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Synthesis and Characterization of Dimolybdenum(II) Complexes: On the Way to Functional Molecular Materials

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Our greatest glory is not in never falling, but in rising every time we fall.

Lernen und es von Zeit zu Zeit wiederholen, ist das nicht auch eine Freude?

Confucius (551–479 BC)



The Rainbow-Arrayed Mo₂-Based Chemistry.

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Deutsche Zusammenfassung

Eine neue Familie mehrfach redoxaktiv Mo₂-Verbindungen mit verschiedenen Liganden wurde ausgehend von der reaktiven Ausgangsverbindung [Mo₂(NCCH₃)₁₀][BF₄]₄ (**1**) hergestellt. Der Schwerpunkt dieser Arbeit liegt auf den Synthesen, Strukturvariationen und elektronischen Eigenschaften, welche Einblicke in die potentielle Verwirklichung von funktionellen molekularen Materialien geben könnten.

Aus der Reaktion von **1** mit Fc-COOH (Ferrocenmonocarbonsäure) ging eine cis-substituierte Verbindung *cis*-[Mo₂(O₂C-Fc)₂(NCCH₃)₆][BF₄]₂ (*cis*-**2**) hervor, welche im Weiteren zu den trans-substituierten Komplexen *trans*-[Mo₂(O₂C-Fc)₂(DPPX)₂][BF₄]₂ (**6a-6c**) umgesetzt wurde (DPPX = *N,N*-Bis(diphenylphosphino)amin (DPPA; **6a**), 1,1-Bis(diphenylphosphino)methan (DPPM; **6b**) und 1,2-Bis(diphenylphosphino)ethan (DPPE; **6c**)). Dieses Substitutionsmuster kann sehr wahrscheinlich durch die sterisch anspruchsvollen Diphosphin-Liganden, welche eine dauerhafte trans-Anordnung erzwingen, erklärt und mit Hilfe von Röntgeneinkristallstrukturanalyse und Dichtefunktionaltheorieberechnungen bewiesen werden. Bei der Umsetzung der Liganden *N,N'*-Diphenylformamidinat (DPhF), *N,N'*-Di(*p*-anisyl)formamidinat (DTfmpF) und *N,N'*-Di(*p*-trifluoromethylphenyl)formamidinat (DAniF) mit *cis*-**2** wurden unter verschiedenen Synthesebedingungen jeweils die Verbindungen *cis*-[Mo₂(O₂C-Fc)₂(DPhF)₂] (*cis*-**7d**), *cis*-[Mo₂(O₂C-Fc)₂(DTfmpF)₂] (*cis*-**7e**), *trans*-[Mo₂(O₂C-Fc)₂(DAniF)₂] (*trans*-**7f**), [Mo₂(DTfmpF)₃(O₂C-Fc)] (**8e**), und [Mo₂(DAniF)(O₂C-Fc)₃] (**9f**) isoliert. Neben den oben erwähnten Mo₂-Verbindungen wurde durch die Reaktion von *cis*-**2** und HOOC-Fc-COOH (Ferrocendicarbonsäure) das vierecksförmige Makromolekül [(CH₃CN)₄Mo₂(O₂C-Fc-CO₂)₄][BF₄]₈ (**3**), welches durch axiale Verknüpfung mit BF₄-Anionen eine aromatische molekulare Röhre bildet, hergestellt. Elektrochemische Eigenschaften der Komplexe *cis*-**2** und **6-8** wurden bezüglich Ligand, Elektrolyt und Lösungsmittel systematisch untersucht. Bei der Betrachtung der Oxidationspotentiale $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ aller gemessenen Mo₂-Komplexe konnte eine Abnahme der Ligandbasizität in der Reihenfolge DAniF⁻ > DTfmpF⁻ > Fc-CO₂⁻ > DPPX >

CH₃CN festgestellt werden. Bezüglich des Oxidationspotentials von Fc-CO₂⁻ fällt auf, dass $E_{1/2}(\text{Fc}/\text{Fc}^+)$ unabhängig von anderen Liganden in den Verbindungen größtenteils unverändert bleibt, was darauf hinweist, dass die verschiedenen Liganden hauptsächlich die direkt gebundenen Mo₂-Einheiten beeinflussen.

Bemerkenswerterweise wurde in allen trans-substituierten Mo₂-Komplexen eine elektronische Kopplung beobachtet, wohingegen diese Kopplung nicht in allen cis-substituierten Komplexen eindeutig beobachtbar ist. Dies könnte zu der Annahme führen, dass die trans-Anordnung von Fc-Einheiten elektronische Kopplung bevorzugt. Daher kann die Herstellung von redoxaktiven Komplexen, vor allem von diesen, die für „molecular wires“ verwendet werden sollen, von diesen trans-konfigurierten Verbindungen ausgehen.

English Abstract

A new family of multi redox-active mixed-ligand Mo₂ compounds has been sequentially synthesized by reactions starting from the reactive precursor [Mo₂(NCCH₃)₁₀][BF₄]₄ (**1**). The major focus of this thesis is placed on the syntheses, structure variations, and electrochemical properties that might give some insights into the realization of functional molecular materials. The reaction of **1** with ferrocenemonocarboxylic acid resulted in a *cis*-positioned compound *cis*-[Mo₂(O₂C-Fc)₂(NCCH₃)₆][BF₄]₂ (***cis*-2**), which was further reacted and exclusively isolated as *trans*-positioned series *trans*-[Mo₂(O₂C-Fc)₂(DPPX)₂][BF₄]₂ (**6a-6c**) (DPPX = *N,N*-bis(diphenylphosphino)amine (DPPA; **6a**), 1,1-bis(diphenylphosphino)methane (DPPM; **6b**), and 1,2-bis(diphenylphosphino)ethane (DPPE; **6c**), respectively). This exclusive *trans*-rearrangement is most likely due to the bulky diphosphine ligands DPPX, as evidenced by X-ray crystallography and density functional theory calculations. When ligands of *N,N'*-diphenylformamidinate (DPhF), *N,N'*-di(*p*-trifluoromethylphenyl)formamidinate (DTfmpF), and *N,N'*-di(*p*-anisyl)formamidinate (DAniF) were reacted with ***cis*-2**, *cis*-[Mo₂(O₂C-Fc)₂(DPhF)₂] (***cis*-6d**), *cis*-[Mo₂(O₂C-Fc)₂(DTfmpF)₂] (***cis*-6e**), *trans*-[Mo₂(O₂C-Fc)₂(DAniF)₂] (***trans*-6f**), [Mo₂(O₂C-Fc)(DTfmpF)₃] (**7e**), and [Mo₂(O₂C-Fc)₃(DAniF)] (**8f**) were respectively isolated under different synthetic conditions. Besides the above mentioned complexes, a square-shaped tetramer [(CH₃CN)₄Mo₂(O₂C-Fc-CO₂)₄][BF₄]₈ (**3**) that forms an aromatic tube when axially linked by BF₄ anions was produced by reacting ***cis*-2** and ferrocenedicarboxylic acid.

Electrochemical properties of complexes ***cis*-2** and **6-8** were systematically studied with respect to ligand, electrolyte, and solvent. Given their oxidation potential $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ values, a ligand basicity decreasing in the order DAniF⁻ > DTfmpF⁻ > Fc-CO₂⁻ > DPPX > CH₃CN was observed. With regard to the oxidation potential of Fc-CO₂⁻, it is apparent that $E_{1/2}(\text{Fc}/\text{Fc}^+)$ remains largely unchanged regardless of the other ligands in the compounds, indicating that the mixed-ligand mainly influences the directly bonded Mo₂ moiety. Noteworthy, electronic coupling was observed in all *trans*-directed Mo₂ complexes, however, it was not clearly

observable in cis-positioned species. This leads to the assumption that the trans-arrangement of Fc units favors electronic coupling. Therefore, further synthetic design of redox-active complexes can be based on this trans-arranged compounds, especially for those which are intended for molecular wires.

List of Abbreviations

ap ⁻	2-anilinopyridinate
BF ₄ ⁻	tetrafluoroborate
CH ₃ CN	acetonitrile
CV	cyclic voltammetry
DAniF ⁻	<i>N,N'</i> -di(<i>p</i> -anisyl)formamidinate
DArF ⁻	<i>N,N'</i> -diarylformamidinate
DFT	density functional theory
DmAmiF ⁻	<i>N,N'</i> -di(3-methoxyphenyl)formamidinate
DMBA ⁻	<i>N,N'</i> -dimethylbenzamidinate
DPhF ⁻	<i>N,N'</i> -diphenylformamidinate
DPPA	<i>N,N</i> -bis(diphenylphosphino)amine
DPPM	1,1-bis(diphenylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPX	bulky diphosphine ligands
DPV	differential pulse voltammetry
DTfmpF ⁻	<i>N,N'</i> -di(<i>p</i> -trifluoromethylphenyl)formamidinate
EPR	electronic paramagnetic resonance
Fc	ferrocene
Fc-CO ₂ ⁻	ferrocenemonocarboxylate
Fc-COOH	ferrocenemonocarboxylic acid
Fc-(COOH) ₂	ferrocenedicarboxylic acid
HOMO	highest occupied molecular orbital
IR	infrared spectroscopy
IVCT	intervalence charge transfer
<i>K</i> _c	comproportionation constant
LUMO	lowest unoccupied molecular orbital

M ₂	dimetal
MCM	mobile crystalline material
Me	methyl
MLCT	metal-to-ligand charge transfer
Mo ₂	dimolybdenum
MOFs	metal-organic frameworks
NMR	nuclear magnetic resonance
OPE	oligophenylene ethynylene
PCT	photochemo therapy
PW	paddle-wheel
r.t.	room temperature
Rh ₂	dirhodium
ROMP	ring-opening metathesis polymerization
Ru ₂	diruthenium
SAM	self-assembled monolayer
SBU	secondary building unit
SQUID	superconducting quantum interference device
STM	scanning tunneling microscopy
TCNE	tetracyanoethene
TG-MS	thermogravimetry mass spectrometry
TTF	tetrathiofulvalene
UV–vis	ultraviolet-visible

Table of Contents

Acknowledgement	IX
Deutsche Zusammenfassung.....	XI
English Abstract	XIII
List of Abbreviations.....	XV
1 Introduction.....	1
1.1 From Dinuclear Molecules to Functional Molecular Materials: A Teaser	1
1.2 From Dinuclear Molecules to Supramolecular Structures	3
1.2.1 Metal-Organic Frameworks (MOFs).....	3
1.2.2 Mo ₂ -Based Macromolecules.....	5
1.3 New Trend of Dinuclear Complexes: Electronic Structure and Application Exploration 9	
1.3.1 Electronic Structure Investigation	9
1.3.2 Application Exploration	11
1.4 Dinuclear-Based Molecular Wires	12
1.4.1 What is A Molecular Wire?.....	12
1.4.2 What Molecules Can Be Targeted as Molecular Wires? — Electronic Coupling ..	15
1.4.3 Electronic Coupling in Mo ₂ -Based Compounds	20
2 Objective	22
3 Results and Discussion.....	23
3.1 Publication Summaries.....	23
3.1.1 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers	23
3.1.2 Rational Synthesis and Characterization of Dimolybdenum(II) Compounds Bearing Ferrocenyl-Containing Ligands toward Modulation of Electronic Coupling	25

3.1.3 Synthesis and Electrochemical Properties of <i>cis</i> - and <i>trans</i> -[Mo ₂ (O ₂ C-Fc) ₂ (DArF) ₂] (O ₂ C-Fc = Ferrocenecarboxylate; DArF = <i>N,N'</i> -diarylformamidinate)	27
3.1.4 Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series [Mo ₂ (DArF) _n (O ₂ C-Fc) _{4-n}] (DArF = <i>N,N'</i> -Diarylformamidinate; O ₂ C-Fc = Ferrocenecarboxylate)	29
3.2 Reprint Permissions.....	33
4 Summary and Outlook	39
5 Bibliographic Data of Complete Publications	43
5.1 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers	43
5.2 Rational Synthesis and Characterization of Dimolybdenum(II) Compounds Bearing Ferrocenyl-Containing Ligands toward Modulation of Electronic Coupling	44
5.3 Synthesis and Electrochemical Properties of <i>cis</i> - and <i>trans</i> -[Mo ₂ (O ₂ C-Fc) ₂ (DArF) ₂] (O ₂ C-Fc = Ferrocenecarboxylate; DArF = <i>N,N'</i> -Diarylformamidinate).....	45
6 References	46
7 Curriculum Vitae and Publication List	51
7.1 Curriculum Vitae.....	51
7.2 Publication List	53
7.3 Talks and Poster Presentations	54

1 Introduction

1.1 From Dinuclear Molecules to Functional Molecular Materials: A Teaser

Paddle-wheel (PW) compounds containing two transition metal centers, each with an octahedral configuration, have been largely investigated during the last half century.¹ These multiply bonded dinuclear compounds adopt four equatorial bridging ligands in most cases, forming the Chinese-lantern-like structures. These transition metals usually can be found in the groups of 4, 5, and 6 in the periodic table (Figure 1.1), with the compound type incorporating $[M_2]^{n+}$ units commonly found when n equals 4, 5, and 6. This means that the oxidation state of each metal center is between 2 and 3. Each metal adopts several d electrons so that the overall electrons can fill in the open-shell molecular orbitals (σ , π , δ , δ^* , π^* , and σ^*), resulting in variable metal-metal bond orders and electron configurations of the $[M_2]^{n+}$ unit.

24	25	26	27	28
Cr	Mn	Fe	Co	Ni
42	43	44	45	46
Mo	Tc	Ru	Rh	Pd
74	75	76	77	78
W	Re	Os	Ir	Pt

Figure 1.1: The most common transition metals for dinuclear compounds. The elements in bold will be interpreted in detail over the whole thesis.

After the first quadruply bonded dimetal complex $[Re_2Cl_8]^{2-}$ was discovered half a century ago,² the prosperous field of dinuclear paddle-wheel complexes possessing a quadruple bond (electron configuration of $\sigma^2\pi^4\delta^2$; e.g. Cr, Mo, and W) emerged.¹ Particularly for the $[Mo_2]^{4+}$ system, the electron configuration of $\sigma^2\pi^4\delta^2$ results in the easy oxidation of the metal centers to $[Mo_2]^{5+}$, whereas a reduction to $[Mo_2]^{3+}$ is difficult. The more electronic donating the ligands

are, the more easily the $[\text{Mo}_2]^{4+}$ can be oxidized. More electrochemical properties will be further discussed in section 1.4.

With regard to diruthenium compounds ($[\text{Ru}_2]^{n+}$; pioneering dimetallic unit incorporated into organometallic molecular wires³), the moiety valence is not invariable, usually with $n = 4, 5,$ and $6,$ respectively. For $[\text{Ru}_2]^{6+}$ moieties, there are generally four possible electron configurations: $\sigma^2\pi^4\delta^2\pi^{*2}, \sigma^2\pi^4\delta^2\pi^{*1}\delta^{*1}, \sigma^2\pi^4\delta^2\delta^{*2},$ and $\pi^4\delta^2\pi^{*4},$ depending on the order of the π^* and δ^* molecular orbital levels and their energy separation. This usually can be analyzed via magnetic moments and Ru–Ru bond lengths. For instances, complexes of $[\text{Ru}_2]^{6+}$ cores are usually diamagnetic (as it is shown by their normal ^1H NMR spectra)^{4,5} and have a relatively long Ru–Ru bond length, a single bond with the electron configuration of $\pi^4\delta^2\pi^{*4}$ can be proposed. Compounds containing $[\text{Mo}_2]^{4+}$ and $[\text{Ru}_2]^{n+}$ cores will be further discussed as part of section 1.4, since they are deemed as molecular wire candidates due to their versatile redox properties.

