2013

Tetrathiafulvalene-Annulated Phenanthroline and Its Complexes with Transition Metals

Lawrence Keith Keniley Jr

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TETRATHIAFULVALENE-ANNULATED PHENANTHROLINE AND ITS
COMPLEXES WITH TRANSITION METALS

By

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A Dissertation submitted to the
Department of Chemistry & Biochemistry
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Degree Awarded:
Summer Semester, 2013
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To whom I owe the world, my grandmother Jacquelyn S. Keniley, I would have never began to realize my potential without your incessant communication and positive reinforcement throughout my young life. Your support throughout the years has been invaluable in making me the man I am today. I am most appreciative for your presence today to realize my achievements.

To my loving parents, Debra L. Keniley and Lawrence K. Keniley, Sr., I would have never made it to today without your guidance through the rough reality of my childhood. Your methodic discipline and immutable positive outlook for my future has been instrumental in teaching me how to succeed in the face of adversity. I have paved my road to success to pay tribute to your providing the required patience and unconditional love throughout the years.
ACKNOWLEDGEMENTS

This dissertation not only represents my work in the lab and at the computer over the past six years, but also the work of the many people who made this work possible. Since my arrival in Tallahassee, just short of six years ago, on that hot and sunny Wednesday morning of July 4th, 2007, I have encountered dozens of remarkable individuals that I wish to acknowledge herein. It is through their collective hard work and personal support that I wish to present this dissertation.

First and foremost, I wish to thank my advisor, professor Michael Shatruk for taking a chance on such a young man lacking direction, and doing so at such an early stage of his own career here at FSU. Aside from being the most integral part in forming the scientist standing before you today, Dr. Shatruk has literally shown me the world. He enabled my many travels abroad, including my month stay in Geneva, Switzerland, which in itself changed me as a person and how I view the world abroad. Through our personal interactions, Dr. Shatruk has been able to show me the true definition of the word patience. He stood strong and confident during those times I had all but given up on myself. Words cannot describe the amount of appreciation and reverence I have formed for this man through the years of our acquaintance.

In addition, I would like to thank my dissertation committee members: Dr. Albert E. Stieigman, Dr. Ken L. Knappenberger, Jr., and Dr. James S. Brooks for the many discussions and suggestions regarding the direction of my research over the years.

I would also like to thank all of the current and former members of the Shatruk Group for their seemingly endless support in all aspects of the lab. I wish you all the best in your future endeavors. A special thanks to our collaborators abroad Andreas Hauser, Nathalie Dupont, Jie Ding, and Pradip Chakraborty for making my stay in Geneva an experience I will cherish forever.

I would also like to thank my loving and supportive family, as if not for you, this accomplishment may be worth much less to me.

I would like to extend my gratitude to the many friends I have had through these years, both inside and outside of the Chemistry department. Charles J. Porter, you could not have been a better man or confidant in my eyes, I owe you tremendously. Danielle R. Hay, a man could not have asked for a more understanding and supportive friend as I have found in you. James P. Williamsen, your humility and amicable nature were all that one could seek in a roommate. And amongst the others: John Watts, Nichole Revis, Jeremiah Revis, Tara Weber and my beautiful godchildren Cale and Teagan, Ruthie Flynn, Mike Peoples, Kandace Cox, Jamie Goodsen, Jeff Swedenhjelm. And those whose names I have forgotten, I thank you all!
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ABSTRACT

Recent interest in designing multifunctional transition metal complexes that incorporate the redox-active tetrathiafulvalene (TTF) molecule stems from the perspective of embedding specific localized properties of transition metal ions into TTF-containing substructures characterized by extended delocalized conduction pathways. This dissertation reports on the synthesis of tetrathiafulvalene, a ubiquitous component of organic conductors, fused directly to 1,10-phenanthroline, one of the most popular ligands in transition metal chemistry. We have devised and implemented a synthetic pathway to this unique ligand, which then was used to obtain complexes with Ru(II) and Fe(II) ions. Chapter 1 of this dissertation provides an introduction to the chemistry of TTF and its metal complexes. Chapter 2 describes the most important methods of characterization employed in this research project. Chapter 3 is devoted to the preparation and properties of the TTF-annulated phenanthroline ligands. Chapter 4 describes a detailed study of a Ru(II) complex of TTF-phenanthroline, including its structural, photophysical, and electrochemical properties. [Ru(bpy)$_2$(edt-TTF-phen)](PF$_6$)$_2$ exhibits a unique helical packing of molecules in the crystal structure. In contrast to its TTF-free analogues, this complex contains a TTF-centered highest occupied molecular orbital, and the electrochemical data show that the first two oxidations of the complex are TTF-based. Examination of the photophysical properties revealed that this Ru(II) complex experiences excited-state luminescence quenching via reductive electron transfer from the TTF to the Ru$^{3+}$ center, which opens up a path for non-radiative relaxation to the ground state through the low-lying intra-ligand charge transfer state. We also describe an unusual photoreactivity of this complex that leads to the cleavage of the central C=C bond of the TTF unit in solution. Such reactivity was monitored by the evolution of NMR, UV-visible, emission, and transient absorption spectra. Chapter 5 describes spin-crossover behavior of [Fe(NCS)$_2$(L)$_2$] (L = edt-TTF-phen or hexS$_2$-TTF-phen) and parent Fe(II) complexes. The complex with hexyl substituents is highly soluble and exhibits reversible oxidations centered on the TTF fragments. The observed spin transition was elucidated with variable-temperature Mössbauer and infrared spectroscopies.
CHAPTER ONE
INTRODUCTION

1.1 Multifunctional Materials

Multifunctionality represents one of the central themes in contemporary materials science. Imparting different functions to the same material and achieving synergetic interaction between them constitute an innovative line of attack for the development of new technologies and devices.\textsuperscript{1-6} The rational assembly of building blocks with desired physical properties to form materials that combine these properties or enhance them via synergistic interactions is especially feasible in the case of molecule-based materials, taking into account the synthetic tunability of molecular components. Specifically, coordination chemistry provides an appealing approach to the design of multifunctional materials via a simple combination of properties characteristic of a metal ion and a ligand bound together in a coordination compound.

Spanning almost all traditional scientific disciplines, there is a wide variety of research efforts that share the common aim of producing multifunctional materials. Silicon-coated nanowoven fabrics produce flexible batteries with good performance in combination with high strength and light weight.\textsuperscript{7} Varieties of multifunctional metal-oxides form multiferroic materials that simultaneously exhibit both ferromagnetism and ferroelectricity.\textsuperscript{8,9} Many industrial applications produce carbon-based nanomaterials with inherently high strength for electronic devices and for biomedical engineering including drug delivery systems and cancer targeting molecules.\textsuperscript{10,11} With relevance to the work herein, materials containing heterocyclic sulfurous compounds, such as quinoidal thiophenes and tetrathiafulvalenes, have been used to produce multifunctional magnetic conductors.\textsuperscript{2,12,13}

1.2 Tetrathiafulvalene (TTF)

1.2.1 Introduction

Tetrathiafulvalene (TTF), shown in Figure 1.1, is one of the most widely studied heterocycles, as it constitutes a ubiquitous component of synthetic conductors based on redox-active organic donor and acceptor molecules.\textsuperscript{5,14-17} Aside from its use for the preparation of synthetic metals, pronounced electron-donating ability of TTF has caused its frequent use as a sensor and luminescence quencher. With such an array of interesting properties, it is not
surprising that the studies involving TTF span the different branches of science from research in chemistry and condensed-matter physics to biology and medicine.

Figure 1.1: Tetrathiafulvalene (TTF).

1.2.2 General Aspects of TTF

1.2.2.1 History of TTF. The first studies of TTF appeared in the literature almost 90 years ago in the works by Hurtley and Smiles.\textsuperscript{18,19} Nevertheless, it was only half a century thereafter that TTF and its derivatives started to appear in the literature more regularly. The “TTF era” was incited by reports on the preparation of the organic donor in the research labs of both Coffen\textsuperscript{20} and Wudl\textsuperscript{21} in 1970. Wudl \textit{et al.} reported TTF as “an unusually stable organic radical cation”.

The electron-donating nature of TTF stems in part from its inherent gain of aromatization energy upon oxidation from the dithiolylidene moiety in the neutral state to the aromatic dithiolium ring(s) in the oxidized states as depicted in Figure 1.2.

\begin{center}
\includegraphics[width=0.8\textwidth]{figure1_2.png}
\end{center}

\textbf{Figure 1.2:} The sequential and reversible oxidations of neutral TTF to its stable radical cation TTF\textsuperscript{+} and subsequent oxidation to the stable dication TTF\textsuperscript{2+}.

Shortly thereafter in 1972, Wudl \textit{et al.} reported the room temperature electrical conductivity of a single crystal of TTF in an externally applied electric field (resistivity, $\rho = 10^{12}$ $\Omega$ cm).\textsuperscript{22} A year later, in 1973, Ferraris \textit{et al.} reported that a reaction between TTF and the electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetonitrile resulted in precipitation of a 1:1 complex in the form of shiny black crystalline plates. A partial charge transfer (CT) between the TTF donor and TCNQ acceptor resulted in unprecedented electrical conductance that was several orders of magnitude higher than that reported for any other known molecular organic material. Furthermore, the authors showed that such conductivity stemmed from a band structure that
contained features normally found in metals. It was this finding that labeled the material as the first “organic metal”.\textsuperscript{23} Later the same year (1973), Heeger \textit{et al.} claimed, although never substantiated, the same donor acceptor complex, TTF-TCNQ, to display superconducting fluctuations above 57 K.\textsuperscript{24} These two publications in 1973 were the catalyst that initiated the explosion of studies on TTF and its derivatives.

The following decade produced some rather important milestones in TTF chemistry as well. The first occurred in 1980 with the discovery of superconductivity in the CT salt of a TTF analogue, tetramethyltetraselenafulvalene (TMTSF), by Bechgaard \textit{et al.}\textsuperscript{26-28,30,31} A few years later, in 1983, Cava \textit{et al.} reported the superconducting properties of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) that, till today, is one of the most studied organic superconductors.\textsuperscript{32} The major milestones in the studies of TTF are listed in Table 1.1.

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
Year & Event \\
\hline
1926 & The first TTF derivative, dibenzo-TTF was synthesized as part of a general study of five-membered ring systems.\textsuperscript{18,19} \\
1965 & Deprotonation of 1,3-dithiolium salts afforded TTF derivatives for the first time.\textsuperscript{34} \\
1970 & First observation of parent TTF that was found to form a stable purple-colored radical cation upon reaction with chlorine gas.\textsuperscript{21} \\
1973 & First observation of metallic conductivity in an organic solid TTF-TCNQ; conductivity = 1.47\times10^4 \text{ S/cm at 66 K}.\textsuperscript{23} \\
1980 & Superconductivity observed in a TTF analogue at 1.4 K: tetramethyltetraselenafulvalene hexafluorophosphate ([TMTSF]$_2$PF$_6$).\textsuperscript{26-28} \\
1980 & TTF was derivatized extensively in the search for organic (super-)conductors.\textsuperscript{35} \\
Since 1985 & Macro cyclic TTF-based systems investigated with the aim of making molecular devices, sensors, switches, and shuttles.\textsuperscript{33} \\
\hline
\end{tabular}
\caption{A summary of the major milestones in TTF chemistry according to the literature.\textsuperscript{33}}
\end{table}

In the recent years and with relevance to this dissertation, a focus has been directed at preparing TTF-functionalized materials with novel magnetic and optical properties. Altogether, over 10,000 scientific publications discuss TTF and its derivatives, attesting to the prolific science afforded by this family of compounds.

1.2.2.2 \textbf{Theoretical considerations on the chemical structure of TTF}. Since the discovery of TTF, much research has been focused on uncovering efficient synthetic pathways towards this
molecule and its derivatives. Despite the large number of such studies, relatively few of them focused on the resulting structure adopted by the TTF-based molecule. It had been generally accepted that TTF was essentially planar, adopting $D_{2h}$ symmetry. In 1994, however, a gas phase electron diffraction study was published that proved that the planar conformation was not preferred for neutral TTF, which adopts a non-planar boat conformation of $C_{2v}$ symmetry.\(^{35}\)

In 1999, Katan reported an investigation of the structure and vibrational frequencies for TTF in different oxidation states.\(^{36}\) These results, along with the theoretical studies by Liu and co-workers,\(^{37}\) confirmed that neutral TTF can often adopt the boat-like $C_{2v}$ equilibrium geometry. In contrast, the radical cationic species TTF$^{+}$ appears to prefer the planar conformation. Furthermore, the energy difference between the two conformations is quite small in the neutral state: 0.02 eV from the DFT calculations at the local density approximated (LDA) level and 0.04 eV with the BP gradient (exchange and correlation energy’s) correction.\(^{37}\) These results are collected in Table 1.2 (see Figure 1.3 for the corresponding numbering scheme of the TTF molecule).

![Figure 1.3: Numbering of atoms in the TTF molecule.\(^{36}\)](image)

Such a small energy difference between the planar and boat conformations suggests that the TTF molecule is indeed quite flexible and, depending on the surrounding intermolecular interactions, can readily adopt either of these conformations. Additionally, the theoretical results indicate a linear correlation between charge and geometry of TTF based on variation of either a single bond length, or a function of several alterations (with the central C=C bond most affected) upon transformation from neutral to cationic species.\(^{37}\)
Table 1.2: Calculated bond lengths (Å) and angles (deg) for the TTF molecule in comparison with gas phase electron diffraction results.36

<table>
<thead>
<tr>
<th></th>
<th>TTF</th>
<th>TFF\textsuperscript{a}</th>
<th>TTF\textsuperscript{b}</th>
<th>TTF</th>
<th>TFF\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>1.095(5)</td>
<td>1.095</td>
<td>1.096</td>
<td>1.092</td>
<td>1.092</td>
</tr>
<tr>
<td>C\textsubscript{1}–C\textsubscript{2}</td>
<td>1.354(3)</td>
<td>1.372</td>
<td>1.393</td>
<td>1.36(6)</td>
<td>1.378</td>
</tr>
<tr>
<td>C\textsubscript{1}–S\textsubscript{1}</td>
<td>1.733(7)</td>
<td>1.720</td>
<td>1.706</td>
<td>1.777(8)</td>
<td>1.761</td>
</tr>
<tr>
<td>C\textsubscript{3}–S\textsubscript{1}</td>
<td>1.72(2)</td>
<td>1.708</td>
<td>1.698</td>
<td>1.76(6)</td>
<td>1.753</td>
</tr>
<tr>
<td>C\textsubscript{3}–C\textsubscript{4}</td>
<td>1.339(9)</td>
<td>1.343</td>
<td>1.348</td>
<td>1.351(1)</td>
<td>1.354</td>
</tr>
<tr>
<td>C\textsubscript{2}C\textsubscript{1}S\textsubscript{1}</td>
<td>122.7(6)</td>
<td>122.5</td>
<td>122.5</td>
<td>122.4(1)</td>
<td>122.1</td>
</tr>
<tr>
<td>S\textsubscript{1}C\textsubscript{3}S\textsubscript{4}</td>
<td>114.5(8)</td>
<td>114.9</td>
<td>114.9</td>
<td>115.2(9)</td>
<td>115.9</td>
</tr>
<tr>
<td>H\textsubscript{1}C\textsubscript{3}S\textsubscript{1}</td>
<td>117.9(8)</td>
<td>118.0</td>
<td>118.1</td>
<td>117.5(5)</td>
<td>117.6</td>
</tr>
<tr>
<td>C\textsubscript{1}S\textsubscript{1}C\textsubscript{3}</td>
<td>94(5)</td>
<td>95.4</td>
<td>95.8</td>
<td>93.6(9)</td>
<td>94.3</td>
</tr>
<tr>
<td>C\textsubscript{6}C\textsubscript{3}S\textsubscript{4}</td>
<td>117.2(5)</td>
<td>117.1</td>
<td>116.8</td>
<td>118(8)</td>
<td>117.8</td>
</tr>
<tr>
<td>(\theta)</td>
<td>17</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

\(\theta\) corresponds to the dihedral angle between SCS and SCCS planes.

1.2.2.3 Electronics within TTF. The driving force behind the widespread efforts on the chemistry of TTF and its analogues resides in their ability of these molecules to form purely organic CT materials that display metallic properties. These efforts have been realized by exploiting TTF’s electron donating properties in combination with either (a) appropriate electron acceptors or (b) oxidizing agents to generate radical cation salts.\textsuperscript{22,23,38} The electron donating ability of TTF can be explained by considering its electronic structure.

Despite being a \(4n + 2\), or \(14-\pi\) electron system, neutral TTF is a non-aromatic molecule consisting of two heterocyclic rings joined by a double bond. The parent unsubstituted TTF molecule exhibits two redox waves at \(E_{1/2}^{(1)} = –0.10\) V for the \(\text{TTF}^+ / \text{TTF}\) couple and \(E_{1/2}^{(2)} = 0.27\) V for the \(\text{TTF}^{2+} / \text{TTF}^+\) couple vs Fc\textsuperscript{+}/Fc in CH\textsubscript{2}Cl\textsubscript{2} (Fc = ferrocene). The oxidations of TTF occurring at fairly modest potentials can be rationalized by the formation of a six \(\pi\)-electron aromatic 1,3-dithiolium cationic ring, as each successive electron is removed. It should be noted that it is the presence of highly polarizable sulfur atoms and the aromaticity of the cation that renders TTF susceptible to such facile oxidation.

