(\text{OC}_{18}\text{H}_{37}\)) to the \([\text{N}_2\text{O}_3]\) ligand framework so that it will enhance water repulsion. Furthermore, instead of Langmuir-Blodgett, the self-assembly technique can be implemented during film deposition. This is based on the hypothesis that chemisorption of the metallosurfactants will improve the film stability.
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## APPENDIX B.

Table A1. Geometry optimized structures of the simplified models of [Fe$^\text{III}_{2}(L^{\text{N4O6}})](1)$ and [Cu$^\text{II}\text{Fe}^\text{III}$] in Chapter 4.

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C

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H

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Table A2. Coupling results: X-ray and simplified models of [Fe^{III}_2(L^{N4O6})](I) and [Cu^{II}Fe^{III}] in Chapter 4.

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Table A3. Bond lengths for $[\text{Fe}^{\text{III}}_2(L^{N4O6})]$ in Chapter 4.

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ABSTRACT

FERMI-SOMO/HOMO AND FERMI-LUMO ARGUMENTS ON CURRENT RECTIFICATION AND CORROSION INHIBITION USING LANGMUIR-BLODGETT FILMS OF PHENOLATE-BASED METALLOSURFACTANTS

by

A. D. K. ISURI WEERARATNE

August 2021

Advisor: Prof. Claudio N. Verani

Major: Chemistry (Inorganic)

Degree: Doctor of Philosophy

The work reported in this thesis focused on the use of redox-active metallosurfactants for current rectification and redox-innocent metallosurfactants for corrosion inhibition. These studies were done based on the hypothesis that redox-active metallosurfactants can promote electron transport, while redox-innocent metallosurfactants can hinder electron transport. As such, new redox-active phenolate based iron(III), chromium(III), oxovanadium(IV) and redox-innocent gallium(III) and zinc(II) complexes were synthesized and characterized for the aforementioned applications.

First, we studied the current rectification ability of a homobimetallic iron(III) hydrophobe with \([\text{N}_4\text{O}_6]\) ligand environment. This complex displayed rectification with rectification ratio ranges from 2.6 to 9.8 between -2.0 and 2.0 V and 4.5 to 15.5 between -4.0 and 4.0 V. Solid state calculations suggested that SOMO energies are energetically compatible with electrode Fermi energy and electron transport can happen through that orbital. In this mechanism, metallosurfactant get reduced first. However, in this study, we did not see an enhancement in the rectification compared to monometallic iron(III) complexes due to only certain molecules directly in contact with the electrodes. In order to further modulate the Fermi/SOMO/HOMO gaps, we have
synthesized and characterized chromium(III), and oxovanadium(IV) complexes with \([N_2O_3]/[N_2O_2]\) ligand environments. Devices were fabricated by sandwiching LB monolayers of each complex, and current-voltage (I-V) measurements were taken. All three complexes showed rectification, with the rectification ratio ranges from 3.08 to 17.22 between -2 to +2V. Solid state calculations displayed that HOMO energies are energetically comparable with electrode Fermi level for all three complexes. That suggested that electron transport can happen through HOMOs. In this mechanism, metallosurfactants get oxidized first.

Similarly, the use of LB films in corrosion inhibition was investigated using redox-innocent gallium(III) and zinc(II) complexes. We studied the corrosion inhibition ability of these complexes on both iron and aluminum surfaces. Iron corrosion inhibition was investigated using SEM, ferroxyll staining, potentiodynamic polarization and impedance spectroscopy studies in both acidic and basic media. Both complexes acted best as inhibitors in saline medium, while in acidic medium, inhibition was present but less pronounced. Aluminum corrosion was studied using SEM, potentiodynamic polarization and impedance spectroscopy studies in the saline medium. Both complexes inhibited aluminum corrosion. However, zinc complexes exhibited superior inhibition compared to gallium during both iron and aluminium corrosion inhibition studied. These observations suggested that redox-innocent metallosurfactants can hinder electron transfer, and orderly physisorbed Langmuir-Blodgett film can act as a barrier against environmental influences.

The work presented herein highlights the significance of modulating the Fermi-SOMO/HOMO and Fermi-LUMO energy gaps while developing current rectifiers and corrosion inhibitors.
AUTOBIOGRAPHICAL STATEMENT

EDUCATION
2015-2021 Wayne State University, Detroit, MI  Ph.D. in Chemistry
2009-2014 University of Sri Jayewardenepura, Sri Lanka  B.S. in Chemistry

HONORS AND AWARDS
- The Summer Dissertation fellowship - Academic year 2020
- The Tomas C. Rumble Graduate Fellowship - Academic year 2019/2020
- Awarded with a High Distinction at Australian National Chemistry Quiz - 2007

PUBLICATIONS

SELECTED PRESENTATIONS
- “Corrosion Mitigation Using Films of Redox-innocent Metallosurfactants” Mar. 2020, 10th Annual Graduate and Postdoctoral Research Symposium, Wayne State University, MI, USA. (poster presentation)
- “Films of Redox-innocent Metallosurfactants as Surface Pretreatment Coatings for Corrosion Mitigation” Dec. 2019, Detroit Science and Networking Symposium, MI, USA. (poster presentation)
- “Development of Molecular Rectifiers Using Langmuir-Blodgett Films of Phenolate-rich Metal-containing Surfactants” Nov. 2019, NOBCChE 46th Annual Meeting, St Louis Union Station, MO, USA. (oral presentation)
- “Early Transition Metal Complexes as Molecular Rectifiers” Mar. 2019, 9th Annual Graduate and Postdoctoral Research Symposium, Wayne State University, MI, USA. (poster presentation)
- “Early Transition Metal Bisphenolate and Triphenolate Complexes for Molecular Rectification” Nov. 2018, Ohio Inorganic Weekend, The Ohio University, Athens, OH, USA. (poster presentation)
- “New Molecular Precursors for Current Rectification using Langmuir-Blodgett Monolayers of Early Transition Metal Complexes” Nov. 2017, Ohio Inorganic Weekend, The Ohio State University, Columbus, OH, USA. (poster presentation)