As a very copious synthetic chemistry, dimetal entities can be coordinated either equatorially or axially, resulting in thousands of novel dimetal compounds.¹ Although the synthetic chemistry of dimetal compounds has developed for decades, the applied chemistry in this area appears to be not largely advanced. Therefore, the focus is directed towards functional molecular materials in recent years.⁶⁻⁸

To the best of my knowledge, these molecular materials in the area of dimetal compounds can be approximately divided into several categories: 1) molecular wires;^{3,7-26} 2) molecular magnets;²⁷⁻²⁹ 3) application in biochemistry;³⁰ and 4) application in catalysis,³¹⁻³³ among which the synthesis of molecular wires is the aim of my doctoral project, which will be further introduced in detail in section 1.4. With regard to molecular magnets, magnetism measurement (SQUID) is largely applied, and electron paramagnetic resonance (EPR) measurement is utilized to further explore their electronic structures.³⁴⁻³⁸ For both molecular wires and magnets, electronic structures are largely correlated with their intermolecular electronic interactions, and control of the intermolecular interactions permits modification of the bulk properties of these materials. Therefore, better understanding of electron configuration, for instance, the above

mentioned discussion concerning both $[\text{Mo}_2]^{4+}$ and $[\text{Ru}_2]^{n+}$ cores, becomes necessary. Regarding the application in both biochemistry and catalysis, only limited discoveries have been reported in the literature.³⁰⁻³³ Hence, it might be a promising area to step forward.³⁹

1.2 From Dinuclear Molecules to Supramolecular Structures

1.2.1 Metal-Organic Frameworks (MOFs)

During the last few decades, an enormous variety of macromolecular compounds containing dimetal paddle-wheel units that possess both equatorial and axial coordination sites have been reported.^{12,39-49} The focus of this research was laid on the controllable synthesis of 1D polymers, which of course is the basis toward more complicated 2D polymers and 3D MOFs. MOFs are inorganic-organic hybrid complexes, encompassing metallic centers as nodes and organic or organometallic bridges as linkers. Among the published results, a plethora of transition metals (shown in Figure 1.1) have been applied in MOFs for multiple applications so far,^{41,50-57} while the key metal relative to the MOFs in this thesis will be focused on Mo and will only be introduced from the synthetic and structural point of views.^{50,53}

On the synthetic basis, it can be discriminated between two moieties: the Mo_2 nodes that are named as the inorganic “secondary building unit (SBU)” and the linker. The most basic Mo_2 node unit resembles the yellow air-stable compound $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ (shown in Figure 1.2; $\text{R} = \text{Me}$) that is readily available from the synthesis of $[\text{Mo}(\text{CO})_6]$ and acetic acid/acetic anhydride.⁵⁸ The construction of MOFs will be based on this Mo_2 node that has four perpendicular neighboring bridging ligands. Generally, the SBUs applied for MOFs are obtained by reacting $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ with variable dicarboxylate ligands, resulting in different building blocks. Therefore, the design of linkers is of great significance.

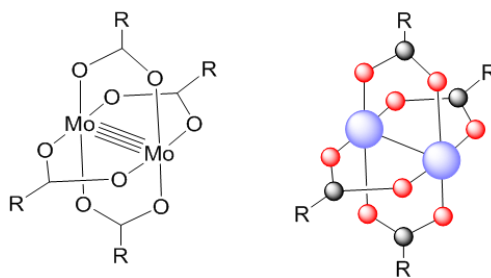


Figure 1.2: The basic PW-structure of Mo₂ node unit for MOFs.

Design of linkers in this area mainly focuses on the bridging dicarboxylate that can be interpreted from two directions: the bridging angle determined by position of the functional groups and the bridging size, which has been deeply discussed in Prof. Zhou's research.⁵⁰ Figure 1.3 exhibits the MOF assemblies from its basic SBU.⁵³ This MOF shows an anticuboctahedral cluster with a composition of Mo₂₄(BDC)₂₄ (BDC = 1,3-benzenedicarboxylate). Each cluster contains 12 Mo₂ units, forming a paddle-wheel building block that is combined with the 120° ditopic ligand BDC. A similar MOF is as well obtained when the ditopic linker was exchanged by 4-*tert*-butyl-1,3-benzenedicarboxylate (BBDC). However, the resulting MOF cluster [Mo₂₄(BBDC)₂₄](py)₁₂ is cuboctahedral. Both compounds Mo₂₄(BDC)₂₄ and [Mo₂₄(BBDC)₂₄](py)₁₂ were reported to be synthesized using solvothermal methods based on the above mentioned yellow node [Mo₂(O₂CMe)₄],⁵⁸ since the ligand acetate can be easily exchanged.

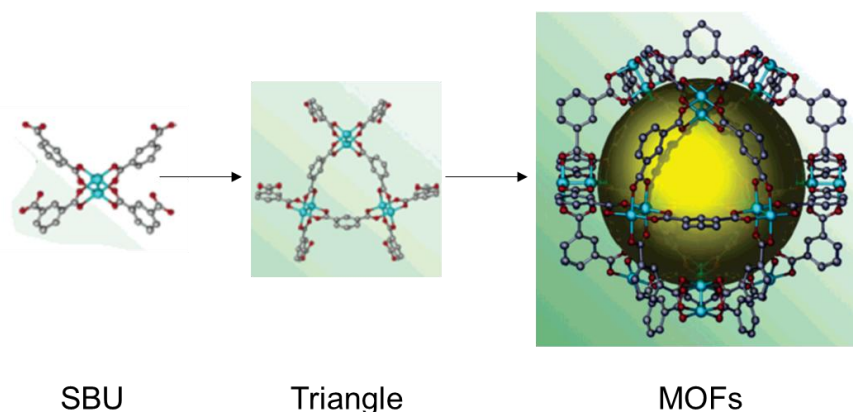


Figure 1.3: The formation of MOF clusters derived from a Mo₂-based SBU. Excerpt from reference 53.

Systematic studies of 12 dicarboxylate linkers were conducted in Prof. Zhou's group in order

to enrich this research area besides the topic of Mo_2 nodes.⁵⁰ These 12 bridging dicarboxylate ligands were designed to have different sizes with bridging angles of 0, 60, 90, and 120° , respectively. Representative examples are shown in Figure 1.4. Consequently, 13 molecular architectures of a linear-shape, triangle, octahedron, and cuboctahedron/anticuboctahedron were displaced therein.⁵⁰

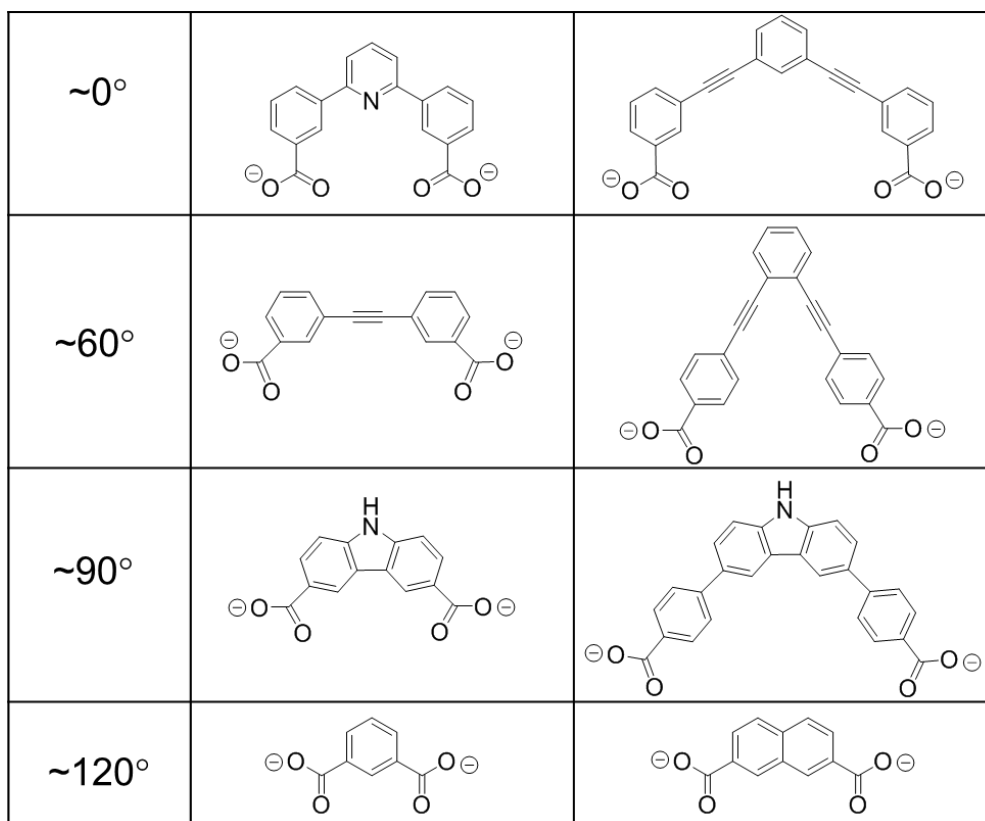


Figure 1.4: Examples of bridging linkers with angles of 0, 60, 90, and 120° , respectively.⁵⁰

1.2.2 Mo_2 -Based Macromolecules

Besides the above mentioned MOFs formed via Mo_2 nodes and dicarboxylate linkers, the major Mo_2 -based published results found so far are focused on the synthesis of macromolecules. Prof. Cotton and his co-workers have devoted several decades to synthesize macromolecules containing Mo_2^{4+} skeleton, which are equatorially coordinated by a couple of bidentate bridging ligands, either charged or neutral (Figure 1.5).

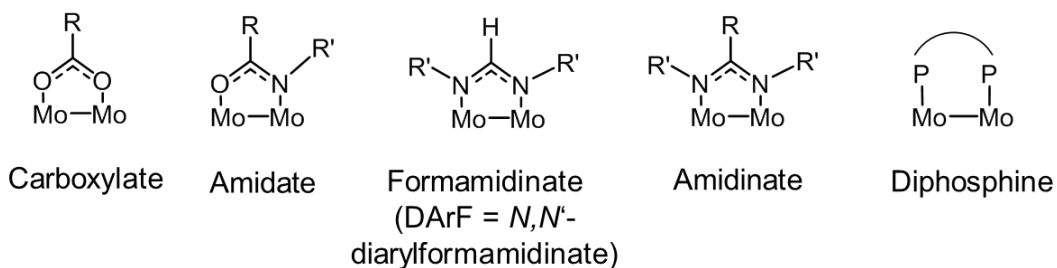
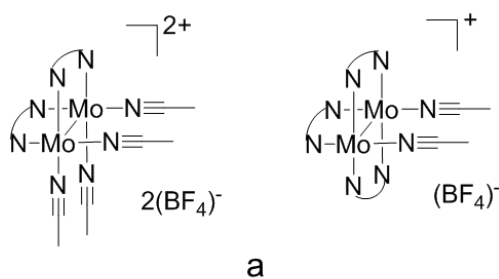


Figure 1.5: Mo₂-based structural entities equatorially coordinated by bidentate ligands.

Such Mo₂ skeletons can form variable types of structural motifs via linkage of dicarboxylate ligands with their respective starting materials, shown in Figure 1.6. Generally, strongly coordinated bridging ligands, such as *N,N'*-diformamidinate (DArF⁻), have been largely applied in the synthesis of structural motifs, in order to avoid unwanted side reactions. Two frequently applied Mo₂ compounds, *cis*-[Mo₂(DArF)₂(NCCH₃)₄][BF₄]₂ and [Mo₂(DArF)₃(NCCH₃)₂][BF₄], have been frequently used for synthesizing macromolecules, illustrated in Figure 1.6. The tris-coordinated compound [Mo₂(DArF)₃(NCCH₃)₂][BF₄] can be applied to synthesize dimers of dimers,⁵⁹ while the *cis*-coordinated compound *cis*-[Mo₂(DArF)₂(NCCH₃)₄][BF₄]₂ can be used for the synthesis of molecular loops,^{60,61} triangles,^{62,63} and squares (Figure 1.6).^{64,65}



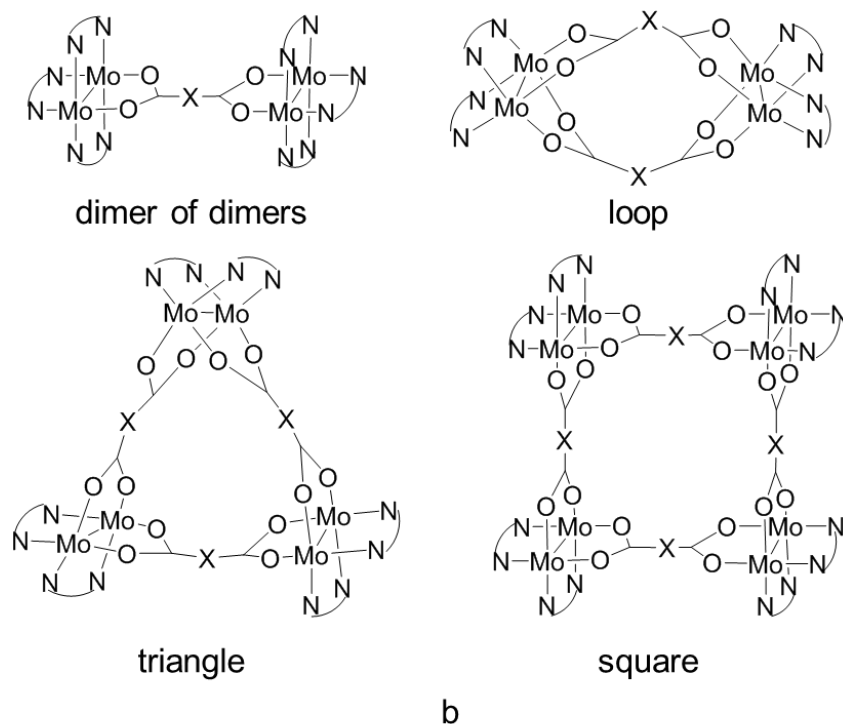


Figure 1.6: a) Synthetic precursors $cis\text{-}[\text{Mo}_2(\text{DArF})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ and $[\text{Mo}_2(\text{DArF})_3(\text{NCCH}_3)_2][\text{BF}_4]$; b) building blocks derived from reactions with respective precursors.

However, the side protectors (DArF^-), on the other side, appear to block the molecule extension into a three dimensional framework, which can be easily distinguished between both triangle structures shown in Figures 1.3 and 1.6b, respectively, where structures in the latter figure are blocked by DArF^- protectors. Therefore, only low-dimensional structures, such as 1D linear or tubular polymers can be obtained via axial linkage (Figures 1.7a and 1.7b).^{21,22,24,25,64-68}

There is one example in the literature reporting the synthesis of an equatorially connected linear oligomer by reacting a trans-coordinated precursor $trans\text{-}[\text{Mo}_2(\text{DArF})_2(\text{OCMe})_2]$ and a dicarboxylic acid, although with limited success (Figure 1.7c).²³ This synthetic strategy provides more insights into the synthesis of linear oligomers, including not only the axially connected polymers that are usually of weak linkage, but also the stronger bonded equatorially bridged structures.

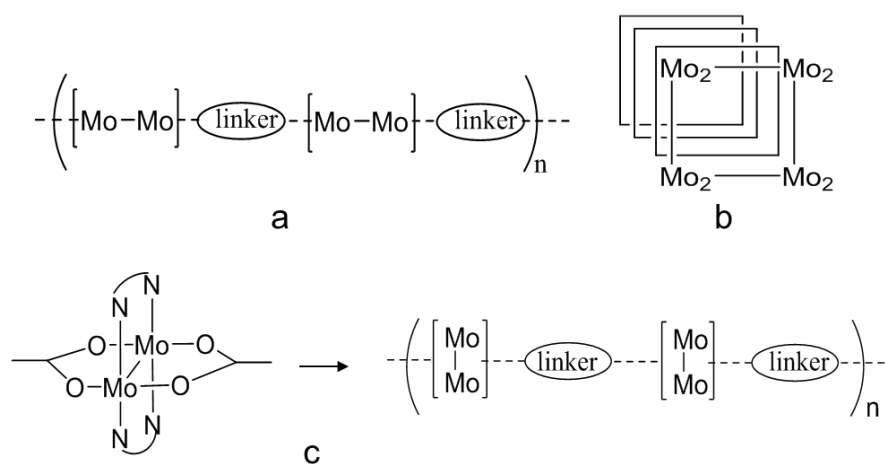
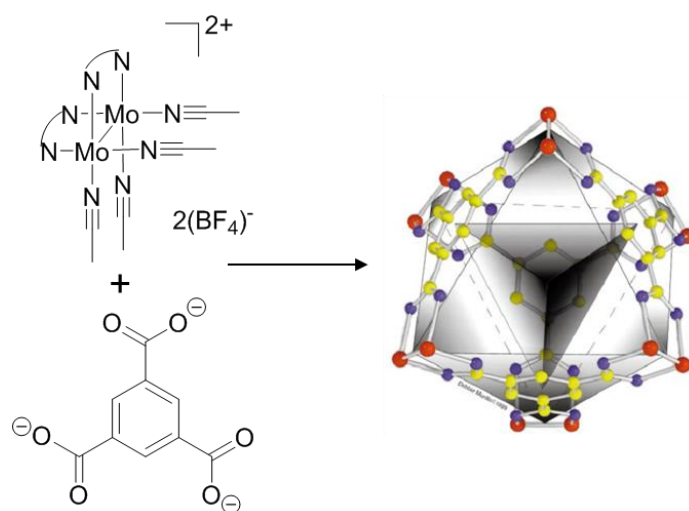


Figure 1.7: Assembly of a) linear oligomer formed by axial linkage; b) 1D tubular polymer formed by axial connection; and c) linear oligomer formed by equatorial linkage.