1.2.2.4 Key aspects of TTF chemistry. Among many attributes of TTF, we may point out the following as the most important: (1) its excellent electron donating ability that is instrumental to the high electrical conductivity witnessed in many TTF-based materials, (2) the ability of neutral non-aromatic TTF to form a stable aromatic radical cation \(\text{TTF}^+\) and dication \(\text{TTF}^{2+}\) in a reversible and step-wise manner, at easily accessible potentials, (3) the ability to fine-tune the observed oxidation potentials through synthetic modifications of the parent TTF molecule, (4) the high degree of symmetry displayed by TTF, which effectively minimizes Coulombic...
repulsions and promotes charge delocalization, (5) the planarity of TTF that allows optimization of intermolecular $\pi-\pi$ stacking and $S\cdots S$ interactions in the solid state, ultimately underlying the charge hopping mechanism of conductivity, (6) the distinctive spectral absorption and emission changes realized upon formation of $\text{TTF}^+$ or $\text{TTF}^{2+}$, as well as upon the formation of charge-transfer complexes, and (7) the robustness of TTF towards a variety of synthetic transformations, although care must be taken to avoid oxidizing or strongly acidic conditions.

### 1.2.3 TTF-Based Materials

Since the initial reports on the synthesis of TTF some 40 years ago, the $\pi$-electron donor has gained much attention as a component of conducting charge transfer salts, the most notable being TTF-TCNQ.\textsuperscript{23,39-43} Surprisingly, the potential of TTF as an intramolecular electron donor has only been realized over the last two decades. According to Bryce, the main cause behind the late blooming of such chemistry is the synthetic difficulty of obtaining reasonable quantities of the desired functionalized TTF molecules.\textsuperscript{44} The situation has been changed due to several key advances in synthetic chemistry of TTF: (1) the parent molecule can now be synthesized from readily available starting materials on a relatively large (20 g) scale;\textsuperscript{45} (2) optimizations in the methodology involving electrophilic substitutions of TTFs have provided many monosubstituted derivatives in high yield;\textsuperscript{46} and (3) advancements in selective protection-deprotection chemistry of thiolates provide key routes to multi-gram quantities of versatile TTF building blocks.\textsuperscript{47,48} Many reviews have been dedicated to the record-keeping of the array of synthetic routes toward functionalized TTFs, some even appear in the form of books,\textsuperscript{49} illustrating the sheer size of the database of TTF derivatives accessible to researchers today. Fanghánel et al. have produced three specific reports, totaling over 500 pages, that track the advances in the synthesis, reactions, and characterizations of tetrachalcogenfulvalenes,\textsuperscript{50-52} one of which contained a useful scheme summarizing many of the synthetic routes toward functionalized TTF, shown below in Figure 1.4.\textsuperscript{52}

These synthetic advances allow design of molecular architectures that may afford materials with specific properties of interest. Some areas where TTFs have been traditionally used are collected in Figure 1.5, in addition to some less traditional areas realized recently such as self-assembling materials,\textsuperscript{53,54} field-effect transistors,\textsuperscript{55-58} non-linear optics,\textsuperscript{59} supramolecular switches,\textsuperscript{60} solar cell dyes or copolymers,\textsuperscript{61,62} sensors for explosives detection,\textsuperscript{63} or magnetoimmunosensors.\textsuperscript{64}
Discussed below are some of the most important milestones in the discovery of TTF-based materials.

1.2.3.1 TTF-TCNQ. TTF and its derivatives are widely accepted as essential components in the preparation of organic conductors and superconductors. In 1973 the charge transfer salt...
TTF-TCNQ was discovered and reported as the first organic metal. Since then, there has been a plethora of other synthetic conductors described in the literature.

The charge transfer salt TTF-TCNQ consists of two uniform segregated stacks, one of each molecular component, that run parallel to one another (Figure 1.6). The columnar architecture is stabilized by extensive intermolecular π–π and S⋯S overlaps. These interactions cause the unpaired electrons to partially delocalize along the one-dimensional molecular stack, resulting in significant conductivity. Such stacking, however, tends to limit the observed conductivity to one dimension. In addition, the segregation of the individual components limits orbital overlap between adjacent stacks and thus minimizes interchain electron delocalization. This characteristic gives rise to insulating transitions in both stacks at low temperatures.

![Figure 1.6: The chemical structure of TCNQ (a) and the top (b) and side (c) views of the segregated molecular stacks in the crystal structure of TTF-TCNQ.](image)

1.2.3.2 TMTSF. With the discovery of TTF-based conductors came a surge in the study of other tetrachalcogenafulvalenes, especially selenium-containing analogues. A review by Jerome in 1979 presented the preparation of a series of conducting salts based on TMTSF (Figure 1.7a), of the general formula (TMTSF)$_2$X (X = PF$_6^-$, AsF$_6^-$, SbF$_6^-$, TaF$_6^-$, BF$_4^-$, ClO$_4^-$, ReO$_4^-$). All of these materials, except for the ClO$_4^-$ salt, exhibited a characteristic metal-insulator transition at temperatures ranging from 180 K for the ReO$_4^-$ salt, to 12 K for the PF$_6^-$ salt (shown in Figure 1.7b). Moreover, the PF$_6^-$ salt showed a superconducting transition under applied pressure at 1 K, and the ClO$_4^-$ salt was shown to exhibit a superconducting transition under
ambient pressure at 1.3 K.\textsuperscript{26-28,30,31} Although all the salts crystallize in the same triclinic space group $P\overline{1}$ and exhibit similar crystal packing motifs, they show an array of different properties at low temperature and/or high pressure. This is direct proof that despite the anions having no part in the actual conduction mechanism that occurs through the $\pi-\pi$ and Se…Se interactions, they can dramatically influence the resulting conductive properties due to subtle differences in the crystal packing forces.

![Figure 1.7: The chemical structure of TMTSF (a) and crystal structure of (TMTSF)$_2$PF$_6$ (b) illustrating how the PF$_6^-$ counterions separate the stacks of TMTSF cations.]

1.2.3.3 (BEDT-TTF)$_3$[Mn$^{II}$Cr$^{III}$(ox)$_3$]. Over the last decade, there has been a growth of interest in using TTF-based molecules for the preparation of multifunctional molecular solids, in which conductivity is combined with other useful properties such as optical activity, electrochemical response, or magnetic bistability.\textsuperscript{14,66} The most notable, and arguably groundbreaking, effort was offered by the Coronado group, who combined BEDT-TTF with oxalate-bridged Mn$^{2+}$ and Cr$^{3+}$ ions to achieve metallic conductivity and ferromagnetism in the same material (Figure 1.8a-d).\textsuperscript{2} This approach relied on interleaving a polymeric anionic metal-oxalato network, as opposed to discrete molecules, with the conducting cationic BEDT-TTF layers. The researchers expected to produce novel magnetoresistant material due to the internal magnetic field produced by the ferromagnetic metal oxide layers, which would have obvious effects on the resulting conduction electrons. Indeed, as depicted in Figure 1.8e, the material behaves as a ferromagnet below 5.5 K and is metallic down to at least 0.2 K.
Figure 1.8: The chemical structure of BEDT-TTF (a) that is incorporated into a multilayered structure of the ferromagnetic metal (BEDT-TTF)$_3$[MnCr(ox)$_3$] (b). The crystal structure analysis reveals the layers are not bound to one another and exist as separate entities as shown in the top-view of the organic ($\beta$ phase) (c) and inorganic layers (d). Magneto-resistance measurements of the ferromagnetic metal (BEDT-TTF)$_3$[MnCr(ox)$_3$] at 0.7 K for the applied field perpendicular ($\theta = 90^\circ$) and parallel ($\theta = 0^\circ$) to the ferromagnetic layers (e).

The Coronado’s report of the molecule-based conducting ferromagnet was followed by many efforts toward the production of truly multifunctional materials. Nevertheless, the majority of these approaches relied on the assembly of molecular components through weak supramolecular interactions such as van der Waals forces, $\pi$-$\pi$ interactions, or hydrogen bonding. Such approaches typically resulted in little or no synergy between the properties that each component has to offer to the resulting material. Therein lays the surge in research involving the preparation of ligands that allow the direct connection of TTF to metal centers via coordination and covalent bonding. It is not hard to imagine that such a direct connection will impart better communication between the inorganic and organic substructures and thus the synergistic modification or enhancement of the materials final properties.

1.2.4 Chelating Ligands with TTF

1.2.4.1 TTF-dithiolates. Numerous studies focused on the design of molecules, in which a TTF-containing fragment connected to a chelating ligand affords robust binding to a metal ion, with a geometrically predictable arrangement of the TTF subunit. Thiolates were the first ligands ever used to attach TTF to a metal center. In 1979, Rivera et al. reported the preparation of a Ni(II) bis(TTF-dithiolene) complex that exhibited an unusually high room temperature
conductivity of 30 S cm\(^{-1}\).\textsuperscript{70} Several decades later in 2001, TTF-dithiolates were again recognized with the discovery of [Ni(tmdt)\(_2\)] (tmdt = trimethylenetetrathiafulvalenedithiolate) (Figure 1.9a), a single component molecular metal with three-dimensional conductivity. The single crystal (Figure 1.9b,c) exhibited room temperature conductivity of 400 S cm\(^{-1}\) and displayed metallic behavior down to 0.6 K (Figure 1.9d). Even a sample of compacted powder of [Ni(tmdt)\(_2\)] exhibited fairly high room temperature conductivity of 200 S cm\(^{-1}\) and displayed metallic behavior down to 70 K.\textsuperscript{71-73} This complex exemplifies the benefits gained by the exclusion of counterions, a regular component in charge-transfer complexes, from the molecular structure. In the absence of counterions, the TTF moieties come into closer contact thus allowing 3D conductivity to ensue.

![Image](image.png)

**Figure 1.9:** The chemical structure of [Ni(tmdt)\(_2\)] (a) used in the preparation of the very first example of single component molecular metal with 3D conductivity. Also shown is the crystal structure of [Ni(tmdt)\(_2\)] viewed along the \(b\) axis (b) and the molecular long axis (c). Color scheme: Ni, green; S, yellow; C, dark gray; and H, white. The red lines indicate the unit cells. The plot in (d) shows temperature dependences of resistivity and magnetic susceptibility.

### 1.2.4.2 TTF-Phosphines.

The first metal complexes to incorporate TTF-containing phosphines or carboxylates also appeared in the literature during the late 20\(^{th}\) – early 21\(^{st}\) century.\textsuperscript{74,75} Since then there has been a variety of complexes prepared in which TTF is functionalized with the diphenylphosphino group(s) (Figure 1.10), which exhibit greater stability than alkylphosphine ligands.
Figure 1.10: Chemical structure of the dm-TTF-dpp\textsubscript{2} ligand (a) and the anionic (b) and cationic (c) fragments in the crystal structure of [Re\textsuperscript{III}Cl\textsubscript{2}(dm-TTF-dpp\textsubscript{2})\textsubscript{2}][Re\textsuperscript{II/III}Cl\textsubscript{6}(dm-TTF-dpp\textsubscript{2})].\textsuperscript{76}

Upon reaction of dm-TTF-dpp\textsubscript{2} with (TBA)[Re\textsubscript{2}Cl\textsubscript{8}], Uzelmeier et al. obtained the [Re\textsuperscript{III}Cl\textsubscript{2}(dm-TTF-dpp\textsubscript{2})\textsubscript{2}][Re\textsubscript{2}\textsuperscript{II/III}Cl\textsubscript{6}(dm-TTF-dpp\textsubscript{2})] complex that, as of today, remains the only known TTF-containing species incorporating a paramagnetic 5\textit{d} ion.\textsuperscript{76} This structure is composed of a mononuclear cationic complex and a dinuclear mixed-valent anionic complex (Figure 1.10).

1.2.4.3 TTF-acacs. Acetylacetone (acac) is a common chelator found in many transition metal complexes. The appendage of TTF to the anionic bidentate acac\textsuperscript{–} ligand allows for the formation of neutral metal complexes. The novel ligand 3-(dimethylthio-TTF-thio)-2,4-pentanedione (DMT-TTF-acac) reported in 2006 was used in the formation of a stable homoleptic Mn(II) complex, [Mn(DMT-TTF-acac)\textsubscript{2}].\textsuperscript{77} Subsequently, the TTF fragment in this complex was oxidized with a methanolic solution of I\textsubscript{2} to form an organic-inorganic system consisting of paramagnetic metal ions and organic radicals. Shortly thereafter in 2009, a similar ligand was reported, 3-(4-[4’,5’-(ethylenethio)-5-(methylthio)-tetrathiafulvalenyl]-thio)acetylacetonato (ET-acac).\textsuperscript{78} The electroactive Ir(III) complex, [Ir(dbq)\textsubscript{2}(ET-acac)] (dbq = dibenzo[f,h]quinoxaline), was shown to act as a reversible redox-controlled phosphorescence switch. NOBF\textsubscript{4} and NaBH\textsubscript{4} were added to oxidize or reduce the complex, respectively. Upon oxidation to the cationic
radical, a remarkable enhancement of the emission intensity (~ 8-fold relative to the standard [Ir(dbq)_2(acac)]) was observed that reached a maximum value (corresponding to ~18-fold increase) upon the formation of the dicationic species.

### 1.2.4.4 N-heterocyclic ligands

In recent years, there has been a growth of interest in N-heterocyclic TTF-containing molecules as ligands for a great variety of metal ions (Figure 1.11). The first successful attachment of TTF to 1,10-phenanthroline was achieved by Becher *et al.* and used to prepare precatenate complexes of Cu^I^ and Ag^I^ that act as redox responsive sensors for various metal ions. In 2002 Sako *et al.* reported the preparation and structural characterization of a diazafluorene-functionalized TTF donor ligand for transition metal binding (dmt-TTF-daf). Also in 2002, Campagna *et al.* published a manuscript on multichromophoric light-harvesting Ru^{II} complexes incorporating a TTF-pyrazine ligand ((PenS)₃TTF-bpy). Later in 2007, Goze *et al.* reported on the spectroscopic investigation of a family of Ru^{II} complexes incorporating the fused donor-acceptor ligand dipropylthio-TTF-dipyridophenazine (dpt-TTF-dppz). One of these complexes showed dual luminescence from both the metal-to-ligand charge transfer (MLCT) state and the ligand-to-ligand charge separated (LLCS) state. A year later, the same group reported a new ligand, dpt-TTF-ppb, topologically similar to TTF-dppz but containing two metal-binding pockets. This ligand allowed the preparation of dinuclear Ru^{II}

![Figure 1.11](image.png)

**Figure 1.11:** Some of the relevant N-heterocyclic ligands and their abbreviations.

complexes, which exhibited luminescence quenching via reductive electron transfer from the TTF subunit. In an effort to maximize communication between the TTF moiety and the
photoactive Ru$^{II}$ metal center, this dissertation presents a TTF-annulated 1,10-phenanthroline (TTF-phen) ligand. The Ru$^{II}$ complex of this ligand not only displays luminescence quenching via reductive electron transfer from TTF moiety to the Ru$^{II}$ center, but also exhibits interesting photoreactivity.  

1.3 Ru$^{II}$-TTF

1.3.1 Basics of Spectroscopy

In order to understand the behavior of some complexes reported in this dissertation, it is necessary to investigate their photophysical and photochemical properties by means of optical spectroscopy. In almost all cases, prior to any interaction with light, the molecules exist in the state of lowest possible energy, namely the ground state. The onset of the interaction with light leads to the absorption of radiation whenever incident photons provide the energy necessary to excite the molecule from the ground state at energy $E_0$ to an excited state at energy $E_1$, with the energy of the photon $h\nu = E_1 - E_0$.

Arguably the most important characteristic of a given absorption band is the integrated intensity, which is proportional to the oscillator strength of the transition. Transitions from the ground state to excited states with the same spin multiplicity (2S+1) are spin-allowed transitions. Furthermore, if they are of opposite orbital parity they are also electric dipole allowed. It can therefore be deduced that transitions between states of different spin values and of the same orbital parity (such as $d$-$d$ transitions in metal complexes) are forbidden and as a result give rise to relatively weak absorption bands. The spin-forbidden transitions can acquire intensity via spin-orbit coupling and as a result can have a degree of non-negligible intensity for complexes with the heavier transition metal ions, which are usually characterized by spin-orbit coupling constants that are an order of magnitude larger than those of 3$d$ metals. Transitions that are both spin and parity forbidden have very weak intensity and are only observed in special cases.  

After the initial photon absorption, the electronic configuration in the excited state has an electron that has been promoted from the ground state to a molecular orbital of higher energy. The excited state of these molecules is known to be photophysically and/or photochemically unstable and thus attempts to relax back to the ground state configuration through dissipation of the previously gained excess energy. This can occur in a variety of pathways, or a combination thereof.
1) Via non-radiative relaxation, such as internal conversion and intersystem crossing followed by vibrational relaxation.

2) Via radiative relaxation, which is accompanied by the inherent emission of a photon usually at lower energy than the one originally absorbed by the molecule (explained by Stokes shift\textsuperscript{89} and Kasha’s rule\textsuperscript{90}).

3) Via the disappearance of the original molecule via photochemical reactions.

4) Via interaction with other molecules or species that exist in solution or in solid state, resulting in luminescence quenching processes such as excitation energy transfer or light-induced electron transfer.