One designed large tetrahedral molecule containing six Mo_2 units (Scheme 1.1) has been so far found in the literature by reacting *cis*- $[\text{Mo}_2(\text{DArF})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ and a tritopic linker 1,3,5-tricarboxylatobenzene.⁶⁹ Although this structure is larger than the above mentioned structural motifs (dimer of dimers, molecular loops, triangles, and squares), especially due to its cage-like shape that might be able to capture small molecules, though the dimension of the molecule is still limited because of the attendant ligands (the attendant ligands are not shown in the tetrahedral cage in Scheme 1.1 for clarity).



Scheme 1.1: Assembly of a tetrahedral cage (excerpted from reference 69).

In order to enrich the dimension of Mo₂-based structures, a more reactive precursor is another metal-metal dimer first reported by Cotton *et al.*, namely [Mo₂(NCCH₃)₁₀][BF₄]₄.⁷⁰ This complex has all equally substituted coordination sites free to be exchanged due to the weakly bound acetonitrile ligands, similar to [Mo₂(O₂CMe)₄]. Nevertheless, it is more reactive than the latter. Few reactions have been carried out with this compound in the years after its first publishing, since it was considered as very sensitive and difficult to control.⁷¹⁻⁷³ Some unexpected results that the [Mo₂]⁴⁺ moiety was coordinated by crosswise-bridging acetonitrile molecules support this view.^{74,75} In recent years, it turned out that [Mo₂(NCCH₃)₁₀][BF₄]₄ can be used both as synthetic precursor for macromolecules^{61,76,77} and for less reactive building entities.⁷² In contrast to the protected building blocks synthesized in Cotton's group, however, [Mo₂(NCCH₃)₁₀][BF₄]₄ not only allows to reach structurally very similar (but more reactive) products, but - in principle - should enable further modification of these motifs with the eventual goal of novel MOFs.

The synthetic work of this thesis will be based on this reactive precursor [Mo₂(NCCH₃)₁₀][BF₄]₄, resulting in a series of multi-metallic redox-active molecules that include both Fc and Mo₂ units.

1.3 New Trend of Dinuclear Complexes: Electronic Structure and Application Exploration

1.3.1 Electronic Structure Investigation

Around one decade ago, Prof. Chisholm and his co-workers started to study the electronic structures of linked dimetal complexes,^{35,62,78-83} which was based on the synthetic work of supramolecular structures performed around two decades ago.⁸⁴⁻⁸⁶ Since the electronic structures of compounds M₂(O₂CR)₄ have been studied extensively,¹ Prof. Chisholm *et al.* employed dicarboxylate ligands, O₂C-X-CO₂, as a mediator for electronic structure calculation of these obtained dimers of dimers, aiming at a fuller understanding of the synthesis and bonding in Mo₂···Mo₂ subunits, in addition to the synthesis, characterization, and manipulation

of extended chains or oligomers.⁸² A model compound $(\text{HCO}_2)_3\text{Mo}_2(\mu\text{-O}_2\text{C-CO}_2)\text{Mo}_2(\text{O}_2\text{CH})_3$, was targeted for the electronic structure calculation, in order to discover how these studies may be relevant to the design and construction of molecular devices, such as molecular wires. When two Mo_2 units are linked by a bridging $\mu\text{-O}_2\text{C-CO}_2$ ligand, the filled δ orbitals of the metals and two of the oxalate π orbitals are involved concerning the primary interaction between the Mo_2 units and oxalate bridge. Figure 1.8 exhibits two conformational structures, where the top and bottom ones are the 90° twisted D_{2d} and the 0° planar D_{2h} configurations, respectively.^{79,82}

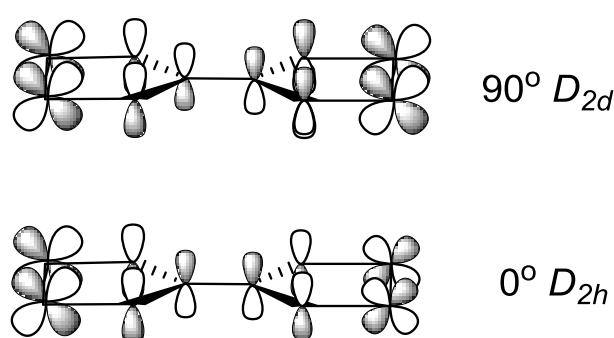


Figure 1.8: Molecular orbitals of D_{2d} and D_{2h} conformations of a $\mu\text{-O}_2\text{C-CO}_2$ linker bridged dimer of dimers, respectively.

The electronic coupling of the two Mo_2 units is very sensitive to the oxalate C–C twist angle (in the range of 0 to 90°). The orbital interaction is maximized in the 0° planar D_{2h} structure, while it is at a minimum in the 90° twisted D_{2d} structure, indicating the planar structure would be favored for electronic coupling over the twisted structure. Therefore, the oxalate bond C–C rotation will act like a rotation “dimmer-switch” with regard to $\text{Mo}_2\cdots\text{Mo}_2$ interaction through the oxalate π system. Such calculation results with regard to conformational structures are largely in accord with my own research that the electronic coupling can be obviously seen in the trans-positioned ferrocene units, while it is not clear in the cis-positioned ones, which will be introduced in detail in chapter 3.

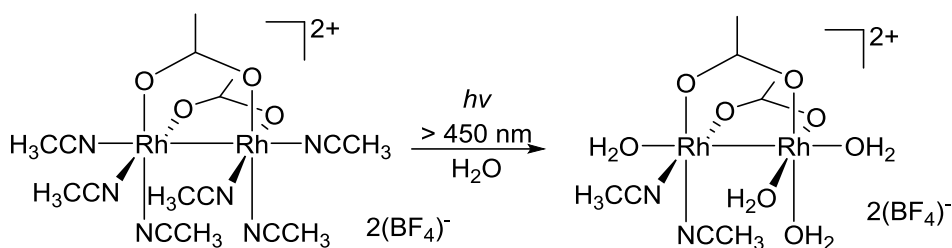
Besides the electronic structure calculation with respect to electronic interactions, those calculations toward photophysical properties have been intensively studied in recent years, aiming to uncover their fascinating optoelectronic properties.^{35,78,83,87-92} This is because conjugated organic polymers have been studied in the past two decades due to their promising

optoelectronic properties, such as field-effect transistors, light emitting diodes, and photovoltaic devices, which aroused the scientists large interest in incorporating metal ions into conjugated organic systems. This procedure resembles the introduction of molecular wires in organometallic chemistry that will be further mentioned in detail in section 1.4. Since no photophysical studies have been carried out in my thesis, the corresponding theory will not be discussed. This chapter is to combine both the calculation and photophysical chemistry that might intrigue more ideas in the future research.

1.3.2 Application Exploration

In the 1990s, McCann *et al.*^{93,94} started to anchor Mo₂ compounds, such as [Mo₂(NCCH₃)₈][BF₄]₄, on SiO₂ as a catalytic initiator for ring-opening metathesis polymerization (ROMP) of norbornene. Later in 2000, a study of heterogenization of this complex on the surface of purely siliceous MCM-41 was presented.⁹⁵ MCM (mobile crystalline material), a silicate material obtained by a template procedure, is ordered to a certain degree and has variable pore sizes.⁹⁶ Very recently, Prof. Mashima and his co-workers consider that the four supporting ligands tightly coordinated to the adjacent two metal centers maintain the dinuclear paddle-wheel skeleton, resulting in the architecture that might be tunable to control redox behavior and catalytic performance. Thus, studies on catalysis by tuning the redox potentials were carried out, with Mo₂ complex catalyzed hydrodehalogenation³¹ and polymerization³² being considered as a new trend in Mo₂-based catalysis.

Some biochemistry-related dimetal complexes have been targeted as new anti-cancer drugs, whose performance is different from that of cisplatin to circumvent resistance issues as well as to find treatments for cancers that are unresponsive to Pt drugs.⁹⁷⁻¹⁰¹ A recent study revealed the potential of the compound *cis*-[Rh₂(O₂CCH₃)₂(NCCH₃)₆][BF₄]₂ as a PCT (photochemotherapy) agent (Scheme 1.2).³⁰ It has been reported that the photolability of the equatorial CH₃CN ligands, which are stable in the dark, is crucial for the formation of the active species upon irradiation with visible light.¹⁰² It appears that this type of compounds has the potential in new drugs, thus, attracting more and more interest in this area.



Scheme 1.2: Structural representation of photochemical process for cis -[Rh₂(O₂CCH₃)₂(NCCH₃)₆]²⁺ upon visible light irradiation in H₂O.

The above mentioned brief introduction of dimetal compounds in application is intended to carry out some insights in the current cutting-edge interest in scientific research, especially for those interdisciplinary studies of biochemistry, photochemistry, and others. To the best of our knowledge, these interdisciplinary topics would definitely top the research hotspot in the near future.

1.4 Dinuclear-Based Molecular Wires

Multiply bonded dimetal complexes enclosed by mixed-ligands have been investigated extensively due to their copious synthetic strategies, which offer access to supramolecular structures and informative electrochemical properties.^{1,10-12,14,17,59,61,62,64,77,103-105} Currently, some intriguing results have been published with regard to the development of molecular wires that can be synthesized via axial linkage on the basis of dimetal compounds.²¹⁻²⁶

1.4.1 What is A Molecular Wire?

Synthesis of active materials for molecular electronic devices, such as molecular wires, has been a focal point of current material research, where much of the progress is based on conjugated organic molecules.¹⁰⁶⁻¹⁰⁸ In Figure 1.9, several organic conjugated molecules with their respective molecular lengths are highlighted.^{109,110}

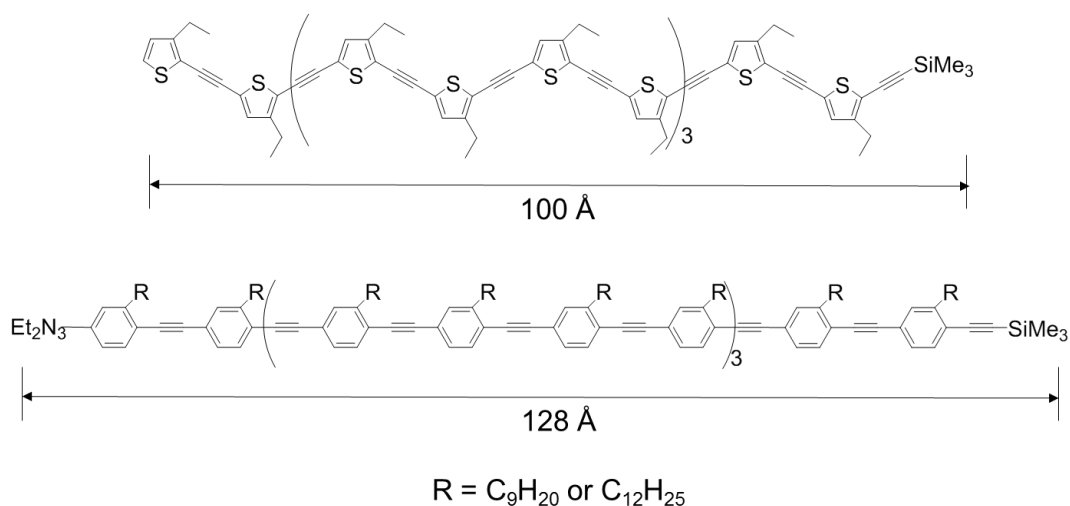


Figure 1.9: Examples of organic molecular wires.^{109,110}

It is noteworthy that the majority of organic molecules applied so far have HOMO-LUMO energy gaps (E_g) ranging from 2.4 to 5.0 eV.¹⁰⁶ It was expected that E_g might be reduced when the metallic unit was incorporated into the backbone of the organic conjugated molecules. Indeed, the series of *trans*-Pt(PR₃)₂(C≡CC₆H₄S)₂ (R = Cy, Ph, Bu, OEt, and OPh) was shown to be potentially more conductive than OPE (oligophenylene ethynylene) of comparable lengths through cross-wire junction measurements.¹¹¹

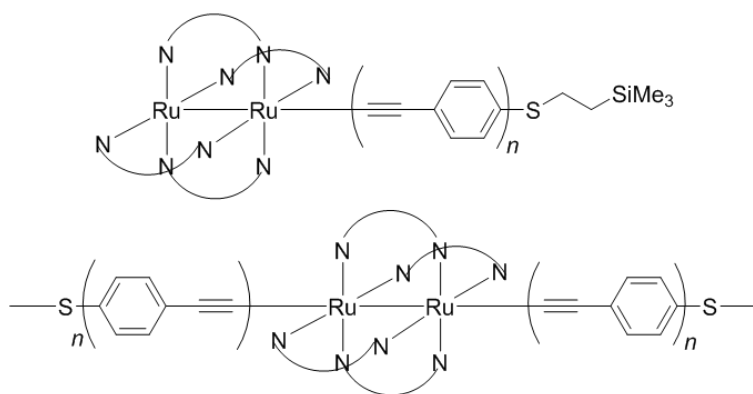


Figure 1.10: Schematic structures of molecular wires including Ru₂⁵⁺ (top)³ and Ru₂⁶⁺ (bottom)⁸ entities.

Paul Weiss and his co-operators firstly reported the testing method of organic molecular wires, which was to insert the aiming molecule into a dodecanethiol SAM (self-assembled monolayer) at the grain boundaries on gold substrate.^{112,113} After massive amount of Ru₂-related

compounds together with their intriguing electrochemical properties published by Ren *et al.*,^{11,13-17,19,36,38,114,115} realization of molecular wires incorporating metallic entities became the top priority. Three precedents incorporating thiol-capped Ru₂ moieties have been found so far,^{3,8,20} which can be exemplarily shown in Figure 1.10. Both SAMs and aiming molecules should include the thiol substituent that can be functionalized on the Au substrate.¹⁰⁸ This technique has permitted the isolation of single molecular wires from their neighbors, resulting in more precise conductance measurement. In addition, it has also allowed the addressing of the vertically arranged systems. Using scanning tunneling microscopy (STM), the molecules could then be individually imaged and addressed. Based on the understanding of this technique, the conductance testing of a Ru₂-incorporated molecular wire can be generally shown in Figure 1.11.

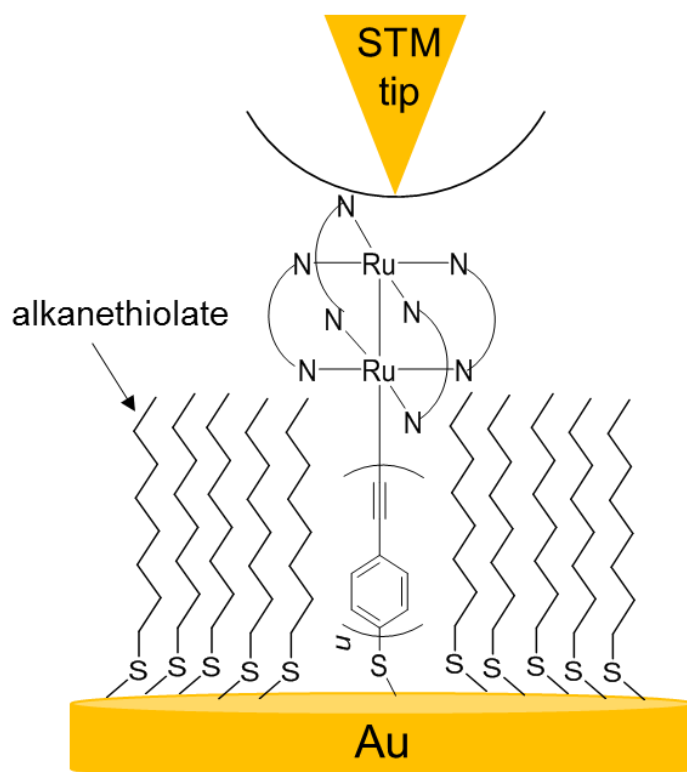


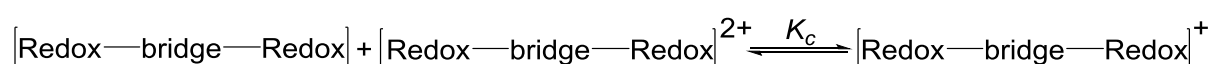
Figure 1.11: STM junction model for a Ru₂ molecular wire inserted into alkanethiol SAMs (as insulator) at grain boundaries on an Au substrate.