The majority of the states involved in photophysical and photochemical processes can be illustrated in a Jablonski diagram, which is a graphical representation of the different energy states of a molecule and transitions between them. The total energy of a specific state of a given molecule is assumed to be the sum of the vibrational, rotational, and electronic energies in reference to the ground state ($E_0$). For reference, a generic Jablonski diagram is offered in Figure 1.12.\textsuperscript{91,92}

Spectroscopy by definition involves the absorption of electromagnetic radiation (from a lamp and/or a laser) by the molecules of interest, and possibly the subsequent photon emission after excitation.\textsuperscript{87} The aforementioned processes underlie two of the most basic forms of spectroscopy, namely absorption and emission spectroscopies. The resulting spectra obtained form either method will consist of peak(s) that represent transitions between different energy states of the analyte. The observed transitions and resulting energy levels obtained from the spectra are characteristic of the analyte and allow identification of the molecular properties.

According to Figure 1.12, two separate relaxation pathways lead to the luminescence (emission of light): either fluorescence (singlet-singlet relaxation) or phosphorescence (triplet-singlet relaxation). In the same manner, the non-radiative relaxation pathways are either internal conversion or intersystem crossing when they occur between states of the same or different multiplicity, respectively. The processes with the same spins in both states involved (i.e. fluorescence and internal conversion) are thus spin-allowed while the paths between states of different spin values (i.e. phosphorescence and intersystem crossing) are spin-forbidden.\textsuperscript{86,87}

It can also be seen in Figure 1.12 that each intramolecular process is characterized by a rate
constant, meaning they have a particular lifetime. Upon excitation, a molecule undergoes fast and 100% efficient radiationless deactivation to the lowest excited singlet $S_1$ (internal conversion, rate constant $k_{ic}$). This excited state can undergo deactivation via three competing processes: nonradiative decay to the ground state ($k_{nr}$), radiative decay to the ground state (fluorescence, $k_{fl}$), or conversion to the lowest triplet state $T_1$ (intersystem crossing, $k_{isc}$). In turn, $T_1$ can undergo deactivation via nonradiative ($k'_{nr}$) or radiative (phosphorescence, $k_{ph}$) decay to the ground state $S_0$. The excited states of a particular molecule thus will have characteristic lifetimes. These lifetimes can help distinguish a plethora of information about the molecular transitions observed for a particular molecule. The lifetimes are defined in equations (1) and (2) below; the variables present in each refer to the corresponding processes as described above.

$$\tau(S_1) = \frac{1}{k_{nr} + k_{fl} + k_{isc}}$$  \hspace{1cm} (1) \\
$$\tau(T_1) = \frac{1}{k'_{nr} + k_{ph}}$$  \hspace{1cm} (2)
For luminescence processes, a quantum yield (i.e. the number of times a specific event occurs per photon absorbed by the system) is defined by equations (3) and (4) below.

\[
\Phi_{fl} = \frac{k_{fl}}{k_{nr} + k_{fl} + k_{isc}}
\]

(3)

\[
\Phi_{ph} = \frac{k_{ph} \times k_{isc}}{(k'_{nr} + k_{ph})(k_{nr} + k_{fl} + k_{isc})}
\]

(4)

Theoretical treatment by means of molecular orbital (MO) theory has turned out to be extremely helpful in assigning the character of various interstate transitions. Different MOs can be conveniently deconvoluted into their atomic orbital contributions or, in more practical terms, into the contributions from specific fragments within the molecule. For metal complexes, two groups can be distinguished: orbitals centered primarily on the ligands (\(\sigma_L, \pi_L, \sigma_L^*,\) and \(\pi_L^*)\) and orbitals primarily centered on the transition metal center (\(t_{2g}\) and \(e_g^*\)). One can thus define the principal excited state transitions as falling under one of five categories:

- Metal centered (MC) \(d-d\) transitions (\(t_{2g} \rightarrow e_g^*\))
- Ligand centered (LC) transitions (\(\pi_L \rightarrow \pi_L^*\))
- Ligand to metal charge transfer (LMCT) transitions (\(\pi_L \rightarrow \pi_M^*, \sigma_M^*\))
- Metal to ligand charge transfer (MLCT) transitions (\(\pi_M \rightarrow \pi_L^*\))
- Ligand to ligand charge transfer (LLCT) transitions (\(\pi_L \rightarrow \pi_{L'}^*\))

### 1.3.2 Basic Photophysics of Ruthenium Polypyridyl Complexes

Complexes in which there exists a strong interaction between the organic and inorganic components tend to be the backbone of multifunctional materials. Ruthenium polypyridine complexes appear in the literature mainly due to their inherently rich photophysical, photochemical, and electrochemical properties. In the majority of these complexes the Ru(II) ion exists in an octahedral coordination environment. \([\text{Ru(bpy)}_3]^{2+}\) (Figure 1.13a) is the simplest and most widely studied Ru(II) complex in the literature, with well-established electronic structure (Figure 1.13b). In light of the work pursued in this dissertation, a discussion of the basic photophysical properties of \([\text{Ru(bpy)}_3]^{2+}\) helps us to better understand other Ru(II) polypyridyl complexes, as many of them are or can be considered to be derived from \([\text{Ru(bpy)}_3]^{2+}\).
The ground state of $[\text{Ru}(\text{bpy})_3]^{2+}$ has a well established absorption spectrum characterized by a low energy MLCT band and some higher energy ligand centered bands (Figure 1.13c). According to the nature of frontier orbitals, three principal optical transitions may occur: (1) the lower energy parity forbidden, metal-centered transition (the $d$-$d$ transition) from the $t_{2g}$ to $e_g^*$ orbitals with $\varepsilon \approx 100$ M$^{-1}$ cm$^{-1}$, (2) the higher energy $\pi$-$\pi^*$ transition localized on the bpy ligands, and (3) the MLCT transition from a $t_{2g}$ orbital of Ru(II) ion to a $\pi^*$ - orbital of bpy with $\varepsilon \approx 20,000$ M$^{-1}$ cm$^{-1}$. All these transitions are spin allowed, but only the latter two are observed in the UV-Vis spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 1.13c). Note that the MLCT band also exhibits a tail extending beyond 500 nm that stems from the spin-forbidden MLCT transitions.\textsuperscript{94-96}
As seen in Figure 1.13b, the frontier orbitals of \([\text{Ru(bpy)}_3]^ {2+}\) are represented by three highest occupied MOs (the HOMO to HOMO-2) localized on the metal center and three lowest unoccupied MOs (the LUMO to LUMO+2) delocalized over the bpy ligands. At ambient temperatures, solutions of \([\text{Ru(bpy)}_3]^ {2+}\) exhibit a broad orange to yellow colored emission with \(\lambda_{\text{max}} = 620\) nm. The photoluminescence of this complex has been the focus of many studies since the late 1960’s and is well understood today.\(^{97-101}\) The observed emission originates from the spin-forbidden \(^3\)MLCT excited state.\(^{95,96,102-104}\) The effective population of the \(^3\)MLCT state becomes possible due to a large spin-orbit coupling, which results in the significant mixing of the singlet and triplet states. It is for this reason that the emission is considered to be from the manifold of spin-orbital states rather than form a pure triplet state.\(^{105,106}\)

### 1.3.3 TTF-Containing Ru(II) Complexes

The photoinduced charge transfer between TTF and the photoactive Ru(II) metal center was demonstrated for the first time in 1982 by Grätzel who observed this phenomenon in a methanolic solution containing the individual constituents, TTF and \([\text{Ru(bpy)}_3]^ {2+}\).\(^{107}\) This study demonstrated for the first time the oxidaiton of TTF to its radical cation by the photoexcitated state of \([\text{Ru(bpy)}_3]^ {2+}\). The lifetime of the charge separated state was 125 ns.

In recent years, a variety of Ru(II) complexes with TTF-containing ligands have been reported. The direct attachment of the redox active molecule to the photoactive metal center should allow for the enhanced synergy between the two substructures.\(^{67,108}\) The \(^3\)MLCT luminescence of the Ru(II) complex can experience a quenching effect via reductive electron transfer from the TTF moiety to the excited state of the Ru(II) chromophore.\(^{69,78,82,109,110}\) In the instance that a complex can overcome this quenching, often times some very interesting properties can be realized in such compounds.

In 2007, the Hauser and Decurtins research groups published a study of three Ru(II) polypyridyl TTF-containing complexes of general formula \([\text{Ru(bpy)}_3-n(\text{TTF-dppz})_n](\text{PF}_6)_2\) \((n=1-3); \text{TTF-dppz} = 4’,5’-bis( propylthio)tetraphiafulvenyl[i]dipyrido[3,2-a:2’,3’-c]phenazine; Figure 1.14a).\(^{83}\) All three complexes displayed intraligand charge-transfer (\(^1\)ILCT) fluorescence \((\tau < 1\) ns) of the TTF-dppz ligand. In addition, an unusual dual luminescence was reported for the member with \(n=1\), which also showed the \(^3\)MLCT luminescence typical of Ru(II) polypyridyl complexes \((\tau = 1040\) ns). The \(^3\)MLCT luminescence was absent for the members with \(n=2,3\) due to the presence of the aforementioned intramolecular TTF \(\rightarrow\) Ru electron-transfer quenching
from a second TTF-dppz ligand. Despite these shortcomings, such electron-transfer quenching leads to the formation of ligand-to-ligand charge-separated (LLCS) states ($\tau = 2.2-2.4 \mu s$). The processes involved are summarized in the respective Jablonski diagrams, shown in Figure 1.14b for $n=1,3$ (the behavior of member with $n=2$ is similar to that of member with $n=3$).

**Figure 1.14:** (a) The chemical structure of [Ru(bpy)$_2$(TTF-dppz)]$^{2+}$ (top) and [Ru(TTF-dppz)$_3$]$^{2+}$ (bottom) and (b) the corresponding Jablonski diagrams depicting the different excited-state relaxation pathways available for the two complexes.

### 1.4 Fe$^{II}$ Spin-Crossover Complexes

#### 1.4.1 Introduction

In addition to potentially interesting photophysical properties of Ru-TTF hybrid materials, an appealing avenue to explore is the combination of conductive TTF-based structures with paramagnetic metal centers, thus forming magnetic multifunctional materials. Of particular interest to this dissertation is the combination of the TTF-containing ligands with the $d^4$-$d^7$ transition metal ions that undergo switching between high-spin (HS) and low-spin (LS) states, a phenomenon known as spin crossover (SCO). Research on transition metal complexes that exhibit SCO is driven by the interest in functional materials that hold potential in such
applications as chemical sensors and memory devices. The occurrence of the HS → LS transition is realized upon careful selection of ligand and metal centers that give rise to a situation in which the ligand field splitting between the metal’s $e_g^*$ and $t_{2g}$ orbitals becomes comparable to the electron pairing energy. In short, the ligand field and the mean spin pairing energy govern the occurrence of a spin transition in coordination compounds of transition metal ions, as discussed in more detail below.

Upon the original observation of a HS to LS interconversion in Fe$^{3+}$ dithiocarbamate complex in 1931, the phenomenon went relatively dormant for about thirty years. The interest in SCO compounds really took off in the 1960’s when the explanation to the observed changes in the temperature-dependent magnetic moment was provided based on the ligand-field theory. Shortly thereafter, a number of Fe$^{II}$ complexes were shown to undergo temperature-induced SCO. Thermal spin transitions are almost exclusive to 3$d$ transition metal ions. Ligand field theory explains that for 4$d$ and 5$d$ ions the ligand field splitting increases dramatically relative to the splitting for the 3$d$ ions and, as a result, is much greater than the spin pairing energy. Thus, almost all 4$d$ and 5$d$ transition metal complexes exhibit LS behavior.

Although SCO complexes have been prepared with various $d^4$-$d^7$ metal ions, more than 90% of SCO complexes reported to date involve Fe$^{2+}$ ions, and thus we limit our discussion to this metal ion. Under octahedral coordination environment, the $d$ orbitals of the metal center diverge into two sets of degenerate orbitals, namely $e_g^*$ and $t_{2g}$. The resulting energy difference between these sets of orbitals is known as the ligand field splitting energy, $10Dq$, or $\Delta_o$. Generally, the $\sigma$-symmetry orbitals that extend directly along the coordination axis between the lone pairs of the ligand and the metal center are destabilized to a more significant extent than the orbitals of $\pi$-symmetry. Figure 1.15 shows the crystal field splitting for an octahedrally coordinated metal center. The $d_{x^2}$ and $d_{x^2-y^2}$ orbitals ($e_g^*$) exhibit $\sigma$-symmetry overlaps with the ligand orbitals and thus become higher in energy than the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals ($t_{2g}$).

The ligand field splitting energy, $\Delta_o$, depends on the nature of metal ion and its oxidation state, the symmetry of the coordination environment of the metal ion, and the nature of the ligands surrounding the metal center. In the first approximation, the ligand field strength can be estimated from the spectrochemical series:

$\Gamma^< S^2^- < NO_3^- < OH^- < C_2O_4^- < H_2O < NCS^- < NH_3 < bpy < PPh_3 < CN^- < CO$
Figure 1.15: a) Ligand field splitting of $d$-orbitals in an octahedral coordination environment. b) Electron distribution in the HS and LS states of the Fe$^{2+}$ $d^6$ metal ion. Adapted from literature.\\n
Ligands toward the left side of the series are generally $\pi$-donors and impose a weak field on the metal center by destabilizing the $t_{2g}$ orbitals. For the Fe$^{2+}$ ion in a weak field environment, electrons will spread across the three lower energy weakly bonding $t_{2g}$ orbitals and the two higher energy antibonding $e_g^*$ orbitals before pairing up according to Hund’s rule (Figure 1.15b), resulting in a HS paramagnetic complex with four unpaired electrons ($S = 2$). In contrast, ligands toward the right side of the spectrochemical series are good $\pi$-acceptors and impose a strong ligand field on the metal center by stabilizing the $t_{2g}$ orbitals, thus producing LS diamagnetic complexes ($S = 0$) for the $d^6$ Fe$^{2+}$ ion (Figure 1.15b). Thus, all six $d$-electrons will commence to pairing only if the pairing energy ($P_E$) is smaller than the crystal field splitting energy ($\Delta_o$), otherwise Hund’s rule is obeyed explicitly.

The depletion of the electron density in the antibonding $e_g^*$ orbitals upon a HS $\rightarrow$ LS transition, and thus simultaneous increase in the electron density in the lower lying weakly bonding $t_{2g}$ orbitals, causes a shortening of the metal-to-ligand bond distances and thus reduces the molecular volume.\(^{118,119}\) For Fe(II) complexes ($\Delta S = 2$), this change in metal–ligand bond length is quite drastic, about 10% of the bond length ($\Delta r = r_{\text{HS}} - r_{\text{LS}} \approx 220 - 200 \approx 20$ pm), which may result in a 3-4% change in the unit cell volume.\(^{120}\) Consequently, the metal-ligand bonds are strengthened, and so the transition can obviously be monitored with variable-temperature crystallography, but also via variable-temperature vibrational and optical spectroscopy. A classical example is provided by the IR spectrum of [Fe(NCS)$_2$(phen)$_2$],\(^{121,122}\) for which the HS $\rightarrow$ LS transition is accompanied by a loss of intensity of the strong doublet at $\sim$2060-2070 cm$^{-1}$ (the C-N stretch of NCS$^-$ in the HS state) and an appearance of a new stretch at 2100-2110 cm$^{-1}$ (of the LS state) upon cooling the sample below the transition temperature.
Another boost to the field of SCO occurred in the mid-1980’s upon the discovery of the photoinduced LS-HS conversion in \([\text{Fe(ptz)}_6](\text{BF}_4)_2\).\textsuperscript{123} This phenomenon became known as light-induced excited spin state trapping (LIESST). \([\text{Fe(ptz)}_6](\text{BF}_4)_2\) was originally shown to exhibit a thermal spin transition around 135 K, accompanied by a change in the color of the crystal (Figure 1.16a) and thus the resulting absorption spectrum. During this study, it was observed for the first time that a LS to HS conversion in a solid SCO compound could be initiated by irradiation with light. The irradiation led to a metastable HS state with exceptionally long lifetime, lasting for days at temperatures below 20 K. The color of the crystal, as well as the absorption and Mössbauer spectra recorded for the photogenerated HS state were similar to the properties observed for the high-temperature HS state (Figure 1.15).

1.4.2 Fe-TTF Complexes

The motivation herein lies in making multifunctional materials that contain the redox-active TTF moiety attached to an Fe\(^{2+}\) metal center via ligand groups that can lead to the occurrence of SCO. It is envisioned that the magnetism of the Fe\(^{2+}\) ion can be selectively activated through perturbation with temperature, pressure, or light. The complex can then be studied in terms of the interplay between the SCO (and thus the change in the magnetic moment) and the conductivity propagated by the TTF substructure in the solid state. It was not until recently, in 2011, that Oshio \textit{et al.} reported the first example of an Fe\(^{2+}\) complex that exhibited both electrical conductivity and SCO.\textsuperscript{124} Other than that, there are very few reports on the combination of TTF with Fe\(^{2+}\) metal centers.\textsuperscript{119}

In 2005, Faulmann \textit{et al.} described a salt obtained by co-crystallization of the redox active \([\text{Ni(dmit)}_2]\) anion (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato; Figure 1.17a, left) and the \([\text{Fe}^{\text{III}}(\text{sal}_2\text{-trien})]^+\) SCO cation (Figure 1.17a, right).\textsuperscript{125} The material exhibited a cooperative spin transition around 240 K with a wide hysteresis loop (30 K). The authors also mentioned that preliminary electrocrystallization experiments had afforded crystalline material that could be suitable for the preparation of switchable SCO molecular conductors, but this claim has not been followed by any other publication since then.

In 2006, Ouahab et. al. reported the preparation of a new ligand that appended BEDT-TTF to 2,2’-bipyridine (bpy-BEDT-TTF).\textsuperscript{126} They followed this with the preparation and characterization of the first Fe\(^{II}\) coordination compound with a redox active TTF-containing ligand, namely \([\text{Fe(NCS)}_2(\text{bpy-BEDT-TTF})_2]\) (Figure 1.18a). The Mössbauer spectroscopic
Figure 1.16: The compound \([\text{Fe}(\text{ptz})_6](\text{BF}_4)_2\) has been shown to undergo a thermal spin transition, followed by a transition back into the HS state via irradiation with light. This change was accompanied by a change in the crystal color (a), the absorption spectrum (b), and the Mössbauer spectrum (c). Also shown is the Jablonski diagram explaining the observed transitions and the LIESST effect (d).

Analysis revealed the coexistence of HS and LS Fe\(^{II}\) species with a ratio of 40:60 at 80 K (Figure 1.18b). The magnetic measurements revealed that this ratio remains essentially the same between 300 and 2 K (Figure 1.18c). The drop in the magnetic moment at lower temperature is due to zero-field splitting effects.

In early 2013, the Hauser and Decurtins research groups published their findings on a novel TTF-containing complex, \([\text{Fe}(\text{phen})_2(\text{TTF-dppz})_2]^{2+}\) (Figure 1.19a).\(^{127}\) The complex is of interest for engineering materials that combine the SCO with light-induced electron transfer. The authors were able to show, with transient absorption spectroscopy, that photoexcitation into the MLCT
band of the LS complex results in the population of a HS state of Fe(II), with a decay lifetime of 15 ns. This HS state, however, is in direct competition with the $^3\text{ILCT}$ charge separated state that can also be realized upon direct excitation with higher energy. The Jablonski diagram in Figure 1.19b illustrates how complicated the behavior and analysis of these systems can be.

Figure 1.18: The chemical structure of [Fe(NCS)$_2$(bpy-BEDT-TTF)$_2$] (a), the corresponding Mössbauer spectrum showing the coexistence of HS and LS Fe$^{II}$ (b) and the thermal variation of $\chi_M T$ (c).

Figure 1.19: The chemical structure of [Fe(phen)$_2$(TTF-dppz)]$^{2+}$ (a) and the corresponding Jablonski diagram illustrating the complexity of the relaxation pathways available in this complex (b).

1.5 Research Objectives

The principal theme and focus of this dissertation is the design and preparation of a novel heterocyclic ligand that allows a close attachment of TTF to a metal center, and the exploration of photophysical and magnetic properties of such complexes. The great deal of motivation for
studying these complexes lies in the aforementioned design of multifunctional molecule-based materials that could be of interest in applications involving solar energy conversion or molecular electronic devices.

Considering the growth of interest in TTF-containing compounds and their inherent potential as components in multifunctional molecule-based materials, this dissertation pursues the following research objectives:

1. In an effort to maximize the observed synergy between the TTF moiety and the metal center of interest, it is thought necessary to minimize the distance between the two subunits. To address this issue, we devise a synthetic route to TTF-functionalized 1,10-phenanthroline (phen) in which the TTF is fused directly onto the outer rim of the chelating phen ligand.

2. The ligand obtained in realization of aim (1) is used to prepare transition metal complexes with the photoactive Ru$^{2+}$ metal center. This allows the study of the interplay between redox behavior of TTF and photoactivity of Ru$^{2+}$ ion. In its photoexcited state, the Ru center acts as a strong oxidizing agent. In order to be conductive, the TTF substructure should be partially oxidized. Thus it seems inevitable that these subunits be combined into a single multifunctional material.

3. In order to explore the potential of the TTF-phen ligand for magnetic multifunctional materials, studies of its complexes with the Fe$^{II}$ ion are presented. The goal herein is to create systems that combine the redox properties of TTF with the spin-crossover at the metal center. This approach has the potential to uncover a novel material that exhibits a combination of magnetic switching and conductivity, with a possible enhancement of the resulting properties due to synergistic effects. We also describe efforts directed at the isolation and characterization of related Fe$^{II}$ complexes of the type [Fe(NCS)$_2$(R-phen)] (R represents various functionalities covalently linked to the backbone of phen). The potential to modify the character of the spin transition by changing the nature of the phen-based ligand is demonstrated.
CHAPTER TWO
EXPERIMENTAL METHODS

2.1 Methods for the Characterization of Ligands and Complexes

This chapter presents various techniques used for the characterization of physical and chemical properties of the molecules and complexes studied in this thesis.

2.1.1 NMR Spectroscopy

$^1$H NMR spectra were measured on either a Bruker 400 or Bruker 600 spectrometer operating at 400 and 600 MHz, respectively, with chemical shifts internally referenced to the residual proton signals of the deuterated solvent CDCl$_3$ (7.26 ppm) or CD$_3$CN (1.94 ppm).$^{128}$ $^{13}$C NMR spectra were measured on either a Mercury 300 or Bruker 600 spectrometer operating at 75.5 and 151 MHz respectively, with chemical shifts internally referenced to the deuterated solvent signals in CDCl$_3$ (77.2 ppm) or CD$_3$CN (118.3 ppm).$^{128}$ Two-dimensional correlation spectroscopy (COSY) and heteronuclear single quantum coherence ($^1$H-$^{13}$C HSQC) experiments were carried out on a Bruker 600 spectrometer.

2.1.2 Absorption Spectroscopy

All the photophysical measurements on Ru(II) complexes and associated ligands were performed in solutions. Electronic absorption (UV-Vis) spectra were collected in the 200-1000 nm range on a Perkin Elmer Lambda 950 UV/Vis/NIR or a Cary 50 Bio UV/Vis spectrophotometer. The measurements were performed in quartz cells with a path length of 1 cm or 1 mm.

Absorption spectroscopy allows the measurement of the absorption of light as a function of wavelength (nm) or wavenumber (cm$^{-1}$). The amount of light absorbed is related to the sample concentration, $c$ (mol L$^{-1}$ or M) and the optical path length, $b$ (the width of the quartz cuvette used in a particular measurement) (Figure 2.1). If an incident beam of light, with an intensity $I_0$ passes through the sample, the emerging light, after interaction with the molecules, has an intensity $I$, such that $I_0 \gg I$. Equation 2.1 presents the absorbance ($A$) or optical density (OD) as a function of the incident and transmitted light intensity.

$$A = OD = \log \left( \frac{I_0}{I} \right)$$  \hspace{1cm} (2.1)
For a dilute solution, where the interactions between the molecules are negligible, the absorbance can be described by the Beer-Lambert law, which will be the case for the different studies shown in this thesis:

\[ A = \varepsilon b c \]  \hspace{1cm} (2.2)

where \( \varepsilon \) is the molar extinction coefficient. In a double beam spectrometer such as the Perkin Elmer Lambda 950 UV/Vis/NIR, the absorption of the solvent is usually subtracted from the spectrum by either recording a base line with a cell filled with pure solvent or by placing a cell with the pure solvent in the reference beam.

Figure 2.2: Single crystal UV-Vis spectra of the SCO compound \([\text{Fe}(ptz)_6](\text{BF}_4)_2\). At 300 K the crystal is white and in the HS state (a). The absorption spectrum shows a weak \( ^5T_2 \rightarrow ^5E \) band at ca. 12000 cm\(^{-1}\) (b). At 80 K the crystal is red-purple and in the LS state (c). The spectrum exhibits two spin-allowed d-d bands, \( ^1A_1 \rightarrow ^1T_1 \) and \( ^1A_1 \rightarrow ^1T_2 \), above 20000 cm\(^{-1}\) (d), while the HS \( ^5T_2 \rightarrow ^5E \) band around 12000 cm\(^{-1}\) is no longer observed.
Solid-state optical absorption spectroscopy is useful for the study of SCO materials. The color of a particular complex in the solid state will usually change upon the occurrence of SCO as a result of the altered electronic configuration. Such a change opens the window for a variety of spectroscopic methods that can be used to monitor the dynamics of SCO. As an example, Figure 2.2 shows the crystal images and the UV-vis spectra recorded for the SCO compound, [Fe(ptz)$_6$](BF$_4$)$_2$ (ptz = 1-propyltetrazole), above (300 K) and below (80 K) the spin transition temperature.\textsuperscript{123,129}

2.1.3 Emission Spectroscopy

For luminescence measurements the solutions were deoxygenated by purging with N$_2$ gas for 30 min prior to recording the spectra, in order to avoid emission quenching by molecular oxygen. Emission and excitation spectra were recorded on a Horiba JobinYvon FluoroMax-4 spectrofluorometer. Luminescence lifetime experiments were performed in the laboratory of Prof. Andreas Hauser at the University of Geneva, Switzerland. The spectra were recorded on the nanosecond time scale by exciting the samples at 458 nm using the third harmonic of a pulsed Nd:YAG laser (Quantel Brilliant, 7 ns pulse width) to pump an OPO (Opotek Magic Prism). The system used for detection consisted of a single monochromator (Spex 270M), a photomultiplier (Hamamatsu R928), and a digital oscilloscope (Tektronix TDS 540B) with a time resolution of 15 ns. The reported values for the luminescence quantum yields of complexes 1-3 were calculated using [Ru(bpy)$_3$](PF$_6$)$_2$ as a standard with quantum yield of 6.2% in CH$_3$CN at room temperature. The above instrumental description was used for the collection of both excitation and emission spectra, as illustrated in a general sense in Figure 2.3.

\textbf{Figure 2.3}: Schematic diagram showing the principal instrumental components utilized in the collection of luminescence spectra. The detector resides in a position orthogonal to the excitation beam to avoid detection of the beam and its false assignment as luminescence from the sample.
For the excitation spectrum, the sample is excited by light of variable wavelength, while the emission is monitored at constant wavelength chosen by a user. The obtained spectrum thus shows the intensity of emission at the specific wavelength as a function of the excitation wavelength emitted by the source. The intensity of the excitation light is monitored at the exit of the excitation monochromator by a photodiode and the measured emission signal is divided by the signal from the photodiode in order to normalize the spectral distribution of the light source and the response curve of the excitation monochromator.

For the emission spectrum, the excitation wavelength is kept constant, and the intensity of the light emitted by the sample is recorded as a function of wavelength. A built-in response curve corrects the spectra for the spectral response of the system within the monitored wavelength region.

Collection of the emission spectra of a sample (s) allows for the determination of the luminescence quantum yield ($\Phi_s$). In order to determine $\Phi_s$, a reference compound (r) with a well-known quantum yield ($\Phi_r$) is required. It is important that the absorbance spectrum of the sample be recorded prior to measuring the emission spectrum for the determination of the quantum yield. In this absorbance spectrum, it is pertinent that the optical density is < 0.1 at the excitation wavelength. In this instance, the concentration and thus absorbance being low, the attenuation of the excitation intensity in the sample is negligible, which minimizes the instrumental errors introduced into the measurement. The known parameters of the experiment can then be used to determine the luminescence quantum yield of the sample using equation 2.3.

$$\frac{\Phi_s}{\Phi_r} = \frac{I_s \cdot \varepsilon_{\lambda ex}^r c_r}{I_r \cdot \varepsilon_{\lambda ex}^s c_s}$$

where $I_s$ and $I_r$ are integrated emission intensities, $\varepsilon_s$ and $\varepsilon_r$ are extinction coefficients at the excitation wavelength, and $c_s$ and $c_r$ are concentrations of the sample and the reference compound, respectively.

2.1.4 Electrochemistry

Cyclic voltammetry (CV) was performed on a CH Instruments 600D electrochemical analyzer at the sweep rate of 0.100 V·s⁻¹, with 0.100 M (Bu₄N)PF₆ electrolyte solution. The voltammograms were recorded using a standard three-electrode configuration, with a Pt-disk
working electrode, a Pt-wire counter electrode, and an Ag⁺(0.01 M AgNO₃)/Ag non-aqueous reference electrode (Figure 2.4). All the potentials were referenced to the standard Fe⁺/Fe couple (Fc = ferrocene).

Figure 2.4: A schematic of the three-electrode electrochemical cell used to perform CV experiments (a) and the actual setup used for the CV experiments described in this dissertation (b).

A CV experiment consists of measuring the current (the rate of electron flow) versus a varying applied potential (voltage or energy of electrons). The potential is provided by the difference in energy of the working and reference electrodes, measured in volts (V) or millivolts (mV). CV is essentially used to characterize the ease with which a compound can be oxidized or reduced (i.e. the energy required to lose or gain an electron, respectively). It can also provide information on the reversibility of the observed redox reactions, as well as information about the kinetics and mechanism by which these redox reactions proceed.¹³⁰

In a typical experiment, the 10 mL electrolyte solution of the 0.100 M (Bu₄N)PF₆ was placed in an electrochemical cell and capped with a special lid equipped with holes that accept the electrodes used in the experiment. An inert gas (N₂) was bubbled through the solution for ~10 min to ensure that there was no oxygen present that could contaminate or obscure the observed results. With the electrodes immersed in the solution and connected to the corresponding leads, a background spectrum was first collected. (It is important, and often times the most time consuming part of the experiment, to obtain a clean background, free of any adventitious redox
processes.) Once a clean background spectrum was obtained, a small amount of the desired analyte was added and the solution was stirred to facilitate dissolution of the sample. Once dissolved, the CV curve was recorded again at the same sweeping potential. The observed spectrum usually displayed anodic and/or cathodic peaks at potential(s) characteristic of the analyte. The experiments were repeated several times to obtain a reproducing voltammograms of sufficient quality. A generic spectrum illustrating a reversible redox process that one would encounter during a typical experiment is presented in Figure 2.5.

![Generic cyclic voltammogram](image)

**Figure 2.5**: A generic cyclic voltammogram illustrating a reversible redox process. $E_{pc}$ and $E_{pa}$ are the cathodic and anodic potentials respectively; $i_{pc}$ and $i_{pa}$ are the cathodic and anodic currents respectively. The average of the $E_{pc}$ and $E_{pa}$ values provides the half-wave potential ($E_{1/2}$) that is reported as the potential at which the particular redox process occurs.

The experiments herein utilized Fc as an internal standard that was added to the electrolyte upon completion of each CV experiment. Upon collection of a voltammogram from the resulting solution, the feature corresponding to the Fc$^{+/}$Fc redox couple could be easily identified, being much more intense than the signal from the analyte. All potentials provided in this dissertation are thus reported relative to the Fc$^{+/}$Fc internal standard.

### 2.1.5 X-ray Crystallography

In a typical experiment, a selected single crystal was suspended in Paratone-N oil (Hampton Research) and mounted on a cryoloop, which was placed in an N$_2$ cold stream and cooled down at 5 K/min to 173 K. The data sets were recorded as $\omega$-scans at 0.3° stepwidth and integrated with the Bruker SAINT software package.$^{131}$ In all the experiments, a multi-scan adsorption correction was applied based on fitting a function to the empirical transmission surface as
sampled by multiple equivalent measurements (SADABS). Determination of the space group, solution, and refinement of the crystal structures was carried out using the SHELX suite of programs. The final refinement was performed with anisotropic atomic displacement parameters for all but hydrogen atoms. The H atoms were placed in calculated positions.

2.1.6 Theoretical Calculations

DFT calculations were performed with the Gaussian 03 package, using the B3LYP hybrid functional and the LanL2DZ basis set. Starting geometries were taken from the refined crystal structure parameters. All geometries were optimized in the ground state without symmetry restraints, using the conducting polarized continuum medium (CPCM, CH$_3$CN) solvation model to include solvent polarization effects. The default Gaussian self-consistent field (SCF) convergence criterion was used, i.e. $10^{-8}$ Hartree on the final energy. Single-point time-dependent DFT (TD-DFT) calculations were carried out on the optimized geometries. The UV-Vis spectra were calculated with the SWizard program, revision 4.7, using the pseudo-Voigt peak profiles. The half-bandwidths, $\Delta_{1/2}$, were set equal to 3000 cm$^{-1}$. Molecular fragment contributions to frontier orbitals were calculated using the AOMix program.

2.1.7 Magnetic Measurements

The magnetic susceptibility measurements were carried out on polycrystalline samples using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL). The DC susceptibility was measured in an applied field of 0.1 T in the 1.8-300 K temperature range. Field-dependent magnetization was obtained at 1.8 K with the magnetic field varying from 0 to 7 T. The data were corrected for diamagnetic contributions using tabulated constants. Magnetic measurements provide the most direct method for the observation of spin-state changes in the Fe(II) complexes. The large difference in the magnetic moment between the HS ($S = 2$) and LS ($S = 0$) states of the $3d^6$ ion allows for detection of SCO from the plot of $\chi T$ vs. $T$ ($\chi$ – molar magnetic susceptibility).