1.4.2 What Molecules Can Be Targeted as Molecular Wires? — Electronic Coupling

Compared to the vast organic conjugated molecular wires, in which electrons are delocalized in the whole molecules, molecular wires incorporating metallic entities should possess electronic coupling, at least electron transfer inside the molecule itself. Ren and his co-workers have dedicated a whole decade to look for potential candidates and the focus was put on Ru₂-related complexes.^{11,13-17,19,36,38,114,115} Electronic coupling in this thesis will be discussed in terms of $\Delta E_{1/2}$ value and intervalence charge transfer (IVCT).

1.4.2.1 $\Delta E_{1/2}$ Value

The linked bis-terminal redox-active complexes examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) typically show two successive redox processes of the terminal entities, if the electrons in the molecule are finely coupled. In general, the first redox process is reversible and the second quasi-reversible. The separation of the first and second waves, $\Delta E_{1/2}$ (measured in millivolts), can be used to determine a comproportionation constant (K_c) representing the stability of the singly oxidized/reduced complex in relation to an equilibrium with the neutral and doubly oxidized/reduced complexes (Scheme 1.3).¹¹⁶



Scheme 1.3: Redox reaction of bis-terminal redox-active compounds, where $K_c = e^{\Delta E_{1/2}/25.69}$.¹¹⁶

It is important to bear in mind that K_c is only a thermodynamic equilibrium constant that represents the stability of the mixed-valence intermediate derived from its neutral and doubly oxidized/reduced form, in contrast to a direct measure of electronic communication. Such factors as solvent, counter-anion, and number of redox centers can definitely affect the redox reaction, thus any comparison of $\Delta E_{1/2}$ and K_c values must relate to identical systems obtained under similar experimental conditions.^{80,117,118} It can only be deemed as strong communication when $K_c > 10^6$ is available.⁷⁹

The investigation of $\Delta E_{1/2}$ value of Ru_2 compounds can be structurally classified into two aspects, with the redox entities either equatorially or axially coordinated. Both Ru_2 and Fc units are involved for discussion, aiming to find a good molecular wire candidate. Four types of axially coordinated compounds are listed as follows: 1) two Ru_2 units connected by conjugated organic linkers; 2) two Ru_2 units connected by organometallic linkers (Fc); 3) two Fc units connected by conjugated organic linkers; and 4) two Fc units connected by Ru_2 -incorporated linkers, generally shown in Figure 1.12.

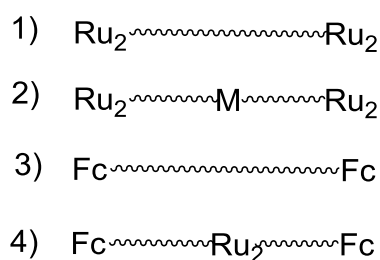


Figure 1.12: Four types of bis-terminal compounds for investigating electronic coupling.

The above mentioned four types of axially coordinated compounds can be exemplarily interpreted in Figure 1.13.^{13,15} The top Ru_2 compound $[Ru_2(DiMeOap)_4]_2(\mu-C_6)$ (ap = 2-anilinopyridinate) bridged by 1,3,5-hexatriyn-diyl ($\mu-C_6$), can result in two analogous compounds, $[Ru_2(DiMeOap)_4]_2[\mu-C\equiv CC(C(CN)_2)-C(C(CN)_2)C\equiv C]$ and $[Ru_2(DiMeOap)_4]_2[(\mu-C_6)(Co_2(DPPM)(CO)_4)]$, by reacting with their corresponding linkers, tetracyanoethene (TCNE) and $Co_2(DPPM)(CO)_6$, respectively.¹³ The 1,1'-diethynylferrocene bridged compound 1,1'- $[Ru_2(ap)_4(C\equiv C)]_2Fc$ shown in the bottom of Figure 1.13 is as well targeted for $\Delta E_{1/2}$ comparison.¹⁵ Among these four compounds, the two terminal Ru_2 of the previous two complexes are connected by conjugated organic linkers, while they are bridged by the organometallic linkers in the latter two complexes. The two organometallic-linker bridged compounds have $\Delta E_{1/2}$ values (reduction potentials) of 200 and 100 mV, respectively. However, only $\Delta E_{1/2}$ value of 180 mV can be found in $[Ru_2(DiMeOap)_4]_2(\mu-C_6)$, while that in TCNE-bridged compound is not directly observed. On the basis of the above mentioned results, it can be assumed that the $\Delta E_{1/2}$ values are accordingly irregular when the terminal Ru_2 are

bridged either by organic or organometallic linkers.

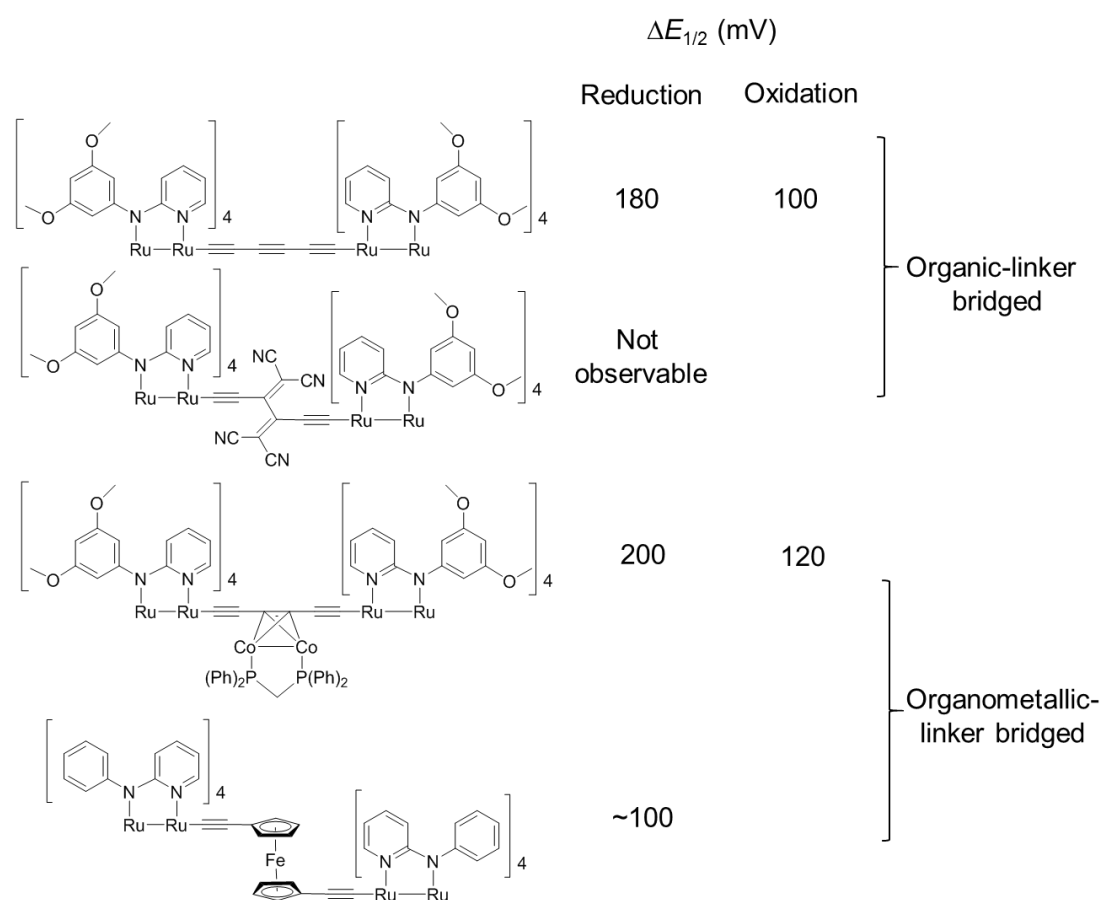


Figure 1.13: $\text{Ru}_2 \cdots \text{Ru}_2$ compounds axially linked by organic and organometallic ligands. $\Delta E_{1/2}$ (Reduction) denotes the difference between $E_{1/2}(\text{Ru}_2^{5+}-\text{Ru}_2^{5+})/(\text{Ru}_2^{5+}-\text{Ru}_2^{4+})$ and $E_{1/2}(\text{Ru}_2^{5+}-\text{Ru}_2^{4+})/(\text{Ru}_2^{4+}-\text{Ru}_2^{4+})$ and $\Delta E_{1/2}$ (Oxidation) denotes the difference between $E_{1/2}(\text{Ru}_2^{6+}-\text{Ru}_2^{6+})/(\text{Ru}_2^{6+}-\text{Ru}_2^{5+})$ and $E_{1/2}(\text{Ru}_2^{6+}-\text{Ru}_2^{5+})/(\text{Ru}_2^{5+}-\text{Ru}_2^{5+})$.

In contrast to the linked Ru_2 compounds shown above, the linked Fc compounds reveal more interesting and intriguing electronic properties. Three Fc compounds connected by conjugated organic linkers have been found (Figure 1.14 left).¹⁶ The oxidation of the terminal Fc units appears as a pseudo-two-electron wave in all three cases, which means no direct observation of $\Delta E_{1/2}$ values can be obtained when connected by conjugated organic linkers containing more than five carbon atoms. Interestingly, $\Delta E_{1/2}$ values can be clearly observed when $\text{Ru}_2(\text{DMBA})_4$ moiety ($\text{DMBA}^- = N,N'$ -dimethylbenzamidinate) is applied to mediate the electron transfer between the terminal Fc units.^{14,17,19} As shown in Figure 1.14 right, all $\Delta E_{1/2}$ values over 200 mV despite of the length of polyyne bridges indicate the retention of strong interferrocene electronic coupling over extended distances. Comparing the $\Delta E_{1/2}$ values between the

conjugated organic and Ru₂(DMBA)₄-mediated Fc compounds, it is easy to assume that Ru₂(DMBA)₄ fragment is among the most efficient mediators of intramolecular electron transfer.

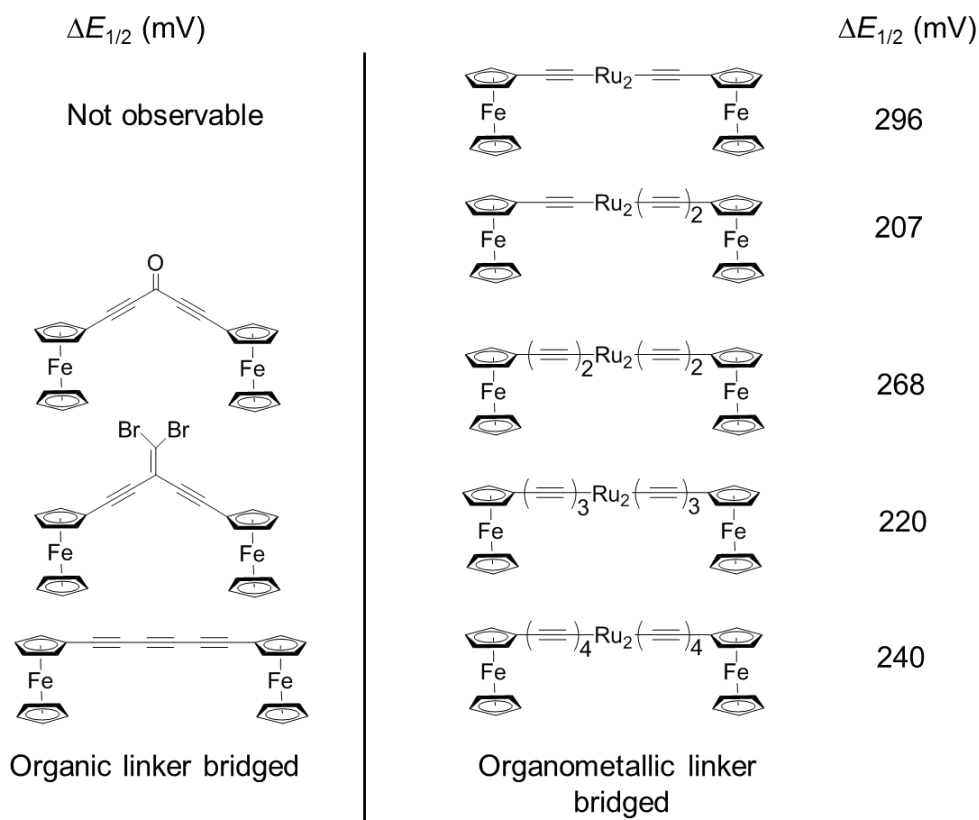


Figure 1.14: Compounds containing bis-terminal redox-active entities. Ru₂ entity represents Ru₂(DMBA)₄. $\Delta E_{1/2}$ denotes the difference between $E_{1/2}(\text{Fc}^+-\text{Fc}^+)/(\text{Fc}^+-\text{Fc})$ and $E_{1/2}(\text{Fc}^+-\text{Fc})/(\text{Fc}-\text{Fc})$.

My previous work of synthesizing a Ru₂-fragment linked compound [Ru₂(DMBA)₄(C≡C–TTFR)₂] (TTFR = 5-ethynyl-2-(4,5-dimethyl-1,3-dithiol-2-ylidene)benzo[d][1,3]dithiole) contains two redox-active organic terminal entities (TTF), which shows a minimal electronic interaction between the two TTF moieties via electrochemical studies (Figure 1.15).¹² Unfortunately, the minimal electronic interaction between two TTF entities might be derived from the additional benzene ring that stabilizes a localized radical cation and prevents interunit coupling. This molecule has a length of 3.3 nm, which is somehow of suitable length for a molecular wire. Especially with its terminal –SMe substituent, this molecule might serve as a good candidate to be functionalized on the STM substrate.

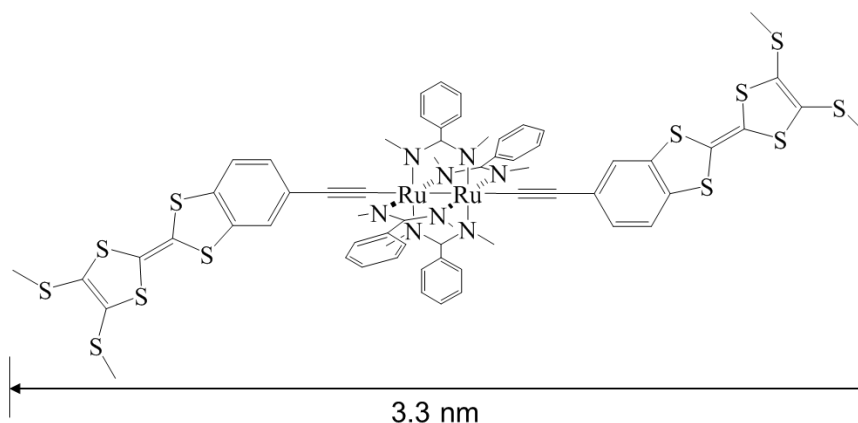


Figure 1.15: Molecular structure of compound $[\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C}-\text{TTFR})_2]$.