The Curie Law that describes the behavior of a specific spin state:

$$C = \chi T = \frac{g^2 S(S+1)}{8}$$  \hspace{1cm} (2.4)

where, $C$ = Curie constant (material-dependent property); $T$ = temperature; $g$ = g-factor (proportionality constant that relates a material’s magnetic moment to the spin of an electron; $S$ =
total spin state (given by the number of unpaired electrons present divided by 2). In the case of Fe$^{2+}$ in the LS state, there are no unpaired electrons, and thus the material exhibits a total spin equal to 0, resulting in $\chi T \sim 0$ emu mol$^{-1}$ K. In the case of Fe$^{2+}$ in the HS state, there exist 4 unpaired electrons providing a value of $S = 2$ and a resulting $\chi T$ of 3.00 emu mol$^{-1}$ K. The experimentally established values of $\chi T$ for the HS Fe$^{2+}$ ion, however, are usually in the range of 3.3-3.8 emu mol$^{-1}$ K, due to the deviation of the g-factor from the free electron value of 2.0023 caused by orbital contribution to the total magnetic moment.

Alternatively, the thermal spin transition is commonly expressed in terms of the molar fraction of HS molecules ($\gamma_{HS}$) as a function of the external parameter (usually temperature) as shown below in equation 2.5.

$$\chi(T) = \gamma_{HS}(T) \cdot \chi_{HS} + (1 - \gamma_{HS}(T)) \cdot \chi_{LS} \quad (2.5)$$

Equation 2.5 relies on the fundamental practice of measuring the magnetic susceptibility as a function of temperature ($\chi(T)$). The $\chi_{HS}$ and $\chi_{LS}$ refer to the magnetic susceptibilities of the sample in the pure HS and LS states respectively. These values can be measured experimentally at sufficiently high and low temperatures, respectively, in the case of a complete spin state transition. With these values and the $\chi T$ vs. $T$ plot, one can readily construct the $\gamma_{HS}$ vs. $T$ spin transition curve. These curves can take on a variety of appearances as shown in Figure 2.6.

**Figure 2.6:** Five possible spin transition behaviors: a) gradual, b) abrupt, c) hysteretic, d) stepwise, and e) incomplete. Each plot shows the molar fraction of the HS state ($\gamma_{HS}$) as a function of temperature. Adapted from literature.\textsuperscript{120}
2.1.8 Mössbauer Spectroscopy

The $^{57}$Fe Mössbauer spectra were collected on constant acceleration instruments over the temperature range of 1.5 – 300 K, in applied external fields up to 8 T. Samples for experiments in low applied magnetic fields (< 50 mT) were prepared by placing polycrystalline solids in Mössbauer cups covered with Teflon lids. For high-field measurements, the solid materials were ground to finely divided powders and suspended in mineral oil. Spectral simulations were generated using WMOSS (WEB Research, Edina, MN), and isomer shifts are reported relative to Fe metal foil at room temperature.

$^{57}$Fe Mössbauer spectroscopy has proved to be a powerful tool in probing the oxidation and spin states of iron in a variety of coordination and extended-structure compounds. The method is based on a resonant absorption of high-energy $\gamma$-rays. The decay of a radioactive $^{57}$Co nucleus produces a $^{57}$Fe nucleus in an excited state, which then relaxes by emitting a $\gamma$-ray. The emitted photon is then absorbed resonantly by the sample containing some amount of the $^{57}$Fe nucleus according to the natural abundance or, if necessary, enriched in the sample.

![Figure 2.7 Thermal SCO in [Fe(ptz)$_6$(BF$_4$)$_2$] recorded at three temperatures. The spin transition temperature is ca. 135 K. The $^{57}$Fe Mössbauer spectra demonstrate the transition between the HS state (quadrupole doublet shown in red) and the LS state (singlet shown in blue) at the spin transition temperature of 135 K.](image)

A Mössbauer spectrum provides parameters such as the isomer shift ($\delta$) and the quadrupole splitting $\Delta E_Q$, which both vary significantly upon Fe(II) HS $\rightarrow$ LS transition. The resonance
signal curves can be deconvoluted into the contributions from the HS and LS states, and each component can be integrated to establish the relative concentrations of the spin states in the sample. An example of such analysis is displayed in Figure 2.7 for the SCO compound \([\text{Fe(ptz)}_6](\text{BF}_4)_2\) for which the Mössbauer spectrum was recorded at three different temperatures. In the plots above, it is easily noticed that the HS state appears as a doublet with much larger quadrupole splitting relative to the LS state. This effect is explained by the gradient electric field experienced by the nucleus that is produced by the asymmetric distribution of electrons across the three degenerate bonding \(t_{2g}\) orbitals of \(\text{Fe}^{2+}\). The HS state has six electrons spread across the five \(d\) orbitals, the three bonding \(t_{2g}\) orbitals containing four electrons. This leads to the unequal filling (i.e. one orbital has a pair of electrons and the other two are singly occupied) of the three degenerate bonding \(d\) orbitals and thus an asymmetric distribution of electrons is felt at the nucleus. This effectively produces an electric field gradient felt by the nucleus and leads to the appearance of quadrupole splitting. In the LS state, all six electrons are paired up in the lower energy degenerate \(t_{2g}\) orbitals and the \(e_g^*\) orbitals are left empty. In this case, the nucleus does not feel an electric field gradient and thus the resulting symmetry of the electron distribution does not provide for quadrupole splitting.

2.1.9 Other Characterization Methods

Electrospray ionization (ESI) and electron impact (EI) mass spectra were acquired on JEOL AccuTOF JMS-T100LC and JEOL JMS600 mass spectrometers, respectively. Infrared (IR) spectra were measured in the 600-4000 cm\(^{-1}\) range as solid samples pressed on a ZnSe crystal of the universal attenuated total reflectance (ATR) sampling accessory on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc. (Norcross, GA).
CHAPTER THREE
PREPARATION AND CHARACTERIZATION OF TTF-ANNULATED 1,10-PHENANTHROLINE

3.1 Introduction

There has been a considerable amount of research dedicated to the production of functionalized TTF’s capable of binding transition metal centers. In the resulting complexes TTF acts as an electron donor. Partial oxidation of the TTF substructure might lead to a conducting multifunctional material, with the additional functionality coming from the metal center of choice. A number of studies have focused on the design of molecules, in which a TTF-containing fragment is connected to a chelating ligand that affords robust binding to a metal ion, with a geometrically predictable arrangement of the TTF subunit. Such architecture may enhance the synergy between the conducting properties of the organic substructure and the optical or magnetic properties of the metal ions. In order to increase the interaction between the TTF and metal center, we aimed to decrease the physical separation between the two moieties. In these efforts, we focused on the direct attachment of TTF to the 1,10-phenanthroline (phen), a common chelating ligands that affords topologically predictable binding to essentially any metal ion. The desired ligand (Figure 3.1, $L_1$) was synthesized via a simple and inexpensive 3-step procedure (Figure 3.1). Also reported is the preparation of the more soluble version of $L_1$, bht-TTF-phen ($L_4$), in which the ethylenedithio bridge was replaced with two hexylthio groups. We note that each intermediate product ($L_2$ and $L_3$) is also of potential use for coordination to a metal center. The corresponding complexes will be discussed in further details in the chapters following. The synthesis and characterization of the resulting ligand $L_1$ is the focus of the current chapter.

3.2 Starting Materials and Syntheses

All reactions were performed in an inert N$_2$ atmosphere using standard Schlenk techniques, unless noted otherwise. Commercially available 1,10-phenanthroline (99%), fuming sulfuric acid (20% SO$_3$), bromine (99.5%), benzylthiol (99%), sodium hydroxide (97%), sodium hydride (anhydrous, 95%), aluminum chloride (anhydrous, 98.5%, Acros), carbon disulfide (anhydrous, 99.9%), potassium (poly)sulfide (>42% K$_2$S basis), mercury(II) acetate (99%, Aldrich), glacial acetic acid (EMD), sodium bicarbonate (99%, Mallinckrodt), 4,5-ethylenedithio-1,3-dithiol-2-
thione (TCI), 1-bromohexane (98%, Aldrich), tetraethylammonium bis(1,3-dithiol-2-thione-4,5-dithiolate)zincate (97%, TCI), were used as received. Triethylphosphite (98%, Aldrich) was distilled under nitrogen prior to use. 4,5-ethylenedithio-1,3-dithiol-2-one was prepared according to the published procedure. Additional purification of anhydrous commercial solvents used in anaerobic reactions was achieved by passing them through a double-stage drying/purification system (Glass Contour Inc.). Otherwise, ACS grade solvents were used.

![Figure 3.1](image)

**Figure 3.1**: A schematic showing the chemical structure of ligands $L_1$, $L_2$, $L_3$, and $L_4$.

**5,6-dibromo-1,10-phenanthroline (Br$_2$phen)**. A 100 mL heavy-wall pressure vessel was cooled in an ice bath and charged with 5.45 g (30.2 mmol) of phen and 44 mL of fuming sulfuric acid. 1.55 mL of bromine (30.2 mmol) were added with a pipette, and the vessel was closed tightly with a Teflon bushing equipped with a chemically resistant o-ring. The vessel was immersed into an oil bath pre-heated to 120°C. After being allowed to react for 12 h at constant temperature, the mixture was cooled down to room temperature. The deep-red solution obtained was poured carefully into 1.5 L of chilled water with vigorous stirring, and the pH was adjusted to 3 with sodium bicarbonate, resulting in precipitation of a solid product. (It is essential that the pH remains below 3.0 to avoid the contamination of the desired product with 1,10-phenanthroline-5,6-dione byproduct.) After filtration, the filter cake was extracted with CH$_2$Cl$_2$ (3×130 mL). The solution was dried over MgSO$_4$ and evaporated to dryness. The product can be recrystallized from ethanol to afford white needles, but the fluffy white powder (crude product) proved to be of sufficient purity to be used in the subsequent reactions. Yield = 62% (6.33 g). *Elem. analysis*: calcd. (found) for C$_{12}$H$_6$N$_2$Br$_2$, wt.%: C, 42.64 (43.04); H, 1.79 (1.89); Br, 47.28 (46.91); N, 8.29
(8.13). \(^1H\) NMR (CDCl\(_3\), 600 MHz), \(\delta\), ppm: 9.20 (dd, 2H, \(J = 1.5, 5.7\) Hz), 8.76 (dd, 2H, \(J = 1.6, 10.0\) Hz), 7.72 (dd, 2H, \(J = 4.3, 12.6\) Hz). ESI-MS, \(m/z\) (relative intensity): 339 ([M+1]^+, 100), 260 ([M–Br+2H]^+, 4), 179 ([M–2Br+H]^+, 49).

**5,6-bis(benzylthio)-1,10-phenanthroline ((SBz)\(_2\)phen).** Sodium hydride (0.238 g, 9.9 mmol) and dry DMF (12 mL) were mixed in a Schlenk tube under nitrogen. After chilling in an ice bath, benzylthiol (1.2 mL, 10.2 mmol) was introduced via syringe with a purge needle in place to release the evolving hydrogen gas. Once gas evolution had ceased, the purge needle was removed, and the obtained light-yellow solution was allowed to warm to room temperature. The solution was then transferred dropwise via cannula to a Schlenk flask containing 1.52 g (4.5 mmol) of 2. After stirring for 12 h, the reaction mixture was filtered, and the yellow filtercake extracted with CH\(_2\)Cl\(_2\) (250 mL), washed with deionized water, and dried (MgSO\(_4\)). The removal of solvent afforded 3 as a yellow solid. Yield = 65%. Elem. analysis: Calcd. for C\(_{26}\)H\(_{20}\)N\(_2\)S\(_2\): C, 73.55; H, 4.75; N, 6.60; S, 15.10. Found: C, 73.19; H, 4.74; N, 6.59; S, 15.02%.

\(^1H\) NMR (CDCl\(_3\), 300 MHz), \(\delta\), ppm: 9.13 (dd, 2H, \(J = 1.7, 4.3\) Hz), 8.95 (dd, 2H, \(J = 1.7, 8.4\) Hz), 7.57 (dd, 2H, \(J = 4.3, 8.4\) Hz), 7.03 (m, 10H, phenyl), 4.04 (s, 4H, CH\(_2\)). ESI-MS, \(m/z\) (relative intensity): 871 ([2M+Na]^+, 25), 447 ([M+Na]^+, 53), 425 ([M+H]^+, 40), 334 ([M–PhCH\(_2\)]^+, 6), 301 ([M–PhCH\(_2\)S]^+, 100), 243 ([M–2PhCH\(_2\)]^+, 73), 225 ([M–Ph\(_2\)CHS]^+, 4).

**1,3-dithiole-2-thiono[4,5-f][1,10]phenanthroline (L\(_2\)). Method 1:** 548 mg (1.30 mmol) of 3 was dissolved in 15 mL of dry benzene under nitrogen. The solution was added dropwise to a Schlenk flask containing a suspension of AlCl\(_3\) (1.38 g, 10.4 mmol) in 7 mL of dry benzene. After stirring for 24 h, the benzene layer was removed via cannula, and 50 mL of chilled and degassed deionized water was added to the brown residue to quench the reaction. To the dark red mixture, 50 mL of 2M NaOH was added under nitrogen and the remaining traces of benzene were removed under vacuum. The resulting mixture was filtered under nitrogen affording a clear dark red solution. 5.0 mL (83 mmol) of CS\(_2\) was added, and the reaction was refluxed under N\(_2\) for 2 h, resulting in the formation of yellow precipitate. After cooling down the reaction mixture, the excess CS\(_2\) was removed under vacuum. At this point, the reaction was opened to air, and the yellow solid was recovered by filtration and extracted with CHCl\(_3\). After filtration, the CHCl\(_3\) solution was dried over MgSO\(_4\) and evaporated to dryness to afford 4 as a yellow solid. Yield = 95%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of 4.
**Method 2**: The compound was prepared according to the literature method with a slight modification of the work-up procedure.\(^{146}\) 7.424 g (28.28 mmol) of 42% \(\text{K}_2\text{S}\) was ground into a powder and dissolved in 185 mL of dry DMF under nitrogen. To this was added 4.7 mL (77.77 mmol) of \(\text{CS}_2\) which immediately reacted turning the dark green solution to a dark orange/brown color. After stirring at room temperature for 2 h, the resulting brown/red colored suspension of potassium trithiocarbonate was transferred via cannula to a flask containing 7.966 g (23.57 mmol) of \(\text{Br}_2\text{phen}\). The reaction mixture was further stirred for 48 h at 50°C under nitrogen. Within 2 h, the reaction had become thick and yellow in color. After 48 h, the flask was put under vacuum to remove excess volatiles that remained after completion of the reaction. The reaction mixture was then poured onto deionized \(\text{H}_2\text{O}\) (275 mL) and filtered affording a yellow filtercake. The filtercake was extracted three times with \(\text{CHCl}_3\) (500 mL portions). The yellow solid obtained from successive extractions with \(\text{CHCl}_3\) contained the desired product \(\text{L}_2\) contaminated with the starting material \(\text{Br}_2\text{phen}\). The latter was removed by washing the mixture with hot ethanol. Yield = 96%. *Elem. analysis*: calcd. (found) for \(\text{C}_{13}\text{H}_8\text{N}_2\text{OS}_3\) (\(\text{L}_2\cdot\text{H}_2\text{O}\)), wt.\%: C, 51.29 (51.29); H, 2.65 (2.53); N, 9.20 (9.16); S, 31.60 (31.35). \(^1\)\text{H NMR} (\(\text{CDCl}_3\), 600 MHz), \(\delta\), ppm: 9.26 (dd, 2H, \(J = 1.6, 5.9\) Hz), 8.08 (dd, 2H, \(J = 1.6, 9.8\) Hz), 7.74 (dd, 2H, \(J = 4.3, 12.5\) Hz). *EI-MS*, \(m/z\) (relative intensity): 286 ([M]+, 100), 242 ([M–CS]+, 25), 210 ([M–CS\(_2\)]+\(^{\text{+}}\), 18). *IR* (ZnSe ATR), \(\nu\), cm\(^{-1}\): 642 (m), 736 (vs), 804 (s), 918 (m), 1063 (s), 1093 (C=S, vs), 1414 (s), 1477 (w), 1495 (m), 1682 (s), 2954 (w).

**1,3-dithiole-2-ono[4,5-f][1,10]phenanthroline (L\(_3\))**: To a clear yellow solution of 123 mg (0.429 mmol) of \(\text{L}_2\) in 150 mL of \(\text{CHCl}_3\) were added sequentially 200 mL of glacial acetic acid and 342 mg (1.07 mmol) of \(\text{Hg(OAc)}_2\). The solution turned to a white cloudy suspension within 5 min. The suspension was stirred for 3 h at room temperature. The white precipitate was removed by filtration. The clear and colorless organic phase was washed with an equal volume of \(\text{H}_2\text{O}\), followed by three sequential washings with equal volumes of a saturated aqueous \(\text{NaHCO}_3\) solution, and then a final washing with \(\text{H}_2\text{O}\). The resulting \(\text{CHCl}_3\) solution was dried over \(\text{MgSO}_4\) and evaporated to dryness to afford \(\text{L}_3\) as a white solid. Yield = 98% (113 mg). \(^1\)\text{H NMR} (\(\text{CDCl}_3\), 400 MHz), \(\delta\), ppm: 9.24 (dd, 2H, \(J = 1.6, 6.0\) Hz), 8.11 (dd, 2H, \(J = 1.6, 9.8\) Hz), 7.73 (dd, 2H, \(J = 4.3, 12.6\) Hz). *IR* (ZnSe ATR), \(\nu\), cm\(^{-1}\): 732 (vs), 790 (vs), 915 (m), 1016 (m), 1259 (m), 1414 (s), 1472 (w), 1490 (m), 1640 (vs), 1701 (C=O, m), 2919 (w).
4',5'-ethylenedithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline (L₁). 222 mg (0.775 mmol) of L₂, 484 mg (2.33 mmol) of 4,5-ethylenedithio-1,3-dithiol-2-one, and 10 mL of P(OEt)₃ were placed in a Schlenk tube and heated at reflux under N₂ for 12 h. The obtained red precipitate was filtered off, washed with cold methanol (3×20 mL), and dried under vacuum. The product was loaded onto a 1-inch thick bed of silica gel and washed with CH₂Cl₂ to remove byproducts. Then the eluent was gradually changed to CH₂Cl₂/MeOH (2:1 v/v), and the collected fraction was filtered through Celite and evaporated to dryness to afford pure L₁ as an orange solid. Yield = 54% (187 mg). Recrystallization from CHCl₃/hexanes resulted in orange crystals of L₁·CHCl₃.

Elem. analysis: calcd. (found) for C₁₉H₁₁N₂S₆Cl₃ (L₁·CHCl₃), wt.%: C, 40.32 (40.37); H, 1.96 (1.89); N, 4.95 (5.15); S, 33.99 (33.64). £H NMR (CDCl₃, 600 MHz), δ, ppm: 9.17 (dd, 2H, J = 1.6, 5.9 Hz), 8.01 (dd, 2H, J = 1.6, 9.8 Hz), 7.68 (dd, 2H, J = 4.3, 12.5 Hz), 3.34 (s, 4H, CH₂). £C NMR (CDCl₃, 75.5 MHz), δ, ppm: 30.5, 80.6, 114.3, 123.9, 124.2, 131.0, 133.3, 145.3, 150.2. ESI-MS, m/z (relative intensity): 917 ([2M+Na]⁺, 14), 469 ([M+Na]⁺, 30), 447 ([M]⁺, 100), 419 ([M–C₂H₄]⁺, 11). UV-Vis (CH₂Cl₂), λₑₓ, nm (log ε): 232 (4.48), 277 (4.37), 310 (4.24), 336 (4.08), 403 (3.51). IR (ZnSe ATR), ν, cm⁻¹: 660(w), 737(vs), 769(m), 790(m), 917(s), 1146(w), 1400(w), 1418(s), 1479(w), 1576(m), 2934(w).

3.3 Results and Discussion

3.3.1 Synthetic Procedures

4',5'-ethylenedithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline (edt-TTF-phen, L₁) was prepared in good yield via a synthetic procedure that employs readily available and inexpensive reactants (Figure 3.1). The synthesis starts with 5,6-dibromo-1,10-phenanthroline (Br₂phen). This reagent was readily produced via a reaction between Br₂ and phen in an acidic environment, a synthetic procedure utilized since the 1970’s.147 Initially, the second step in the procedure involved the isolation of 5,6-bis(benzylthio)-1,10-phenanthroline ((BzS)₂phen, Figure 3.2).

The Almeida group had reported that (SBz)₂phen could be obtained in 71% yield using a Pd₂-(dba)₃-catalyzed reaction between Br₂phen and benzylthiol in the presence of bis[2-(diphenylphosphino)phenyl]ether and t-BuOK (48 h at 120°C).148 Nevertheless, we discovered that a simple reaction between Br₂phen and sodium benzylthiolate (generated in situ from benzylthiol and NaH) provides a comparable yield of (SBz)₂phen but in just 12 h at room temperature and without a catalyst.
Figure 3.2: Synthesis of L₁-L₄: (i) NaH, DMF, benzylthiol, 12 h; (ii) benzene, AlCl₃, NaOH, CS₂, reflux, 2 h; (iii) K₂S, CS₂, DMF, 60°C, 36 h; (iv) Hg(O₂CCH₃)₂, CH₃CO₂H, CHCl₃, 3 h; (v) 4,5-ethylenedithio-1,3-dithiole-2-one, P(OEt)₃, reflux, 12 h; (vi) 1-bromohexane, CH₃CN, reflux, 4 h; (vii) Hg(OAc)₂, CHCl₃, AcOH, 3 h; (viii) 1,3-dithiole-2-thiono[4,5-f][1,10]phenanthroline, P(OEt)₃, reflux, 18 h.

We found the subsequent step in the procedure toward L₁ to be the most synthetically challenging because all attempts to isolate the intermediate 1,10-phenanthroline-5,6-dithiol led to untractable products. Thus, a one-pot approach was used in which the 1,3-dithiole-2-thione functionality was formed by reacting the in situ formed 1,10-phenanthroline-5,6-dithiolate dianion with CS₂ under basic conditions. Thus L₂ was obtained in 95% yield and recrystallized from acetonitrile. Around the same time, the Hudhomme group reported a similar preparation of L₂ in which 5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline was converted to L₂ by cleaving the thioether groups with t-BuOK and converting the obtained dithiolate into 1,3-dithiole-2-thione using thiophosgene, with a resulting yield of 67%. Despite the efforts of both groups, shortly thereafter, a more direct route towards L₂ was proposed (Fig. 3.1), via a reaction between Br₂phen and potassium trithiocarbonate (formed in situ from K₂S and CS₂ in DMF), affording L₂ as a yellow solid in 92% yield.

The ligands L₂ and L₃ provide an entry into synthetic chemistry of TTF-annulated phenanthrolines, as demonstrated by our preparation of the asymmetric ligand L₄ via a triethylphosphite-mediated cross-coupling reaction between L₂ and 4,5-ethylenedithio-1,3-dithiole-2-one (Scheme 1). The same result can be obtained by reacting L₃ and 4,5-ethylenedithio-1,3-dithiole-2-thione in P(OEt)₃. A separation of L₄ from the symmetric
byproduct, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), formed by self-coupling of 4,5-ethylenedithio-1,3-dithiole-2-one, is achieved by using a short column (2.5 cm) and washing out the BEDT-TTF impurity with CH$_2$Cl$_2$, after which the eluent is switched to CH$_2$Cl$_2$/CH$_3$OH (2:1 v/v) to wash out the pure L$_1$ fraction.

### 3.3.2 NMR Spectroscopy

All ligands were unambiguously characterized by NMR spectroscopy. Their $^1$H NMR spectra exhibit three distinct series of peaks in the aromatic region that can be explicitly assigned to the protons on the phen moiety (Figure 3.3). The $^1$H NMR spectrum of L$_1$ shows that the H$_a$ proton of the phen moiety resonates at lowest field ($\delta = 9.17$ ppm), followed by the H$_b$ proton ($\delta = 8.01$ ppm) and the more shielded H$_c$ proton ($\delta = 7.68$ ppm). As can be seen in Figure 3.3, the L$_1$ ligand exhibits an additional peak compared to that of L$_2$ and L$_3$, arising from the two pairs of protons residing on the ethylenedithio bridge on the periphery of the molecule.

### 3.3.3 Crystal Structure

The ligand L$_1$ crystallizes in the chiral orthorhombic space group $P2_12_12_1$. The chirality stems not from the molecular structure, but from the crystal packing. A careful examination of the crystal structure did not reveal any additional symmetry elements. The crystal structure refinement revealed that the compound crystallizes as a racemic twin. The dark-orange crystals exhibit rod-shaped morphology and contain interstitial solvent, resulting in the formula L$_1$·CHCl$_3$. In the crystal structure, the molecule of L$_1$ is almost planar (Figure 3.4a). The root mean square (rms) deviation from a least-squares plane fit through all atoms is 0.035(6) Å. Excluded from the fit was the peripheral ethylenedithio subunit, the carbon atoms of which are disordered over two positions at ~0.4 Å above and below the molecular plane. The molecules are stacked in columns parallel to the $a$ axis in a head-to-tail fashion (Figure 3.4b) and exhibit face-to-face π-π contacts with the interplanar separation of 3.56 Å. Large channels are present along the $a$ axis, which are filled with disordered CHCl$_3$ molecules. The details of data collection and crystal structure refinement are listed in Table 3.1.

### 3.3.4 Electrochemistry

The electrochemical properties of ligand L$_1$ were investigated in a CH$_3$CN/CH$_2$Cl$_2$ (3:2 v/v) solution. (CH$_3$CN was added to avoid the appearance of an irreversible feature associated with ligand absorption on the electrode surface.) Ligand L$_1$ exhibits two reversible one-electron redox processes that are associated with the successive oxidations of the TTF subunit to the radical
cation TTF$^{+*}$ and the dication TTF$^{2+}$ (Figure 3.5). The half-wave potentials of L$_1$ (0.17 and 0.52 V vs. Fc$^+$/Fc) are positively shifted relative to those observed for unsubstituted TTF ($-$0.10 and

Figure 3.3: Selected aromatic and aliphatic regions of the $^1$H NMR spectra of L$_1$, L$_2$, and L$_3$ (CDCl$_3$, room temperature). The residual solvent signals are marked with asterisks.
Figure 3.4: The molecular structure of $L_1$ (a) and crystal packing of $L_1 \cdot CHCl_3$ viewed along the crystallographic $a$-axis (b). Thermal ellipsoids are at the 50% probability level. In (b), the H atoms have been omitted for clarity. Color scheme: Ru = light blue, S = yellow, N = blue, and C = gray.

Table 3.1: Data collection and structure refinement parameters for $L_1 \cdot CHCl_3$ and $L_2$.

<table>
<thead>
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<th></th>
<th>$L_1 \cdot CHCl_3$</th>
<th>$L_2$</th>
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<td>$C_{13}H_6N_2S_3$</td>
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<td>0.35 and −0.34</td>
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</table>
This shift can be explained by the π-accepting nature of the phen moiety which makes the TTF unit less prone to oxidation. The ligand based reductions of the phen moiety are also expected but could not be observed within the electrochemical window of the solvent system used.

Figure 3.5: Cyclic voltammogram of $L_1$ recorded in a 0.100 M solution of (Bu$_4$N)PF$_6$ in CH$_3$CN/CH$_2$Cl$_2$ (3:2 v/v). Potentials are given vs Fc$^+$/Fc.

3.3.5 Density Functional Theory Calculations

DFT calculations of the electronic structure of $L_1$ reveal that the π-type highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are centered on the edt-TTF and phen fragments, respectively (Figure 3.6). This agrees with the makeup of the frontier orbitals reported earlier for a similar compound, TTF-dppz, with a more extended polypyridyl fragment.$^{83,151}$

Figure 3.6: DFT calculated frontier molecular orbitals of $L_1$ (a) and TTF-dppz (b)$^{151}$. 
3.3.6 UV-Visible Absorption

The optical absorption spectrum of \( L_1 \) in CHCl\(_3\) solution is shown in Figure 3.7. The results of DFT calculations allow assignment of the transitions observed. The lowest energy band at 402 nm (~24800 cm\(^{-1}\)) can be assigned to an intra-ligand charge transfer (ILCT) transition from the TTF unit to the phen fragment. The extinction coefficient of this band is ~2000 M\(^{-1}\)cm\(^{-1}\), which is substantially smaller than 10000 M\(^{-1}\)cm\(^{-1}\) reported for the ILCT band in the related TTF-dppz molecule.\(^{151}\) The remaining bands at higher energy are attributed to \( \pi-\pi^* \) transitions localized at phen and TTF units.

![Figure 3.7: UV-visible absorption spectrum of a 0.1 mM solution of \( L_1 \) in CHCl\(_3\) at room temperature (optical path = 1 cm).](image)

The absorption spectroscopy was also used to monitor the chemical oxidation of the ligand with successive additions of the oxidizing agent, NOBF\(_4\) (Figure 3.8a). Upon addition of 0.2 equivalents of NOBF\(_4\), a new absorption band appears around 530 nm (~19000 cm\(^{-1}\)), along with the decrease in the intensity of the ILCT band. This is in line with what was observed earlier for TTF-dppz and can be attributed to the oxidation of the TTF fragment.\(^{151}\) It seems, however, that further addition of NOBF\(_4\) destroys the molecule as the resulting absorption spectrum loses all characteristic features.

In a similar manner, the ligand was subject to electrochemical oxidation in the optical cuvette allowing acquisition of spectroelectrochemical data as function of time (Figure 3.8b). The applied potential was chosen to correspond to one-electron oxidation of \( L_3 \) (Figure 3.5). Thus, one should expect that the resulting spectrum will reflect the formation of the TTF\(^+\) radical cation. In contrast to the chemical oxidation, the electrochemical method gives much better control over the oxidation potential. Just as in the previous experiment, the ILCT intensity
decreased upon oxidation and a new band at lower energy emerged, indicating the formation of the radical cation, TTF$^{+}$.

![Figure 3.8: Absorption spectrum of $L_1$: (a) with successive additions of NOBF$_4$ in CH$_2$Cl$_2$ (0.01 mM) at room temperature (optical path = 1 cm), (b) during electrochemical oxidation in the spectroelectrochemical cell at a constant potential of 640 mV; concentration was 0.1 mM and the optical path of the spectroelectrochemical cell was 0.07 cm.](image)

### 3.3.7 Luminescence Spectroscopy

The luminescence of the ligand $L_1$ was observed in a CH$_2$Cl$_2$ solution at room temperature (Figure 3.9). Excitation at 450 nm resulted in a relatively weak emission band centered at $\sim$18500 cm$^{-1}$. In the original spectrum, Raman scattering of the solvent appeared with comparable intensity, and therefore it was subtracted prior to constructing the plot shown in Figure 3.9. The slight differences observed between the excitation and absorption spectra are attributed to the inherently low intensity of the emission of $L_1$. Nonetheless, the spectral overlap between the observed emission and the ILCT band in the absorption spectrum, allows us to tentatively assign the observed emission to ILCT luminescence from $L_1$.

### 3.4 Conclusion

The attachment of the redox-active TTF to the metal-binding chelator in 1,10-phenanthroline, has been afforded via two different synthetic routes, ultimately providing the stable ligand edt-TTF-phen ($L_1$). Ligand $L_1$ can be used in the direct attachment of the potentially conductive TTF moiety to virtually any metal center. The ligand $L_1$ crystallizes in the chiral orthorhombic space group $P2_1\overline{2}1_2$ and exhibits two reversible one-electron redox
processes that are readily assigned to oxidation of the TTF moiety to the radical cation TTF$^{+}$ and the dication TTF$^{2+}$ during the electrochemical experiments. A separate synthetic route was discovered affording the sister compound in bht-TTF-phen ($L_4$) that exhibits increased solubility due to the replacement of the original ethylenedithio bridge in $L_1$ with the long hexylthio alkyl chains present in $L_4$. This increased solubility allows for further characterization of the ligand and resulting complexes that is not possible in the analogues that utilize the ligand $L_1$. 

**Figure 3.9:** The absorption, excitation, and emission spectra of a 0.1 mM solution of $L_1$ in CH$_2$Cl$_2$ at room temperature (optical path = 1 cm).
CHAPTER FOUR
RU(II) COMPLEXES WITH TTF-ANNULATED PHENANTHROLINE AND RELATED LIGANDS

4.1 Introduction

The combination of TTF-containing conductors with photoactive metal centers such as Ru(II) has been of particular interest in the development of charge separation systems\textsuperscript{83,111,153}, photoredox switches\textsuperscript{44,154}, and, of high current interest, light harvesting antennae for photovoltaic devices\textsuperscript{62,82,153,155-165}. The current chapter describes the synthesis and investigation of photophysical and electrochemical properties of $[\text{Ru(bpy)}_2(L_1)](\text{PF}_6)_2$ (1), as well as two related model complexes 2 and 3. We also use DFT calculations of electronic structure to aid in the understanding of the photophysical behavior for these complexes.

![Figure 4.1: Chemical structure of complexes 1-3.](image)

4.2 Starting Materials and Syntheses

All reactions were performed in an inert N\textsubscript{2} atmosphere using standard Schlenk techniques, unless noted otherwise. The $[\text{Ru(bpy)}_2\text{Cl}_2]\cdot2\text{H}_2\text{O}$ was kindly donated by Prof. Goldsby (FSU) and used as received. Commercially available NH\textsubscript{4}PF\textsubscript{6} (99%, Aldrich) was used as received. Additional purification of anhydrous commercial solvents used in anaerobic reactions was achieved by passing them through a double-stage drying/purification system (Glass Contour Inc.). Otherwise, ACS grade solvents were used.

$[\text{Ru(bpy)}_2(L_1)](\text{PF}_6)_2$ (1). A suspension of $L_1$ (50 mg, 0.112 mmol) in anhydrous ethanol (10 mL) was added to a suspension of $[\text{Ru(bpy)}_2\text{Cl}_2]\cdot2\text{H}_2\text{O}$ (53 mg, 0.102 mmol) in anhydrous ethanol (15 mL). The mixture was refluxed in the dark under N\textsubscript{2} for 12 h, after which time the reaction was cooled down to room temperature and filtered. A solution of NH\textsubscript{4}PF\textsubscript{6} (58 mg, 0.356
mmol) in anhydrous ethanol (25 mL) was added drop-wise to the filtrate. The solution was left undisturbed overnight at –23°C, resulting in precipitation of a brown product. Yield = 76% (89 mg). X-ray quality single crystals were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the complex in the dark. 