Besides the above mentioned axially coordinated Ru_2 compounds, $\Delta E_{1/2}$ values of equatorially coordinated compounds are as well interpreted herein. Shown in Figure 1.16, the top three Ru_2 -based compounds (Ru_2 represents $\text{Ru}_2(\text{DARF})_3\text{Cl}$ for the top two^{114,115} and $\text{Ru}_2(\text{DARF})_2\text{Cl}$ for the third,³⁸ respectively, where $\text{DARF}^- = N,N'$ -di(3,5-dichlorophenyl)formamidinate; $\text{D}(3,5-\text{Cl}_2\text{Ph})\text{F}^-$) are found in the literature, while compounds of the bottom type with two Fc units equatorially connected by a Ru_2 fragment have not been targeted so far. Only a slight $\Delta E_{1/2}$ value of ca. 70 mV was directly found in the third compound, while no obvious $\Delta E_{1/2}$ values in the top two compounds could be observed. When N,N' -di(3-methoxyphenyl)formamidinate (DmAmiF^-) was applied in the third compound instead of $\text{D}(3,5-\text{Cl}_2\text{Ph})\text{F}^-$, the slight $\Delta E_{1/2}$ value disappeared instead.³⁶

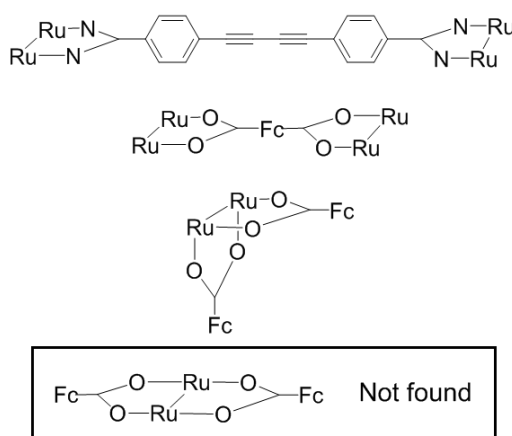


Figure 1.16: Equatorially connected Ru_2 compounds.

1.4.2.2 Intervalence Charge Transfer (IVCT)

It was already mentioned that Kc is only a thermodynamic equilibrium constant that represents the stability of the mixed-valence intermediate derived from its neutral and doubly oxidized/reduced form, other than a direct measure of electronic communication. Therefore, another parameter H_{ab} that can represent the measurement of electronic coupling is necessary to be mentioned and defined. In 1967, Robin and Day first published the influential work wherein the nomenclature of classes I, II, and III was introduced to describe valence trapped, strongly coupled, and fully delocalized mixed valence systems, respectively.¹¹⁹ In the same year, Hush published his pioneering work on the interpretation of the phenomenon of intervalence charge transfer (IVCT) absorptions, which became the theoretical foundation of electronic coupling.¹²⁰

Although no IVCT studies were carried out in my work, it is necessary to make clear the relation between H_{ab} (electronic coupling) and absorptions in the near IR region (IVCT). The electronic coupling parameter H_{ab} can be determined experimentally using the following equation:

$$H_{ab} = (0.0206/d) (\bar{\nu}_{\max} \Delta\bar{\nu}_{1/2} \epsilon_{\max})^{1/2}$$

where d is the electron transfer distance (\AA), $\bar{\nu}_{\max}$ is the energy of the intervalence band (cm^{-1}) at the maximum extinction coefficient, $\Delta\bar{\nu}_{1/2}$ is the peak width at half peak height (cm^{-1}), and ϵ_{\max} is the peak intensity ($\text{M}^{-1} \text{cm}^{-1}$).⁷⁹

1.4.3 Electronic Coupling in Mo₂-Based Compounds

Investigation of electronic coupling in the area of Mo₂ complexes has been largely carried out by Cotton and his co-workers. Most of the compounds mentioned in chapter 1.2.2 have been examined by electrochemical methods. These Mo₂ compounds are only equatorially connected by charged ligands (carboxylate, formamidinate, amidate, etc.), which is the major difference to the Ru₂ area. Therefore, equatorially connected patterns as shown in Figure 1.16 are suitable

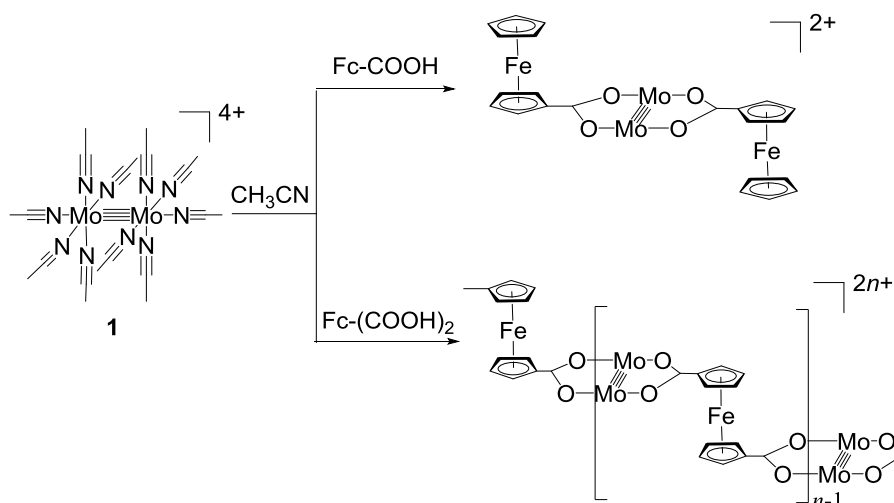
to be studied for Mo₂ compounds. The dimer of dimers in Figure 1.6 can be the best example to interpret $\Delta E_{1/2}$ values for Mo₂ compounds. The largest $\Delta E_{1/2}$ value of 223 mV can be found for compound [Mo₂(DAniF)₃]₂(O₂C–CO₂) (DAniF = *N,N'*-di(*p*-anisyl)formamidinate).⁵⁹ A series of compounds [Mo₂(DAniF)₃]₂(O₂C–X–CO₂), where X represents highly unsaturated, fully conjugated linkers, has been examined, demonstrating that the π system of these dicarboxylate linkers is mediating communication.¹²¹

Since the electronic coupling investigation between two Mo₂ units via organic linkers has been largely investigated, the work in my thesis will be focused on the reversed trend, i.e. the electronic interaction detection between two terminal Fc units via a Mo₂ mediator, especially between the undiscovered equatorially trans-positioned Fc units via the Mo₂ mediator.

2 Objective

The goal of this thesis was to develop a family of multi redox-active mixed-ligand Mo₂ compounds that could be potentially applied for molecular wires. Therefore, oxidizable Fc-CO₂⁻ entity was employed for this purpose. Besides, a dicarboxylate linker Fc-(CO₂⁻)₂ was introduced as well in order to build up supramolecular structures.

It was envisioned to obtain a trans-positioned compound *trans*-[Mo₂(O₂C-Fc)₂(NCCH₃)₄][BF₄]₂ by reacting [Mo₂(NCCH₃)₁₀][BF₄]₄ (**1**) and Fc-COOH at the ratio of 1 to 2, which would be in accord with a possible ferrocenedicarboxylate-linked ladder-type oligomer *trans*-[(CH₃CN)₄Mo₂(O₂C-Fc-CO₂)_n][BF₄]_{2n}, when Fc-(COOH)₂ was reacted with **1** (Scheme 2.1).



Scheme 2.1: Proposed structures (BF₄⁻ anions are deleted for clarity) by reacting **1** and Fc-COOH and Fc-(COOH)₂, respectively.

Afterwards, *trans*-[Mo₂(O₂C-Fc)₂(NCCH₃)₄][BF₄]₂ could be applied as a precursor for further substitution reactions. Since bridging ligands DPPX and formamidinate (DArF) exhibit different steric effects, a new scope of multi redox-active mixed-ligand Mo₂ complexes could possibly be obtained and their corresponding electrochemical properties could be studied. It was expected that the *trans*-positioned Mo₂ compounds would display electronic interaction between the distal Fc units.

3 Results and Discussion

3.1 Publication Summaries

In this chapter, short summaries of the publications prepared during the course of this dissertation are presented. The full manuscripts can be found in the appendix of the thesis and the bibliographic details of the publications in chapter 5.

3.1.1 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers

Xu-Min Cai, Dominik Höhne, Mathias Köberl, Mirza Cokoja, Alexander Pöthig,
Eberhardt Herdtweck, Stefan Haslinger, Wolfgang A. Herrmann, and Fritz E. Kühn

The focus of this manuscript is put on the synthetic route from a small molecule to supramolecular structures.

The reaction of $[\text{Mo}_2(\text{NCCH}_3)_{10}][\text{BF}_4]_4$ (**1**) with four different carboxylate ligands results in four different-shaped complexes, *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ (*cis*-**2**), $[(\text{CH}_3\text{CN})_4\text{Mo}_2(\text{O}_2\text{C-Fc-CO}_2)_4][\text{BF}_4]_8$ (**3**), $[(\text{CH}_3\text{CH}_2\text{CN})_4\text{Mo}_2(\text{O}_2\text{C-C}_6\text{F}_4\text{-CO}_2)_4][\text{BF}_4]_8$ (**4**), and $[(\text{CH}_3\text{CN})_6\text{Mo}_2(m\text{-bdc-F})_3][\text{BF}_4]_6$ (**5**), respectively. All these complexes have been characterized via solution (liquid NMR and UV–vis spectroscopy) and solid state (X-ray crystallography, elemental analysis, and TG-MS and IR spectroscopy) methods, revealing distinct formations in liquid and solid states, respectively (Figure 3.1).

A mixture of *cis* and *trans* products can be obtained when the reaction of precursor **1** and Fc-COOH has been carried out for 20 h, while only the *cis* species could be observed when the reaction was done for three weeks, indicating that the *cis* configuration is thermodynamically stable. In the solid state, complex **2** is axially linked by BF_4^- counter anions, forming the 1D linear oligomer that keeps the *cis* configuration of Fc-CO₂⁻ ligands. For complexes **3** and **4**, both have the square-shaped structures that can be linked into a 1D tubular polymer via BF_4^-

counter anions. With regard to complex **5**, a hexagonal-shaped 2D layer of the trimers can be observed, which goes along with bridging C–H···F interactions between equatorially coordinated acetonitrile molecules and axially coordinated BF₄ anions. Furthermore, a 3D metal-organic framework could be in principle obtained via axial and equatorial interactions between Mo₂ moiety and BF₄[−] counter anion.

The labile disassembly of all solid structures in solution reveals the weak axial bonding via BF₄ anions in the solid state. In order to shed light on the axial interaction strength and compound thermostability, both IR spectroscopy and TG-MS are applied for further interpretation. IR spectroscopy reveals that all the ν_{BF} absorption bands are within the normal range (around 1050 and 1020 cm^{−1}). While thermodynamic analysis of all compounds uncovers higher temperature-stability of compound **5** than that of compounds **2–4**.

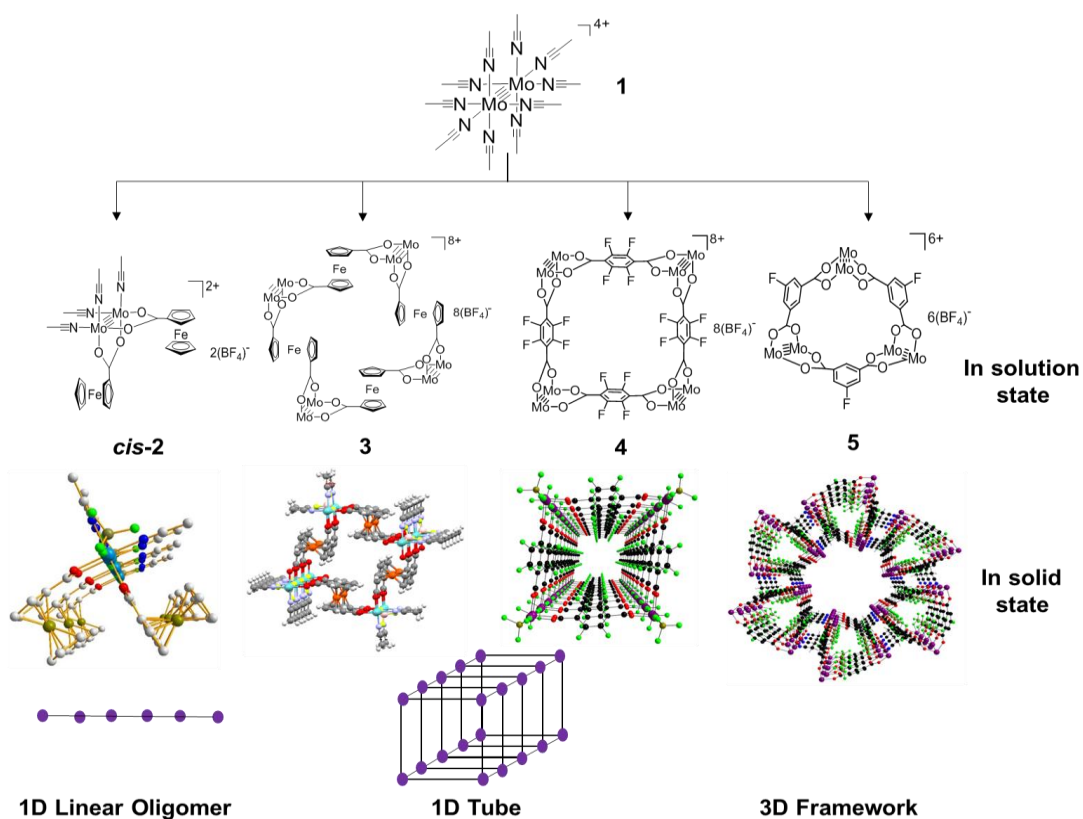


Figure 3.1: Syntheses of compounds **2–5** and their corresponding structures both in solution and solid states.

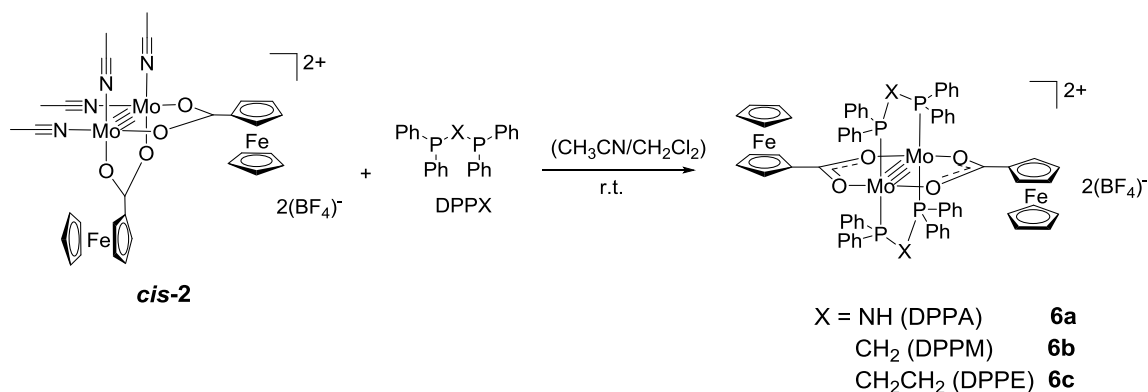
Declaration: Experimental work of synthesizing and characterizing compounds **4** and **5** is from Dominik Höhne and Mathias Köberl.¹²²

3.1.2 Rational Synthesis and Characterization of Dimolybdenum(II) Compounds Bearing Ferrocenyl-Containing Ligands toward Modulation of Electronic Coupling

Xu-Min Cai, Korbinian Riener, Eberhardt Herdtweck, Alexander Pöthig and
Fritz E. Kühn

The work in this manuscript focuses on the rational synthesis of Mo₂ complexes to modulate the electronic coupling between the distal Fc units.

The reaction of *cis*-[Mo₂(O₂C-Fc)₂(NCCH₃)₄][BF₄]₂ (**cis-2**) with three bulky diphosphine (DPPX) ligands [DPPX = DPPA (*N,N*-bis(diphenylphosphino)amine), DPPM (1,1-bis(diphenylphosphino)methane) and DPPE (1,2-bis(diphenylphosphino)ethane)] results in *cis*-to-*trans* converted products of the general composition *trans*-[Mo₂(O₂C-Fc)₂(DPPX)₂][BF₄]₂ (**6a-6c**; Scheme 3.1), which is unambiguously verified by X-ray crystallography (Figure 3.3_right side). All compounds have been characterized by means of NMR, UV-vis and IR spectroscopy as well as TG-MS measurements.



Scheme 3.1: Syntheses of compounds **6a-6c**.