**Elem. analysis:** calcd. (found) for RuC$_{38}$H$_{28}$N$_6$O$_{17}$S$_3$P$_2$F$_{12}$ (1·1H$_2$O), %: C, 39.07 (39.19); H, 2.42 (2.42); N, 7.19 (7.40); S, 16.47 (16.30). $^1$H NMR (CD$_3$CN, 600 MHz), δ, ppm: 8.55 (d, 2H, $J = 8.2$ Hz), 8.52 (d, 2H, $J = 8.1$ Hz), 8.11 (td, 2H, $J = 1.4, 17.4$ Hz), 8.05 (m, 4H), 7.98 (dd, 2H, $J = 0.9, 9.2$ Hz), 7.84 (dd, 2H, $J = 0.7, 6.2$ Hz), 7.66 (m, 4H), 7.47 (m, 2H), 7.34 (m, 2H), 3.32 (d, 4H, $J = 3.0$ Hz).

13C NMR (CD$_3$CN, 151 MHz), δ, ppm: 158.7, 158.4, 153.8, 153.6, 153.4, 148.5, 139.5, 139.5, 134.7, 134.5, 129.1, 129.1, 128.3, 127.0, 125.8, 125.8, 115.1, 113.3, 66.7, 16.1. ESI-MS (CH$_3$OH), $m/z$ (M = [Ru(bpy)$_2$(L)$_1$]$_2^{2+}$, relative intensity): 1005 ([M+PF$_6$]$^+$, 100), 481 ([M–L$_1$+Cl+CH$_3$OH]$^+$, 52), 449 ([M–L$_1$+Cl]$^+$, 30), 430 ([M+2H]$^+$, 24), 416 ([M–C$_2$H$_4$]$_2^{2+}$, 41). UV-Vis (CH$_3$CN), $\lambda_{\text{max}}$, nm (log ε) = 240 (4.73), 253 (4.66), 285 (4.87), 343 (4.06), 450 (4.18). Emission (CH$_3$CN, $\lambda_{\text{exc}} = 450$ nm), $\lambda_{\text{max}}$, nm (quantum yield, $\Phi_F$) = 636 (0.012).

The complexes [Ru(bpy)$_2$(L)$_2$](PF$_6$)$_2$ (2) and [Ru(bpy)$_2$(L)$_3$](PF$_6$)$_2$ (3) were prepared in a similar manner as described above for complex 1.

**[Ru(bpy)$_2$(L)$_2$](PF$_6$)$_2$ (2).** Yield = 93%. 

**Elem. analysis:** calcd. (found) for RuC$_{33}$H$_{23}$N$_6$O$_{10.5}$S$_3$P$_2$F$_{12}$ (2·0.5H$_2$O), %: C, 39.68 (39.75); H, 2.32 (2.33); N, 8.41 (8.73); S, 9.63 (9.44); F, 22.64 (22.75). $^1$H NMR (CD$_3$CN, 600 MHz), δ, ppm: 8.53 (d, 2H, $J = 8.0$ Hz), 8.39 (dd, 2H, $J = 1.1, 9.5$ Hz), 8.15 (dd, 2H, $J = 1.1, 6.4$ Hz), 8.10 (td, 2H, $J = 1.4, 17.3$ Hz), 8.02 (td, 2H, $J = 1.4, 17.3$ Hz), 7.81 (d, 2H, $J = 5.6$ Hz), 7.78 (dd, 2H, $J = 5.3, 13.7$ Hz), 7.56 (d, 2H, $J = 5.0$ Hz), 7.45 (m, 2H), 7.25 (m, 2H). UV-Vis (CH$_3$CN), $\lambda_{\text{max}}$, nm (log ε) = 255 (4.62), 287 (4.85), 372 (4.36), 385 (4.30), 445 (4.21). Emission (CH$_3$CN, $\lambda_{\text{exc}} = 450$ nm), $\lambda_{\text{max}}$, nm (quantum yield, $\Phi_F$) = 632 (0.066).

**[Ru(bpy)$_2$(L)$_3$](PF$_6$)$_2$ (3).** Yield = 78%. 

**Elem. analysis:** calcd. (found) for RuC$_{33}$H$_{27}$N$_6$O$_{13.5}$S$_3$P$_2$F$_{12}$ (3·2.5H$_2$O), %: C, 38.91 (38.87); H, 2.67 (2.56); N, 8.25 (8.25); S, 6.30 (6.16). $^1$H NMR (CD$_3$CN, 600 MHz), δ, ppm: 8.53 (d, 2H, $J = 8.1$ Hz), 8.49 (d, 2H, $J = 8.2$ Hz), 8.40 (dd, 2H, $J = 1.1, 9.5$ Hz), 8.13 (dd, 2H, $J = 1.1, 6.4$ Hz), 8.10 (td, 2H, $J = 1.4, 17.3$ Hz), 8.01 (td, 2H, $J = 1.5, 17.3$ Hz), 7.81 (d, 2H, $J = 4.9$ Hz), 7.77 (dd, 2H, $J = 5.3, 13.7$ Hz), 7.55 (d, 2H, $J = 5.0$ Hz), 7.44 (m, 2H), 7.24 (m, 2H). 13C NMR (CD$_3$CN, 151 MHz), δ, ppm: 187.9, 158.2, 158.0, 154.0, 153.1, 153.0, 147.8, 139.1, 139.0, 134.9, 130.5, 128.7, 128.5, 128.0, 127.4, 125.4,
125.3. *UV-Vis* (CH$_3$CN), $\lambda_{\text{max}}$, nm ($\log \varepsilon$) = 256 (4.61), 285 (4.95), 340 (3.94), 449 (4.16). *Emission* (CH$_3$CN, $\lambda_{\text{exc}}$ = 450 nm), $\lambda_{\text{max}}$, nm (quantum yield, $\Phi_F$) = 628 (0.097).

### 4.3 Results and Discussion

#### 4.3.1 Synthetic Procedures

Due to the never diminishing interest in Ru(II) complexes that incorporate N-heterocyclic polypyridyl ligands, we were incited to investigate the electrochemical and photophysical properties of such complexes prepared with ligands $L_2$ and $L_3$, and especially with the redox-active ligand $L_1$. Reactions between these ligands and [Ru(bpy)$_2$Cl$_2$] in refluxing ethanol result in the formation of the desired complexes that can be isolated as hexafluorophosphate salts, [Ru(bpy)$_2$(L$_i$)](PF$_6$)$_2$ ($i$ = 1, 2, 3) upon addition of an excess of NH$_4$PF$_6$. The crystals of these complexes are obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex.

#### 4.3.2 $^1$H NMR Spectroscopy

In addition to conventional 1D NMR experiments, complexes 1–3 were also examined by 2D $^1$H COSY and $^1$H-$^1$C HSQC methods that allowed unequivocal assignment of signals in the more complicated aromatic region. This region contains signals that can be assigned to the bipyridine and phenanthroline moieties. A representative $^1$H NMR and 2D $^1$H COSY for 1 is shown below in Figure 4.2 and the corresponding NMR for 2 and 3 are collected in the supporting information (Figure S4.1 and S4.2).

Upon coordination of phenanthroline-based ligands to the Ru(II) center, the most dramatic changes are observed for the $\alpha$-protons, whose signals are shifted upfield by $\sim$1.2 ppm. This shift can be explained by shielding arising from the proximity of these protons to the $\pi$-system of bipyridine ligands (Figure 4.3), which is a commonly observed effect in such complexes with chelating polypyridyl ligands. The $^1$H NMR spectrum shows that the two bipyridine ligands are magnetically equivalent and thus produce eight signals identifiable with four protons from each pyridyl moiety. The bipyridine protons were assigned in accordance with previously reported NMR assignments for ruthenium polypyridyl complexes.$^{167}$

#### 4.3.3 Crystal Structure

The mononuclear complex [Ru(bpy)$_2$(L$_1$)](PF$_6$)$_2$ (1) crystallizes as a dark-red acetonitrile solvate, 1·3.6CH$_3$CN (Figure 4.4), in the centrosymmetric monoclinic space group $P2_1/c$ (the
parameters of which are collected below in Table 4.1). Similar to the structure of \( L_1 \), the ligand remains nearly planar in the structure of \( 1 \cdot 3.6\text{CH}_3\text{CN} \), with a

\[
0.12(5) \text{ Å rms deviation from a least-squares plane fit through all atoms but the C atoms of the peripheral dithioethylene bridge. The crystal packing features a unique stacking motif of TTF moieties propagating along the } b \text{ axis (Figures 4.4c and 4.4d). An asymmetric unit includes three}
\]

**Figure 4.2:** \(^1\text{H} 1\)-D and COSY 2-D NMR spectra of the aromatic region of \( 1 \) in CD\(_3\)CN at room temperature.
[Ru(bpy)$_2$(L)]$^{2+}$ dications of the same chirality. An inversion operation generates three dications of the opposite chirality, resulting in a stacking of alternating “triplets” of Δ- and Λ-isomers,

Figure 4.3: Molecular structure of [Ru(bpy)$_2$(L)]$^{2+}$ showing the proximity of the α-protons of coordinated L to the π-system of the bpy ligands.

Figure 4.4: The molecular structure of [Ru(bpy)$_2$(L)]$^{2+}$ dication (a) and crystal packing of 1·3.6CH$_3$CN (b), illustrating the counterions and solvent molecules filling the structural voids between the 1D stacks of dications. The side (c) and top (d) views of the packing of dications, showing the “triplet” of Δ-isomers in the crystal structure of 1·3.6CH$_3$CN. The molecular structure of [Ru(bpy)$_2$(L)](PF$_6$)$_2$·0.8CH$_3$CN (3) is shown with counterions and crystallization solvent present (e). The H atoms have been omitted for clarity in (a)-(d). Color scheme: Ru = light blue, S = yellow, N = blue, C = gray, P = purple, F = green, O = red, H = white. Thermal ellipsoids are at the 50% probability level.
with six dicationic species in a repeat unit of the stack. Thus, the overall structure is indeed centrosymmetric. The plane-to-plane separation between TTF units varies from 3.44 to 3.78 Å.

The crystals of $1 \cdot 3.6\text{CH}_3\text{CN}$ quickly lose crystallinity when removed from mother liquor, which can be explained by the loss of interstitial solvent. The crystals remain indefinitely stable when kept under mother liquor in the dark, but when exposed to light in the presence of air, these dark-red crystals gradually convert to bright-orange crystals of $3 \cdot 0.8\text{CH}_3\text{CN}$. This conversion is described in detail in the section “Photodegradation of the TTF-Containing Complex (1)” below.

The complex $[\text{Ru}(\text{bpy})_2(\text{L}_3)](\text{PF}_6)_2$ (3) crystallizes as an orange acetonitrile solvate, $3 \cdot 0.8\text{CH}_3\text{CN}$ (Figure 4.4e), in the triclinic space group $P\bar{1}$. Since they form spontaneously from crystals of complex 1 when left in mother liquor solution, they seem to remain rather stable in solution as
well as in the solid state. The resulting photochemical and photophysical properties of 3 are discussed in more detail later in this chapter.

**4.3.4 Electrochemistry**

Complex 1 exhibits three reversible oxidation processes (Figure 4.5), in contrast to complexes 2 and 3, which exhibit only one reversible oxidation (Table 4.2). A comparison of the redox behavior of 1 to that of 2, 3, and L₁ indicates that the first two one-electron oxidations in 1 (at 0.26 and 0.58 V) are TTF-based. They are shifted to slightly more positive potentials relative to those observed for L₁ because of the electrostatic inductive effect of the Ru(II) ion bound to L₁. The third oxidation for complex 1 at 1.04 V (and the only oxidation observed for 2 and 3, at 0.97 V and 0.96 V, respectively) thus corresponds to the Ru³⁺/²⁺ redox couple. This couple is also the only oxidation observed for the reference compound [Ru(bpy)₂(phen)](PF₆)₂ at 0.89 V (Table 4.2).³⁶ All three oxidations in 1 are similar to those reported earlier for [Ru(bpy)₂(TTF-dppz)](PF₆)₂ (0.29, 0.61, 0.99 V).²³ Two reversible one-electron reduction waves were observed for 1 in the cathodic region (at –1.54 and –1.92 V). They are also comparable to the reversible reductions observed for the reference compounds, [Ru(bpy)₂(phen)](PF₆)₂ (–1.71 and –1.91 V) and [Ru(bpy)₂(TTF-dppz)](PF₆)₂ (–1.35 and –1.79 V), and attributed to the reduction of the phenanthroline and bipyridine moieties, respectively.

![Cyclic voltammograms of L₁ and 1](image)

**Figure 4.5:** Cyclic voltammograms of L₁ and 1 (dashed blue and solid red lines, respectively) recorded in a 0.100 M solution of (Bu₄N)PF₆ in CH₃CN/CH₂Cl₂ (3:2 v/v). Potentials are given vs. Fe⁺⁺/Fe⁺.
Table 4.2: Redox potentials (V vs Fc+/Fc) of ligand L₁ and complexes 1-3 in CH₃CN/CH₂Cl₂ (3:2 v/v), and of reference compounds, TTF in CH₂Cl₂, [Ru(bpy)₂(phen)](PF₆)₂ in CH₃CN, and [Ru(bpy)₂(TTF-dppz)](PF₆)₂ in CH₂Cl₂/CH₃CN (5:1).³³

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4.3.5 DFT Calculations

DFT and TD-DFT calculations have been shown to be indispensable for the analysis of photophysical behavior of Ru(II) polypyridyl complexes.¹⁴²,¹⁶⁹-¹⁷³ Therefore, we carried out such calculations to elucidate the electronic structure of complexes 1-3 and aid in the interpretation of their photophysical properties. The energy diagram of selected frontier molecular orbitals (MOs) appears in Figure 4.6, while the corresponding orbital energies for each complex are listed in Table 4.2.

Figure 4.6: Frontier molecular orbitals of 1-3. H atoms have been omitted for clarity. All energies have been converted to the NHE scale assuming that the NHE potential is −4.5 V vs. vacuum level.¹³³
Table 4.3: The energies (in eV)\(^a\) and composition (in %) of the frontier molecular orbitals of 1-3.\(^b\)

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</table>

\(^a\) All energies have been converted to the NHE scale assuming that the NHE potential is –4.5 V vs vacuum level.

\(^b\) H = HOMO; L = LUMO.

The most obvious difference between the three complexes appears in the nature of the highest occupied MOs (HOMOs). Complexes 2 and 3 are characterized by the presence of metal-based HOMO, HOMO–1, and HOMO–2, corresponding to the \(d\)-orbitals of the Ru\(^{2+}\) ion, as typical of many Ru-polypyridyl complexes. These three orbitals are preserved in complex 1, but about 0.6 eV above them lays the new \(\pi\)-type HOMO centered entirely on the TTF fragment. This finding is in agreement with the observation of two TTF-centered oxidations that precede the Ru\(^{3+}/2+\) redox couple in 1. The purely TTF-based HOMO and essentially unchanged nature of the metal-centered orbitals in 1 as compared to 2 and 3 (Table 4.3) indicate that the electronic coupling between the Ru\(^{II}\) ion and the TTF fragment is negligible.

In all three complexes, below the three metal-based orbitals appear ligand-centered \(\pi\)-orbitals. In 2 and 3, the HOMO–3 is localized on the dithiocarbonate-phenanthroline (DTC-phen) and trithiocarbonate-phenanthroline (TTC-phen) fragments, respectively, while in 1 the HOMO–4 is centered on the TTF-phen.

The four lowest unoccupied MOs (LUMOs) are similar in all three complexes, corresponding to \(\pi^*\)-orbitals of polypyridyl ligands and spanning a range of only ~0.2 eV. The LUMO and LUMO+1 are centered almost entirely on the phenanthroline fragment. The LUMO+2, LUMO+3, and LUMO+4 are largely bipyridine-based, with the exception of LUMO+3 in 2, which is centered on \(L_2\). It appears that the change from the C=C and C=O bonds in 1 and 3, respectively, to the C=S bond in 2 results in the lower energy of the \(L_2\)-centered \(\pi^*\)-orbital,
which has an important ramification on the appearance of the optical absorption spectrum of 2, as is discussed below.

4.3.6 UV-Visible Absorption

The optical absorption spectra of 1-3 are similar, revealing three major bands centered around 35000 cm$^{-1}$, 29500 cm$^{-1}$, and 22500 cm$^{-1}$. The absorption spectra simulated from the results of TD-DFT calculations reproduce well the character of the experimental spectra (Figure 4.7), and thus can be used to assign the experimentally observed transitions (Tables 4.4-4.6). In each case, the intense absorption band at higher energy (around 35000 cm$^{-1}$) is attributed to spin-allowed intraligand π-π* transitions, with some contribution from ligand-to-ligand charge transfer (LLCT) transitions.

![Figure 4.7: Experimental (red line) and simulated (blue line) optical absorption spectra of 1-3 (top to bottom, respectively). The gray bars indicate the energy and oscillator strength of each electronic excitation.](image)

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Table 4.4: Assignments of the optical absorption bands of 1 based on TD-DFT calculations.