DFT calculations (ground state energy) are used to underpin the experimental results on the thermodynamic stability of the presented complexes. With regard to the *trans*-products, a methylene-bridged diphosphine was subject to the study and the steric bulk of the substituents was gradually increased, from H to methyl to phenyl. Only small energetic differences of *cis*

and trans could be observed for R = H ($\Delta G_{\text{cis/trans}} = 1.1$ kcal/mol), a significant increase could be observed with R = Me, Ph ($\Delta G_{\text{cis/trans}} = 14.6$ and 23.4 kcal/mol, respectively), indicating that the trans-coordination of bulky phosphines is favored, most likely due to steric reasons.

Interestingly, uncommon UV-vis transitions were observed compared to previously reported ones. In literature, the characteristic absorbance of Mo₂ complexes is reported as a $\delta \rightarrow \delta^*$ transition in the region of 400 to 500 nm,^{1,71,72} where the low-energy absorption at around 500 nm can be assigned to a MLCT transition. With regard to these results, the here reported electronic structure seems to be quite different, since the HOMO is uncommonly localized on the ligand (Fc), shown in Figure 3.2.

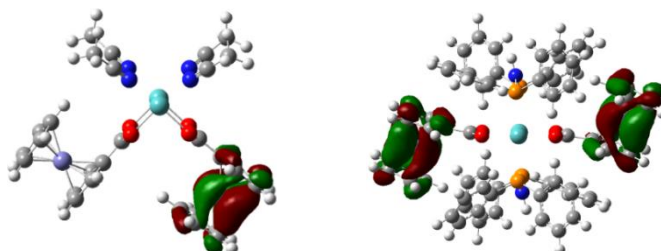


Figure 3.2. HOMOs of compounds *cis-2* (left) and **6a** (right).

As verified by DPVs, all synthesized complexes show two separate one-electron redox processes assigned to subsequent oxidations of the two redox-active Fc-CO₂⁻ ligands, with a split of ca. 70 mV (Figure 3.3 right side). This behavior reveals electronic interaction between the two equatorially *trans*-positioned Fc units.

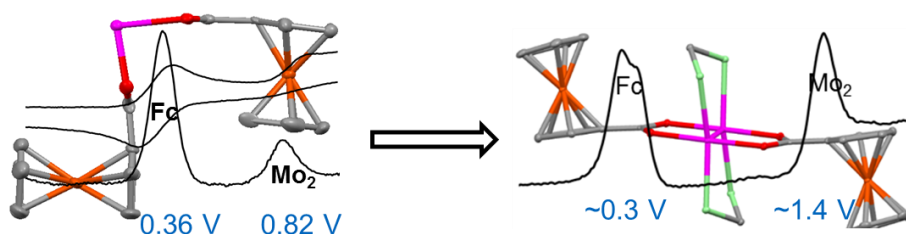


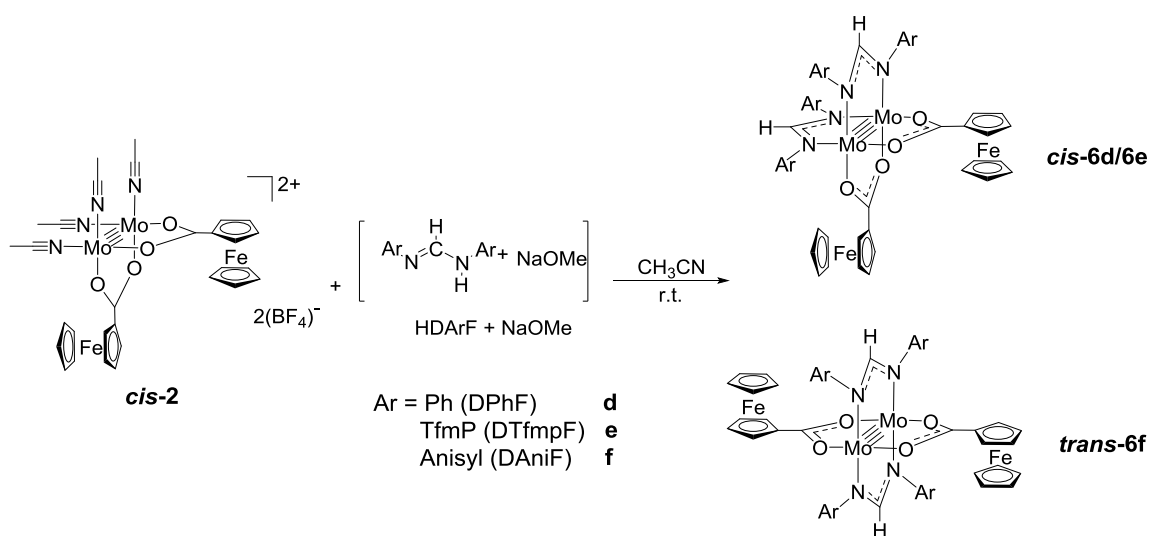
Figure 3.3: A combination of simplified molecular structures and DPVs: from *cis-2* to *trans*-(**6a-6c**).

Declaration: Computational work of all complexes is from Korbinian Riener.

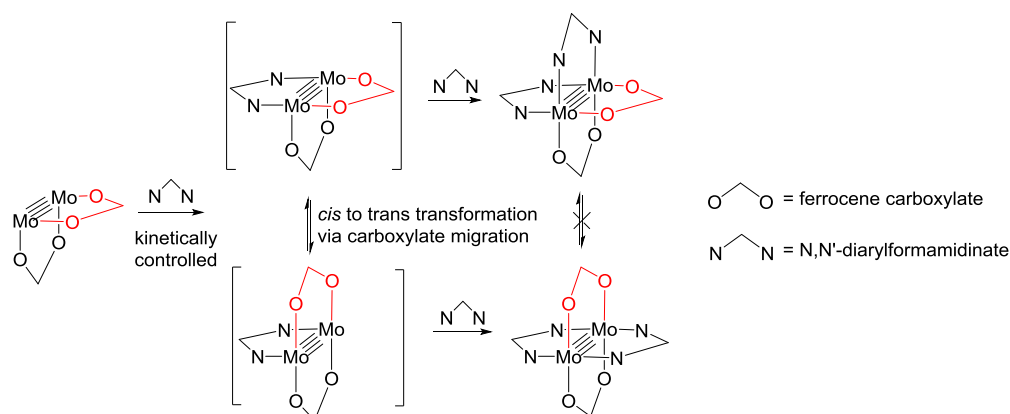
3.1.3 Synthesis and Electrochemical Properties of *cis*- and *trans*-[Mo₂(O₂C-Fc)₂(DArF)₂] (O₂C-Fc = Ferrocenecarboxylate; DArF = *N,N'*-diarylformamidinate)

Xu-Min Cai, Teresa K. Zimmermann, Alexander Pöthig, and Fritz E. Kühn

Three novel mixed-ligand dimolybdenum(II) complexes, *cis*-[Mo₂(O₂C-Fc)₂(DPhF)₂] (*cis*-**6d**), *cis*-[Mo₂(O₂C-Fc)₂(DTfmpF)₂] (*cis*-**6e**), and *trans*-[Mo₂(O₂C-Fc)₂(DAniF)₂] (*trans*-**6f**), [DArF = *N,N'*-diphenylformamidinate (DPhF), *N,N'*-di(*p*-trifluoromethylphenyl)formamidinate (DTfmpF), and *N,N'*-di(*p*-anisyl)formamidinate (DAniF), respectively] were synthesized via the reaction of *cis*-**2** and corresponding DArF⁻ ligands (Scheme 3.2). Even though the *trans*-[Mo₂(O₂C-Fc)₂(DAniF)₂] isomers were originally expected to be the sole products,¹²³ the corresponding *cis*-[Mo₂(O₂C-Fc)₂(DAniF)₂] complexes were isolated as well via crystallization and verified unambiguously by X-ray crystallography. This discovery contrasting previous assumptions concerning the synthesis of *cis*- and *trans*-isomers might be ascribed to the similar basicity of DArF⁻ and Fc-CO₂⁻, both of which are more basic than acetate.^{36,38,123} A reaction mechanism regarding the relevant reaction intermediates is proposed because no interconversion of *cis* and *trans* product could be observed (see Scheme 3.3).



Scheme 3.2: Syntheses of compounds **6d–6f**.



Scheme 3.3. Proposed mechanism for isomerization via intermediate transformation. Equatorial CH_3CN ligands are not shown due to the fast scrambling with solvent CH_3CN .

All DPVs of the products are illustrated in Figure 3.4, along with their corresponding simplified molecular structures. The electron-donating ligand DArF^- enables the oxidation of the $[\text{Mo}_2]^{4+}$ unit prior to that of Fc, while the oxidation sequence is reversed when acetonitrile or diphosphine ligands are coordinated instead of formamidinate. In the case of *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DAniF})_2]$, interactions were found between the two redox-active ferrocenecarboxylate ligands, with a clear $\Delta E_{1/2}$ value originating from the peak-to-peak separation in DPV of around 100 mV with CH_2Cl_2 as solvent. Furthermore, the second oxidation of the Mo_2 -handle $[\text{Mo}_2]^{5+}/[\text{Mo}_2]^{6+}$ was exclusively observed with DAniF^- as ligand. On the basis of the above mentioned results, ligand basicity appears to decrease in the following order: DArF^- ($\sim \text{Fc-CO}_2^-$) $>$ DPPX $>$ CH_3CN .

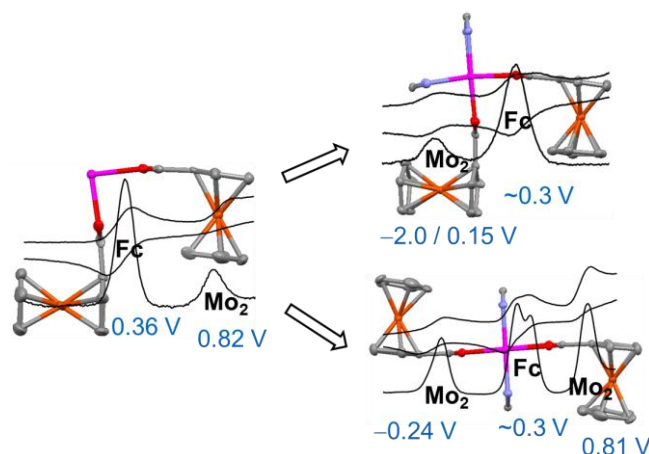


Figure 3.4: A combination of simplified molecular structures and DPVs: from *cis*-**2** to products **6d–6f**.

3.1.4 Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate)

Xu-Min Cai, Teresa K. Meister, Alexander Pöthig, and Fritz E. Kühn

The reaction of *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ (**cis-2**) with two electronically different *N,N'*-diarylformamidinate (DArF) ligands [DArF = *N,N'*-di(*p*-trifluoromethylphenyl)formamidinate (DTfmpF) and *N,N'*-di(*p*-anisyl)formamidinate (DAniF)] was carried out, resulting in the isolation of tris- and mono-substituted complexes $[\text{Mo}_2(\text{DTfmpF})_3(\text{O}_2\text{C-Fc})]$ (**7e**) and $[\text{Mo}_2(\text{DAniF})(\text{O}_2\text{C-Fc})_3]$ (**8f**), respectively, which are unambiguously verified by X-ray crystallography (Figure 3.5) and NMR spectroscopy (Figures 3.6–3.8). The isolation of these two novel complexes completes the series of complexes of the type $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ ($n = 4-0$), thus allowing for quantitative ligand basicity comparison. Both of these two complexes (**7e** and **8f**) were studied by means of electrochemical voltammetry, followed by the comparison with their bis-analogues *cis*-**6e** and *trans*-**6f**, respectively.

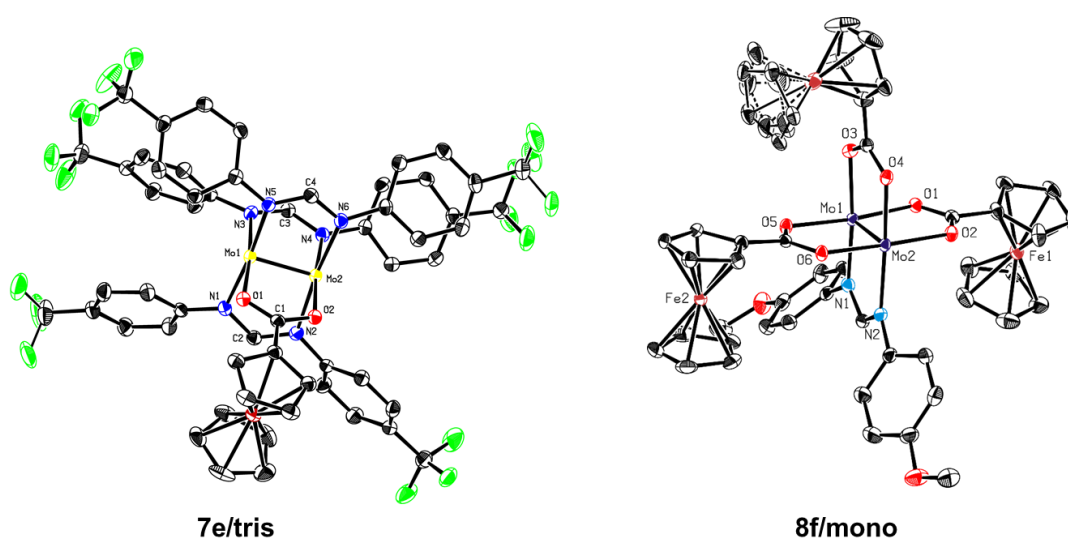


Figure 3.5: Molecular structures of compounds **7e** and **8f**.

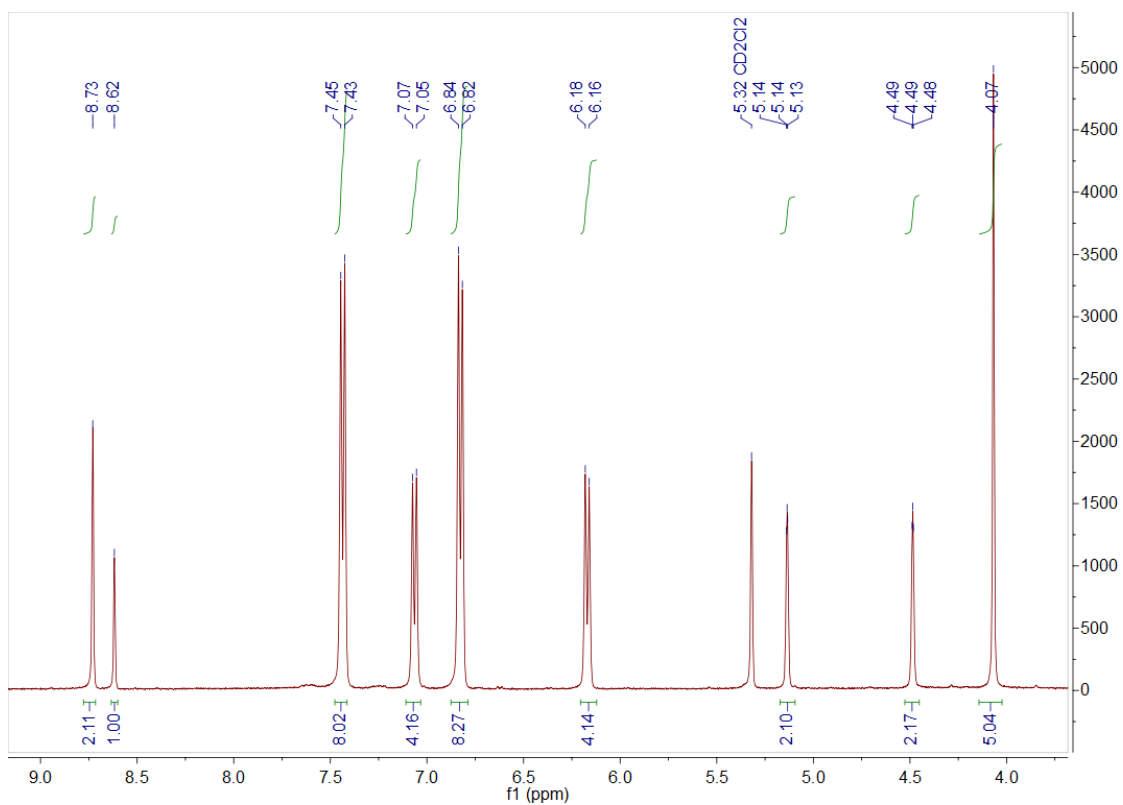


Figure 3.6: ^1H NMR spectrum of **7e** in CD_2Cl_2

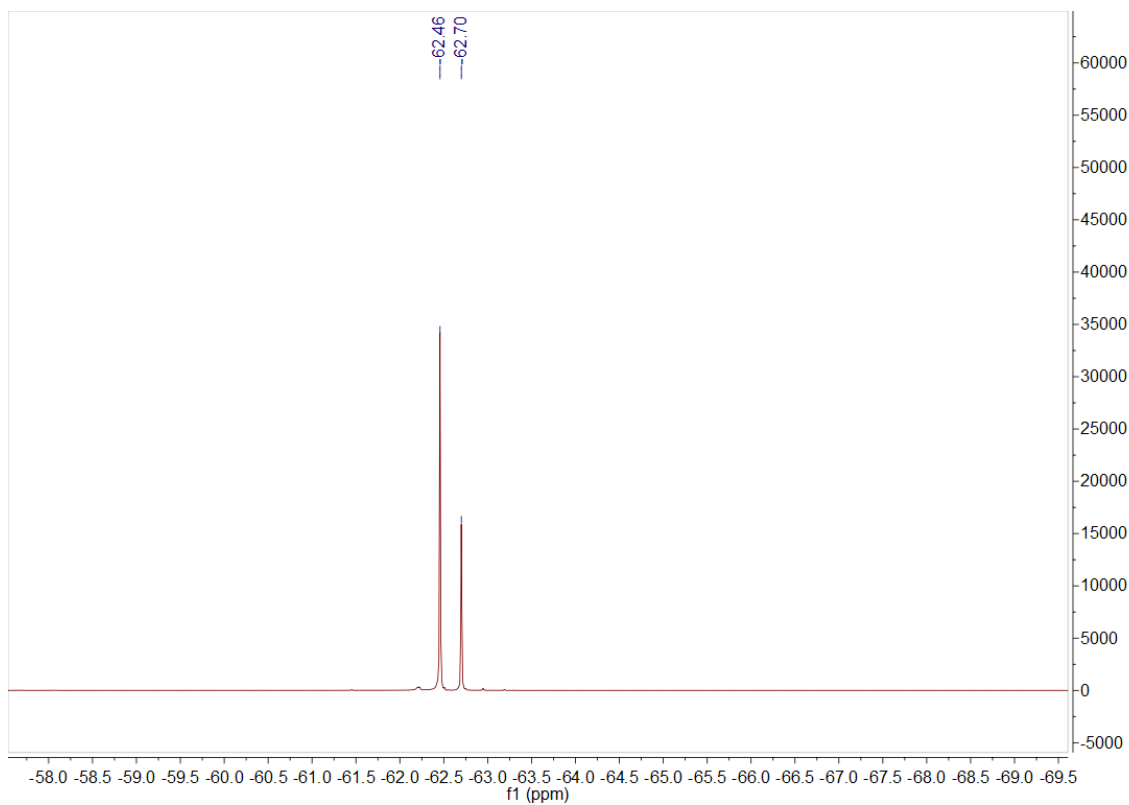


Figure 3.7: ^{19}F NMR spectrum of **7e** in CD_2Cl_2 .

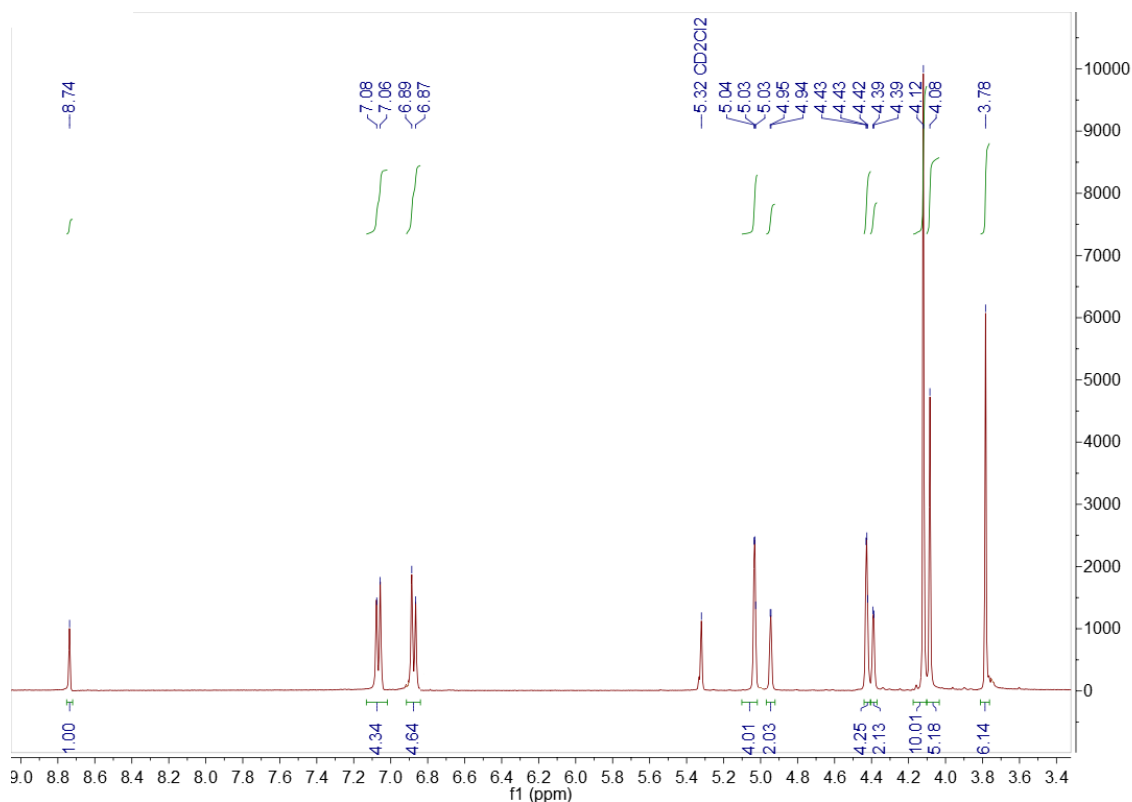


Figure 3.8: ^1H NMR spectrum of **8f** in CD_2Cl_2 .

All CVs and DPVs of **7e** and **8f** are illustrated in Figure 3.9. Complexes *cis-2* and $[\text{Mo}_2(\text{DArF})_2(\text{O}_2\text{C-Fc})_2]$ (**6d–6f**) exhibit oxidation potentials of Fc/Fc^+ at roughly 0.30–0.40 V, although the oxidation potential $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ has been tremendously inverted via ligand exchange of DArF^- over CH_3CN . Similar $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ values are as well found in diphosphine-coordinated complexes *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DPPX})_2][\text{BF}_4]_2$ (**6a–6c**). The mentioned results indicate that the Mo_2 moiety is influenced directly by the ligands DArF^- , DPPX and CH_3CN , while the oxidation potential of Fc-CO_2^- remains largely unchanged regardless of the other ligands in the complex. Given the oxidation potential $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ of all Mo_2 complexes *cis-2*, *cis-6e*, *trans-6f*, **7e** and **8f** (Table 3.1), a precise ligand basicity order decreasing along $\text{DAniF}^- > \text{DTfmpF}^- > \text{Fc-CO}_2^- \gg \text{CH}_3\text{CN}$ is found. In addition, no direct electronic interaction between Fc units in complex **8f** is observed, most likely ascribed to the full overlap of all Fc oxidation processes.

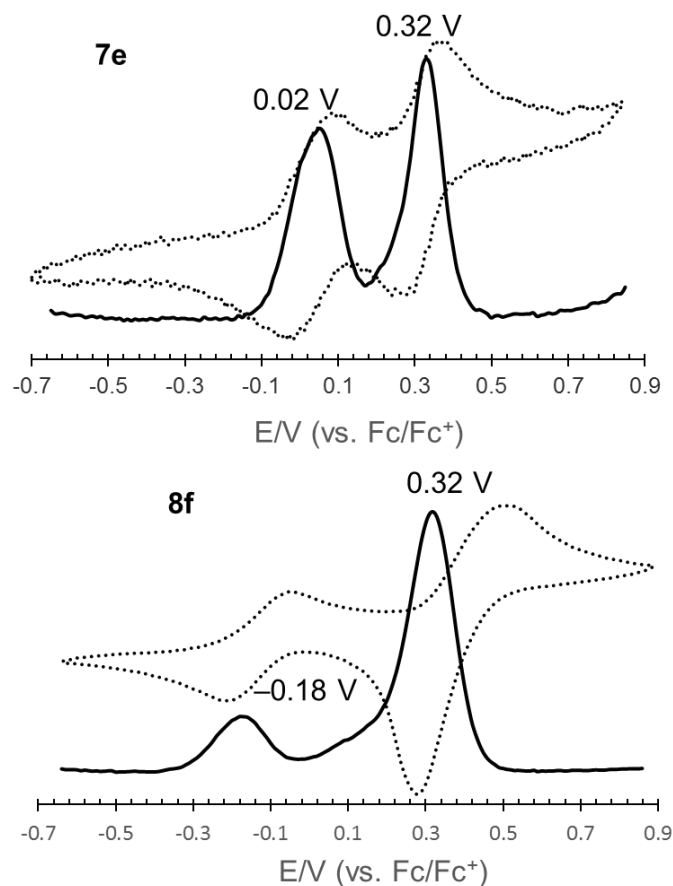


Figure 3.9: CVs and DPVs of compounds **7e** (top) and **8f** (bottom).

Table 3.1: Electrochemical Data^a (in V) for All Compounds (vs. Fc/Fc⁺)

Compd	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$\Delta E_{1/2}^b$ (mV)
	(Mo ₂ ⁴⁺ /Mo ₂ ⁵⁺)	(Fc/Fc ⁺)	(Fc/Fc ²⁺)	(Fc/Fc ³⁺)	(Fc ⁺ /Fc ²⁺)	
cis-2	0.82		0.36			
7e	0.02	0.32				
cis-6e	0.15	0.28			0.38	100
8f	-0.18			0.32		
trans-6f	-0.24	0.30			0.40	100

^a Cyclic and differential pulse voltammograms were recorded in a 0.10 M [*n*-Bu₄N][PF₆] solution (CH₂Cl₂ as solvent) on a Gamry Reference 600 voltammetric analyzer with a platinum working electrode (diameter = 1 mm), a Pt/Ti wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of all the samples was 3.0 mM, and all the potential values were referenced to Fc/Fc⁺.

^b Calculated from the difference between $E_{1/2}(\text{Fc}^+/\text{Fc}^{2+})$ and $E_{1/2}(\text{Fc}/\text{Fc}^+)$ obtained from DPV.

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Author: Xu-Min Cai, Dominik Höhne,
Mathias Köberl, et al

Publication: Organometallics

Publisher: American Chemical Society

Date: Oct 1, 2013

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Publication: Inorganic Chemistry

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Author: Xu-Min Cai, Teresa K. Zimmermann, Alexander Pöthig, et al
Publication: Inorganic Chemistry
Publisher: American Chemical Society
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Author: Xu-Min Cai, Teresa K.
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4 Summary and Outlook

As evidenced, the obtained results are in contrast to the initial proposal. In other words, the reaction of precursor **1** and its corresponding ligands Fc-COOH and Fc-(COOH)₂ resulted in cis-positioned products *cis*-[Mo₂(O₂C-Fc)₂(NCCH₃)₄][BF₄]₂ (*cis*-**2**) and square-shaped *cis*-[(CH₃CN)₄Mo₂(O₂C-Fc-CO₂)₄][BF₄]₈ (**3**) (Figure 4.1), respectively, indicating that the cis-configuration should be thermodynamically favored.

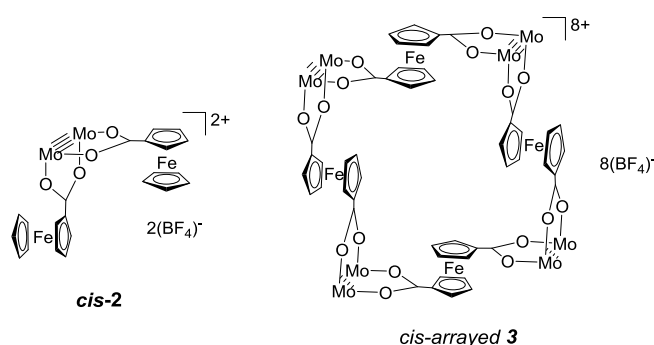


Figure 4.1: Structures of complexes *cis*-**2** and **3**. CH₃CN molecules are deleted in the products for clarity.

The reactions of *cis*-**2** and DPPX (bulky diphosphine ligands) exclusively resulted in the trans-coordinated series *trans*-[Mo₂(O₂C-Fc)₂(DPPX)₂][BF₄]₂ (**6a-6c**). DFT calculations were carried out to determine the energy gap between cis and trans arrangements. As a basis, a methylene-bridged diphosphine (DPPM) was subject to the study and the steric bulk of the substituents was gradually increased, from hydrogen to methyl to phenyl. Only small energetic differences of cis and trans configurations could be observed for hydrogen substituent, while a significant increase could be observed with methyl and phenyl as substituents. This trend supports the assumption that trans coordination is favored, most likely for steric reasons. However, no synthetic selectivity existed when *N,N'*-diarylformamidinate (DARF⁻) was applied as the mixed-ligand. Although a mixture of variable species was observed in the crude products, new compounds *cis*-[Mo₂(O₂C-Fc)₂(DPhF)₂] (*cis*-**6d**), *cis*-[Mo₂(O₂C-Fc)₂(DTfmpF)₂] (*cis*-**6e**), *trans*-[Mo₂(O₂C-Fc)₂(DAniF)₂] (*trans*-**6f**), [Mo₂(O₂C-Fc)(DTfmpF)₃] (**7e**), and [Mo₂(O₂C-Fc)₃(DAniF)] (**8f**) were isolated under different crystallization conditions (Figure 4.2).

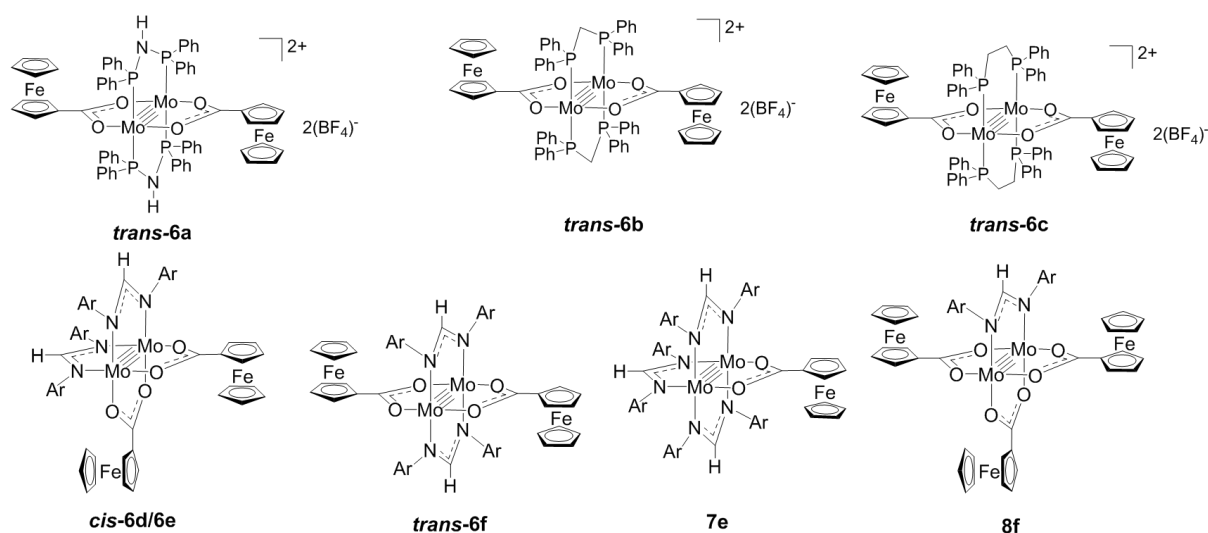


Figure 4.2: Structures of complexes **6-8**.

Electrochemical properties of all mixed-ligand molecules were studied via CV and DPV with respect to ligand, electrolyte, and solvent (Figure 4.3). Based on the oxidation potential $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ of all complexes, a ligand basicity decreasing in the order $\text{DAniF}^- > \text{DTfmpF}^- > \text{Fc-CO}_2^- > \text{DPPX} > \text{CH}_3\text{CN}$ is observed. With respect to the oxidation potential of Fc-CO_2^- , $E_{1/2}(\text{Fc}/\text{Fc}^+)$ remains largely unchanged regardless of the other ligands in the compounds, indicating that the mixed ligand mainly influences the directly-bonded Mo₂ moiety. Interestingly, electronic coupling was observed in all trans-directed Mo₂ complexes with a clear oxidation split in the Fc region, while the coupling was not clearly observable in cis-positioned complexes. This might lead to the assumption that the trans-arrangement of Fc units favors electronic coupling. Therefore, further synthetic design of redox-active motifs can be carried out according to this trans-arrangement pattern, especially for multi redox-active complexes that are intended for the synthesis of molecular wires. Among all these mixed-ligand complexes, **cis-2**, **6a-6c** and **7e** are relatively stable in air, which is in accord with their first oxidation potentials in the positive range.

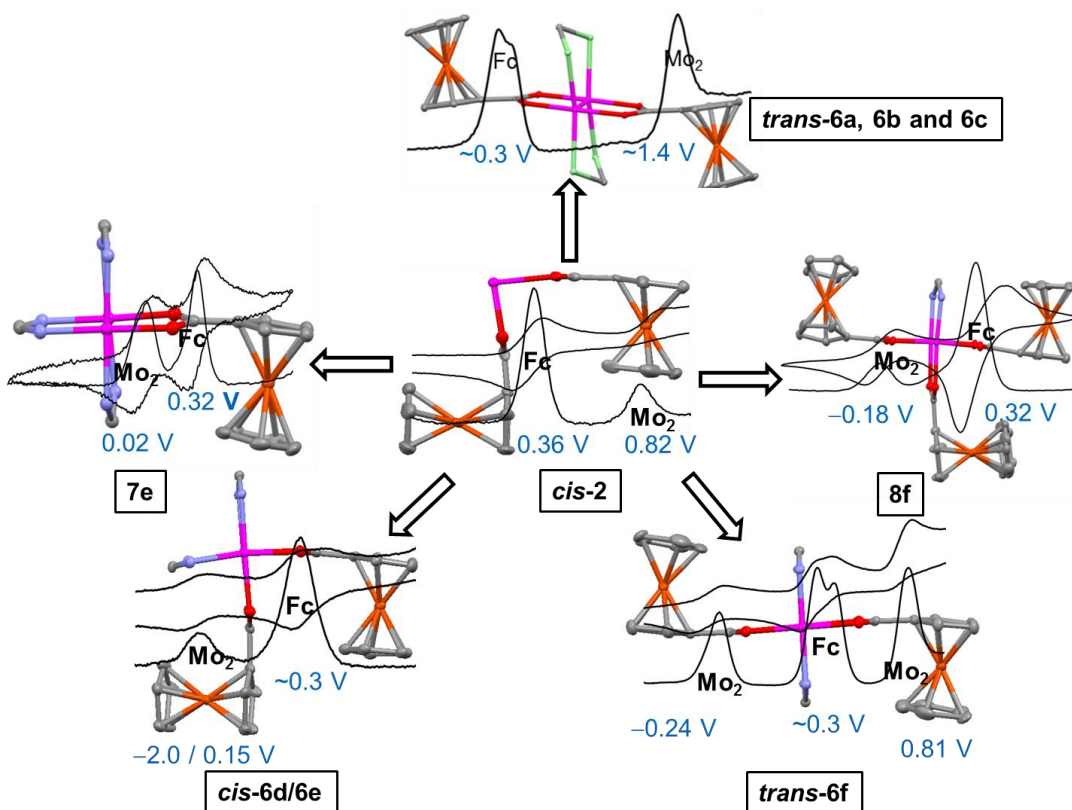
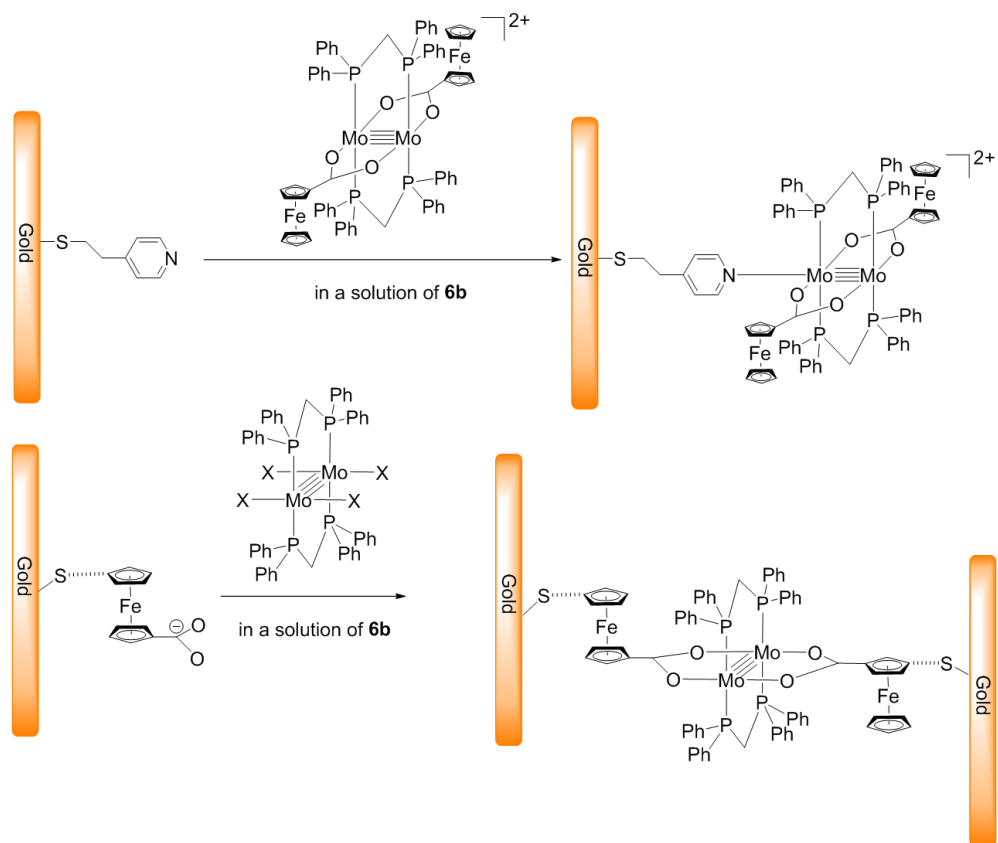


Figure 4.3: CVs and DPVs of Mo₂ complexes (*cis*-2 and 6-8) recorded in a 0.10 M CH₂Cl₂ solution of electrolyte [*n*-Bu₄N][BF₄]. All potential values are referenced to Fc/Fc⁺.

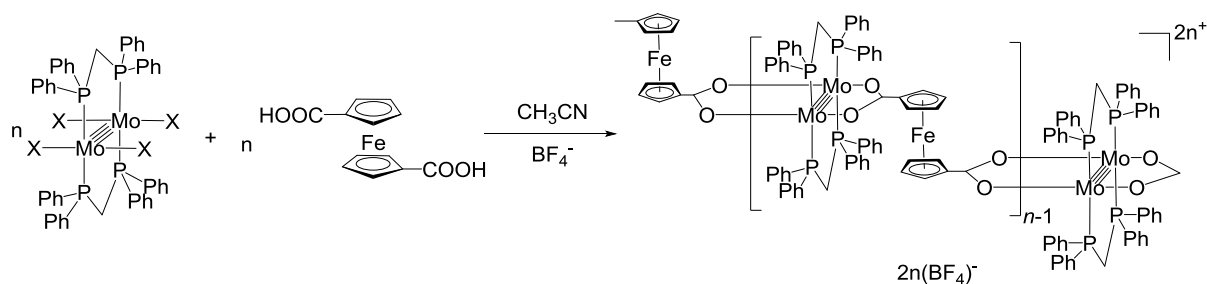
The initial purpose of this thesis was to synthesize functionalized molecules for potential applications as molecular devices. Upon comparison of $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$ and $E_{1/2}(\text{Fc}/\text{Fc}^+)$ values in all monomers, it can be assumed that *trans*-arrangement configuration favors electronic coupling, while ligands DPPX and DTfmpF⁻ have shown to stabilize their corresponding compounds in air. Therefore, the combination of both factors results in the series **6a-6c**, which might be promising candidates for molecular wires.

As briefly introduced in chapter 1.4, STM can be applied for conductance measurement, if the molecule can be functionalized on an Au surface via thiolate (–S) substituents. To date, only three Ru₂ complexes with axial ligand functionalization have been reported.^{3,8,20} Hence, the functionalization of the air-stable compounds **6a-6c** via both axial and equatorial connections is proposed (Scheme 4.1).



Scheme 4.1: Functionalization of compound **6b** on a substituted gold substrate.

Besides the proposed molecular wires mentioned above, a retrosynthetic strategy based on trans-directed precursor **6a-6c** (Scheme 4.2) is proposed in order to achieve the trans-positioned redox-active linear oligomers suggested in the objective of this thesis.



Scheme 4.2: Proposed synthesis of ladder-type oligomer starting from the compound [Mo₂(DPPM)₂X₄] (X = Cl, Br, and I).¹²⁴

5 Bibliographic Data of Complete Publications

This chapter is intended to provide the reader with bibliographic details of the published results summarized in Chapter 3 of this dissertation to allow for retrieval of the complete papers and supporting information.

5.1 Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers

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5.2 Rational Synthesis and Characterization of Dimolybdenum(II) Compounds Bearing Ferrocenyl-Containing Ligands toward Modulation of Electronic Coupling

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5.3 Synthesis and Electrochemical Properties of *cis*- and *trans*-[Mo₂(O₂C-Fc)₂(DArF)₂] (O₂C-Fc = Ferrocenecarboxylate; DArF = *N,N'*-Diarylformamidinate)

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7 Curriculum Vitae and Publication List

7.1 Curriculum Vitae

PERSONAL INFORMATION

Cai, Xumin

Sex: Female | **Date of birth:** 14/12/1986 | **Nationality:** Chinese

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EDUCATION

Doctor	Technical University of Munich, Munich, Germany Inorganic Chemistry, Molecular Catalysis, Department of Chemistry Professor: Fritz E. Kühn	10/2012 – 11/2015
Master	Nanjing University, Nanjing, P. R. China Department of Chemistry and Chemical Engineering Major GPA: 3.58 (overall) Professor: Jing-Lin Zuo Rank: 1/40	09/2010 – 06/2012
Bachelor	Nanjing Forestry University, Nanjing, P. R. China Department of Chemical Engineering and Technology Major GPA: 3.54 (overall) Rank: 1/71	09/2005 – 06/2009

WORK EXPERIENCE

Job-related Skills

- ✓ Internship at “Huzhou Bureau of Quality and Technical Supervision” as a junior inspector, conducting test to inspect the quality of industrial water, 07/2009 – 09/2009.
- ✓ Attendance to a work shop run by BASF in Ludwigshafen: “BASF Days China”, 26/10/15 – 28/10/15.
- ✓ Selected as committed young co-workers to receive TUM Ambassador on the “Forscher-Alumni Forum” event, 28/11/15 – 30/11/15.

Supervision Skills

- ✓ Two master theses 11/2013 – 04/2014; 07/2014 – 10/2014
- ✓ One bachelor thesis 12/2014 – 03/2015
- ✓ One synthetic practical course 04/2014
- ✓ Two inorganic chemistry practical courses (ca. 15 students for each)
10/2013 – 12/2013; 10/2014 – 12/2014

RESEARCH EXPERIENCE (SEE DETAILS IN PUBLICATIONS)

- ✓ Synthesis of Dinuclear Complexes for Multi-functional Molecular Materials.
- ✓ Synthesis of 1D Tubular Polymers Aiming on Functionalized MOFs.
- ✓ Synthesis of arylrhenium(VII) trioxides toward homogeneous multi-catalysis: epoxidation and ring-opening metathesis polymerization (ROMP).

PERSONAL SKILLS

- Mother Tongue(s)** Chinese
- Other Language(s)** English C2 (fluent in both speaking and writing);
German B2 (daily chatting)
- Organizational Skills** Class monitor at university, cooperating with other class leaders for organizing activities.
- Computer Skills** Microsoft Office: Word, Power Point, and Excel
Chemistry-related Program: ChemDraw, MestReNova
X-ray Crystallography Analysis, and Origin
- Driving Licence** Driving license in China

ADDITIONAL INFORMATION

Honors and Awards

- ✓ State Scholarship Fund (China Council Scholarship) for studying abroad, Sep. 2012– Aug. 2015; File Number: 201206190102.
- ✓ State Scholarship for Outstanding Undergraduate, Nov. 2007; File Number: 200728664.
- ✓ People Scholarship for Outstanding Undergraduate, Oct. 2006.
- ✓ “Dushanzi Petrochemical Industry” Scholarship for Outstanding Undergraduate, Otc. 2008.
- ✓ Award of Excellent Student Leader of Nanjing Forestry University, Oct. 2007.

7.2 Publication List

1. “Synthesis and Electrochemical Properties of *Cis*- and *Trans*-[Mo₂(O₂C-Fc)₂(DArF)₂] (O₂C-Fc = Ferrocenecarboxylate; DArF = *N,N'*-diarylformamidinate)”
Xu-Min Cai, Teresa K. Zimmermann, Alexander Pöthig, and Fritz E. Kühn, *Inorg. Chem.* 2015, 54, 6631.
2. “Rational Synthesis and Characterization of Dimolybdenum(II) Compounds Bearing Fc-containing Ligands towards Modulation of Electronic Coupling”
Xu-Min Cai, Korbinian Riener, Eberhardt Herdtweck, Alexander Pöthig, and Fritz E. Kühn, *Inorg. Chem.* 2015, 54, 3272.
3. “Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers”
Xu-Min Cai, Dominik Höhne, Mathias Köberl, Mirza Cokoja, Alexander Pöthig, Eberhardt Herdtweck, Stefan Haslinger, Wolfgang A. Herrmann, and Fritz E. Kühn, *Organometallics* 2013, 32, 6004.
4. “New Linear π -Conjugated Diruthenium Compounds Containing Axial Tetrathiafulvalene-acetylide Ligands”
Xu-Min Cai, Xiang-Yi Zhang, Julia Savchenko, Zhi Cao, Tong Ren, and Jing-Lin Zuo, *Organometallics* 2012, 31, 8591.
5. “Chiral Cyanide-Bridged Cr^{III}-Mn^{III} Heterobimetallic Chains Based on [(Tp)Cr(CN)₃]⁻: Synthesis, Structures, and Magnetic Properties”
Min-Xia Yao, Qi Zheng, **Xu-Min Cai**, Yi-Zhi Li, You Song, and Jing-Lin Zuo, *Inorg. Chem.* 2012, 51, 2140.
6. “Filling a gap: Electrochemical Property Comparison of the Completed Compound Series [Mo₂(DArF)_n(O₂C-Fc)_{4-n}] (DArF = *N,N'*-Diarylformamidinate; O₂C-Fc = Ferrocenecarboxylate)”
Xu-Min Cai, Teresa K. Meister, Alexander Pöthig, and Fritz E. Kühn, *Inorg. Chem.*, in revision, 2015.

7.3 Talks and Poster Presentations

1. **Xu-Min Cai** and Fritz E. Kühn, “Assembly of metal-organic ‘paddle-wheel’-compounds to supramolecular coordination polymers”, talk to conference “1st International Symposium on Energy Challenges and Mechanics, 8-10th July **2014**, UK”.
2. **Xu-Min Cai**, Xiang-Yi Zhang, and Jing-Lin Zuo, “四硫富瓦烯炔基取代的金(I)配合物的合成与性质研究”, poster presentation to “The 28th CCS Congress, 13-16 April, **2012**, Chengdu, China”.