<table>
<thead>
<tr>
<th>λ, nm</th>
<th>E, cm⁻¹</th>
<th>Calculated (osc. strength)</th>
<th>Excitation</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>19194</td>
<td>521 (0.24)</td>
<td>515 (0.014)</td>
<td>H → L+1 (66%)</td>
<td>TTF → phen</td>
</tr>
<tr>
<td>22321</td>
<td>448 (1.62)</td>
<td>447 (0.080)</td>
<td>H→2→L(61%)</td>
<td>Ru → phen</td>
</tr>
<tr>
<td></td>
<td>447 (0.080)</td>
<td>439 (0.102)</td>
<td>H–2 → L+2 (37%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>447 (0.080)</td>
<td>428 (0.163)</td>
<td>H–2 → L+3 (38%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>447 (0.080)</td>
<td>422 (0.118)</td>
<td>H–3 → L+2 (52%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>447 (0.080)</td>
<td>421 (0.104)</td>
<td>H–3 → L+3 (38%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td>29155</td>
<td>345 (1.25)</td>
<td>333 (0.035)</td>
<td>H → L+8 (55%)</td>
<td>TTF → bpy</td>
</tr>
<tr>
<td></td>
<td>333 (0.035)</td>
<td>328 (0.042)</td>
<td>H–1 → L+8 (63%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>328 (0.042)</td>
<td>327 (0.054)</td>
<td>H → L+9 (57%)</td>
<td>TTF → phen</td>
</tr>
<tr>
<td></td>
<td>327 (0.054)</td>
<td>318 (0.062)</td>
<td>H–2 → L+6 (47%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>318 (0.062)</td>
<td>305 (0.152)</td>
<td>H–3 → L+7 (34%)</td>
<td>Ru → bpy</td>
</tr>
<tr>
<td></td>
<td>305 (0.152)</td>
<td>294 (0.108)</td>
<td>H–2 → L+9 (33%)</td>
<td>Ru → phen</td>
</tr>
<tr>
<td>35088</td>
<td>285 (7.78)</td>
<td>286 (0.331)</td>
<td>H → L+1 (33%)</td>
<td>phen → phen</td>
</tr>
<tr>
<td></td>
<td>286 (0.331)</td>
<td>284 (0.233)</td>
<td>H–4 → L+4 (54%)</td>
<td>TTF → bpy</td>
</tr>
<tr>
<td></td>
<td>284 (0.233)</td>
<td>281 (0.259)</td>
<td>H–7 → L+3 (41%)</td>
<td>bpy → bpy</td>
</tr>
</tbody>
</table>

The lowest energy band around 22500 cm⁻¹ is due to the metal-to-ligand charge transfer (MLCT) transitions, as commonly seen in the optical spectra of Ru-polypyridyl complexes. In contrast to 2 and 3, the MLCT band of 1 reveals a low-energy tail that extends below 20000 cm⁻¹. This feature is attributed to the intra-ligand charge transfer (ILCT) excitation from the TTF-centered HOMO to the phenanthroline-centered LUMO+1.

The intermediate-energy band in the optical spectrum of 2 differs significantly from those found in the spectra of 1 and 3. In the latter two complexes, this band appears as a broad shoulder at ~29500 cm⁻¹ on the tail of the intense higher-energy band. In the spectrum of 2, this band is red-shifted to 26000 cm⁻¹. Given the chemical similarity between complexes 2 and 3, one would have to deduce that this bathochromic shift is attributed to the substantial change in the bonding character when going from the C=S bond in 2 to the C=O and C=C bonds in 3 and 1, respectively. Indeed, an examination of excitations that compose the intermediate-energy band confirms this assumption. In the case of 1, this band involves a mix of transitions of MLCT (Ru → phen, Ru → bpy), LLCT (TTF → bpy), and ILCT (TTF → phen) character, which correspond
Table 4.5: Assignments of the optical absorption bands of 2 based on TD-DFT calculations.

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>Observed ($\varepsilon \times 10^{-4}$, M$^{-1}$ cm$^{-1}$)</th>
<th>Calculated (osc. strength)</th>
<th>Excitation</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>22573</td>
<td>443 (1.74)</td>
<td>449 (0.140)</td>
<td>H$^{-1}$ $\rightarrow$ L (50%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>428 (0.142)</td>
<td>H$^{-1}$ $\rightarrow$ L+1 (48%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-2}$ $\rightarrow$ L+2 (42%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-2}$ $\rightarrow$ L+1 (51%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-2}$ $\rightarrow$ L+4 (37%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td>26882</td>
<td>372 (2.41)</td>
<td>361 (0.049)</td>
<td>H$^{-3}$ $\rightarrow$ L+1 (66%)</td>
<td>TTC $\rightarrow$ phen</td>
</tr>
<tr>
<td>25974</td>
<td>385 (2.13) sh</td>
<td>332 (0.031)</td>
<td>H $\rightarrow$ L+6 (60%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330 (0.382)</td>
<td>H$^{-3}$ $\rightarrow$ L+3 (58%)</td>
<td>TTC $\rightarrow$ TTC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>327 (0.038)</td>
<td>H $\rightarrow$ L+8 (61%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>317 (0.057)</td>
<td>H$^{-1}$ $\rightarrow$ L+6 (45%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td>34965</td>
<td>286 (8.09)</td>
<td>289 (0.056)</td>
<td>H$^{-5}$ $\rightarrow$ L+2 (52%)</td>
<td>bpy $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>282 (0.114)</td>
<td>H$^{-7}$ $\rightarrow$ L (57%)</td>
<td>phen $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>278 (0.798)</td>
<td>H$^{-5}$ $\rightarrow$ L+4 (41%)</td>
<td>bpy $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>276 (0.050)</td>
<td>H$^{-3}$ $\rightarrow$ L+5 (59%)</td>
<td>TTC $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>275 (0.065)</td>
<td>H$^{-7}$ $\rightarrow$ L+3 (47%)</td>
<td>phen $\rightarrow$ TTC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>254 (0.053)</td>
<td>H$^{-2}$ $\rightarrow$ L+11 (62%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
</tbody>
</table>

Table 4.6: Assignments of the optical absorption bands of 3 based on TD-DFT calculations.

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>Observed ($\varepsilon \times 10^{-4}$, M$^{-1}$ cm$^{-1}$)</th>
<th>Calculated (osc. strength)</th>
<th>Excitation</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>22573</td>
<td>443 (1.67)</td>
<td>448 (0.088)</td>
<td>H$^{-1}$ $\rightarrow$ L (42%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>427 (0.169)</td>
<td>H$^{-2}$ $\rightarrow$ L+2 (52%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-1}$ $\rightarrow$ L+1 (32%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-2}$ $\rightarrow$ L+1 (53%)</td>
<td>Ru $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$^{-2}$ $\rightarrow$ L+3 (38%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td>29412</td>
<td>340 (0.97)</td>
<td>332 (0.062)</td>
<td>H$^{-3}$ $\rightarrow$ L+1 (63%)</td>
<td>DTC $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>317 (0.057)</td>
<td>H$^{-1}$ $\rightarrow$ L+6 (45%)</td>
<td>Ru $\rightarrow$ bpy</td>
</tr>
<tr>
<td>35211</td>
<td>284 (10.26)</td>
<td>286 (0.065)</td>
<td>H$^{-6}$ $\rightarrow$ L+1 (52%)</td>
<td>DTC $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>281 (0.330)</td>
<td>H$^{-5}$ $\rightarrow$ L+3 (50%)</td>
<td>bpy $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280 (0.263)</td>
<td>H$^{-6}$ $\rightarrow$ L (37%)</td>
<td>DTC $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>277 (0.825)</td>
<td>H$^{-6}$ $\rightarrow$ L (39%)</td>
<td>DTC $\rightarrow$ phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>264 (0.258)</td>
<td>H$^{-3}$ $\rightarrow$ L+4 (60%)</td>
<td>DTC $\rightarrow$ bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>258 (0.109)</td>
<td>H$^{-3}$ $\rightarrow$ L+5 (63%)</td>
<td>DTC $\rightarrow$ DTC</td>
</tr>
</tbody>
</table>
to excitations from the Ru-based HOMO–1, HOMO–2, or HOMO–3, or from the TTF-based HOMO to the polypyridyl-centered π*-orbitals (Table 4.4). In both 2 and 3, this band includes MLCT (Ru → bpy) and ILCT (TTC → phen or DTC → phen, respectively) transitions (Tables 4.5 and 4.6 respectively), but in 2 the band is dominated by a strong HOMO–3 to LUMO+3 excitation that corresponds to the π–π* transition of the TTC fragment. Thus, the red shift of the intermediate-energy band in 2 relative to the corresponding bands in 1 and 3 stems from the stabilization of one of the unoccupied π*-orbitals (LUMO+3 in 2) upon introduction of the additional S atom in L2.

4.3.7 Photophysical Properties

Complexes 1-3 exhibit luminescence in a CH3CN solution at room temperature (Figure 4.8) when excited at 450 nm (22220 cm⁻¹). The emissions appear as broad and structureless bands centered at ca. 600 nm (16670 cm⁻¹), which is characteristic of 3MLCT emission in Ru polypyridine complexes. In comparison to reference complexes [Ru(bpy)₃](PF₆)₂ and [Ru(bpy)₂(phen)](PF₆)₂, the emission maximum (λ_em) of 1-3 is red-shifted by ~400 cm⁻¹. The emission of complex 1 is shifted to lower energy relative to those of 2 and 3, which agrees with the smaller HOMO-LUMO gap in the former. Compiled in Table 4.7 are the photophysical properties of complexes 1-3 and the reference compounds. The emission lifetime (τ_obs) and quantum efficiency (Φ_f) of 1 in de-oxygenated CH3CN at room temperature are 1.77(4) µs and 1.2%, respectively. For 2 and 3, these parameters are 1.47 µs and 6.6% and 2.08(4) µs and 9.7%, respectively.

Table 4.7: Photophysical properties of complexes 1-3 and reference compounds [Ru(bpy)₃](PF₆)₂ and [Ru(bpy)₂(phen)](PF₆)₂.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_abso/λ_abso nm</th>
<th>E_emso/λ_emso nm</th>
<th>E_ST, cm⁻¹</th>
<th>Φ_f, %</th>
<th>τ_abso, µs</th>
<th>τ_r, µs</th>
<th>τ_nr, µs</th>
<th>k_r, s⁻¹</th>
<th>k_nr, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22321 / 448 (1.62)</td>
<td>15723 / 636</td>
<td>6598</td>
<td>1.2</td>
<td>1.77(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22573 / 443 (1.74)</td>
<td>15823 / 632</td>
<td>6750</td>
<td>6.6</td>
<td>1.47(4)</td>
<td>22</td>
<td>1.58</td>
<td>4.5x10⁴</td>
<td>6.4x10⁵</td>
</tr>
<tr>
<td>3</td>
<td>22573 / 443 (1.74)</td>
<td>15823 / 632</td>
<td>6750</td>
<td>6.6</td>
<td>1.47(4)</td>
<td>22</td>
<td>1.58</td>
<td>4.5x10⁴</td>
<td>6.4x10⁵</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(bpy)₃</a>₂</td>
<td>22172 / 451 (1.32)</td>
<td>16260 / 615</td>
<td>5912</td>
<td>6.2</td>
<td>0.86</td>
<td>14</td>
<td>0.92</td>
<td>7.2x10⁴</td>
<td>1.1x10⁵</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(bpy)₂(phen)</a>₂</td>
<td>22271 / 449 (1.57)</td>
<td>16340 / 612</td>
<td>5931</td>
<td>6.0</td>
<td>0.80</td>
<td>13</td>
<td>0.85</td>
<td>7.5x10⁴</td>
<td>1.2x10⁵</td>
</tr>
</tbody>
</table>

*E_abso/λ_abso = energy/wavelength of maximum absorption; E_emso/λ_emso = energy/wavelength of maximum emission; E_ST = Stokes shift; Φ_f = luminescence relative quantum yield under 450 nm excitation, using [Ru(bpy)₃]²⁺ in CH₂CN as standard with Φ_f = 0.062; τ_abso = measured luminescence lifetime; τ_r = calculated radiative lifetime (Φ_f = τ_abso/τ_r); τ_nr = calculated non-radiative lifetime (1/τ_r + 1/τ_nr = 1/τ_abso); k_r = radiative rate constant (k_r = Φ_f/τ_abso); k_nr = non-radiative rate constant (k_r + k_nr = 1/τ_abso).
The radiative lifetimes, $\tau_r$, of 2 and 3 are 22 $\mu$s and 21 $\mu$s, respectively, as calculated from the respective quantum efficiencies and observed lifetimes. These $\tau_r$ values are of the order usually observed for the spin-forbidden transition from the $^3$MLCT state of Ru(II) polypyridyl complexes.\textsuperscript{135} For 1, the observed lifetime ($\tau_{obs}$) is comparable to those of 2 and 3, but the overall luminescence quantum yield is significantly quenched. Based on the absorption spectra of the three compounds, the radiative lifetime of the $^3$MLCT state of 1 is expected to be similar to those calculated for 2 and 3. Therefore, the reduced luminescence quantum efficiency of 1 must be due to a non-radiative decay to a state at lower or similar energy competing with the intersystem crossing from the initially excited $^1$MLCT states to the $^3$MLCT state.\textsuperscript{83}

The luminescence quenching observed for complex 1 may be associated with the different nature of frontier orbitals in 1 as compared to 2 and 3 (see Figure 4 and the related discussion above). In the latter complexes, the lowest energy excitations, Ru$^{2+}\rightarrow$bpy and Ru$^{2+}\rightarrow$phen, correspond to the population of nearly degenerate $^1$MLCT states, bpy/bpy$^*$-Ru$^{3+}$-phen and (bpy)$_2$-Ru$^{3+}$-phen$^*$, respectively, that are known to relax via intersystem crossing (ISC) and interligand electron hopping to the lowest energy emissive $^3$MLCT state.\textsuperscript{32,33} In the case of 1, however, the ISC can be quenched by electron transfer from the TTF donor moiety to the Ru$^{2+}$ center, thus resulting in the decreased luminescence quantum yield. The mechanism of such quenching requires a special attention. The initial excitation from the ground state of 1 also creates two $^1$MLCT states, (bpy)$_2$-Ru$^{2+}$-phen$^*$-TTF$^*$ ($^1$MLCT$_1$) and bpy/bpy$^*$-Ru$^{3+}$-phen-TTF (1MLCT$_2$), which have quite different nature due to the presence of the TTF moiety in the vicinity of the excited electron in $^1$MLCT$_1$ (Figure 4.9). In the $^1$MCLT$_2$ state, the electron can be transferred from TTF to Ru$^{3+}$ to produce, in a cascade, first a lower-energy, charge-separated LLCT state, bpy/bpy$^*$-Ru$^{2+}$-phen-TTF$^+$, and finally a non-emissive ILCT state, (bpy)$_2$-Ru$^{2+}$-phen$^*$-TTF$^*$. For the (bpy)$_2$-Ru$^{3+}$-phen$^*$-TTF ($^1$MLCT$_1$) state, the TTF$\rightarrow$Ru$^{3+}$ electron transfer is expected to be slower, due to the localization of the excited-state electron on the phen moiety. This blockage of the electron transfer results in more efficient ISC to the corresponding $^3$MLCT$_1$ state that undergoes the radiative decay with the characteristic lifetime of 1.77 $\mu$s.

In principle, the TTF$\rightarrow$Ru$^{3+}$ electron transfer can also occur in the corresponding longer-lived $^3$MLCT$_2$ state, and it would be of interest to investigate the possible competition of this process with the radiative decay by combining advanced transient spectroscopy and theoretical calculations. However, based on the spectroscopic and the electrochemical data, the driving force
for electron transfer in the $^3\text{MLCT}_2$ state would be significantly smaller than in the $^1\text{MLCT}_2$ state. Therefore, this process would be slower and would have to compete with the electron localization in the lowest energy $^3\text{MLCT}$ state, namely the $^3\text{MLCT}_1$ state, via interligand electron hopping on the picosecond timescale. But this puts the electron transfer rate into direct competition with the $^1\text{MLCT}$ to $^3\text{MLCT}$ ISC. Thus, we believe that the luminescence quenching in complex 1 stems primarily from the inability of the $^1\text{MLCT}_2$ state to undergo ISC to the corresponding $^3\text{MLCT}_2$ state.

**Figure 4.8:** MLCT absorption bands and corresponding emission spectra of complexes 1-3 (a-c, respectively). The wavelengths of the absorption ($\lambda_{\text{abs}}$) and emission ($\lambda_{\text{em}}$) maxima are indicated by the corresponding spectra.
In an effort to better understand the nature of the luminescence (and thus the quenching mechanism) of 1, time-resolved transient absorption spectra were collected in a deaerated CH$_3$CN solution at room temperature. A 488 nm (20492 cm$^{-1}$) pulse into the tail of the mixed Ru $\rightarrow$ phen/Ru $\rightarrow$ bpy 1MLCT band was used for excitation, and the bleach of this band was monitored at 458 nm (21834 cm$^{-1}$). There is no indication of an intermediate state in the transient signal and the kinetic trace was fit to a single exponential (Figure 4.10) with a lifetime of 1.75(7) $\mu$s, which coincides with the luminescence lifetime of 1 (Table 4.7). Unfortunately, there is no indication of an intermediate charge-separated state that would be sufficiently long-lived on the scale of the detection limits of the instrument (>10 ns). If such a state exists, experiments on a faster timescale will be required to observe it.

We also probed a transient signal at 370 nm (27027 cm$^{-1}$) under 488 nm excitation. At this energy, the reference compound [Ru(bpy)$_3$](PF$_6$)$_2$ exhibits a significant transient absorption signal. In the case of 1, however, we observed only a very weak signal at 370 nm, which decayed at a single-exponential rate but with a high degree of uncertainty: 1.6(8) $\mu$s (Figure
S4.3). This observation reinforces our assumption that the luminescence observed for 1 is of the $^3\text{MLCT}$ nature.

![Figure 4.10: Kinetic profile of the difference absorbance spectrum of 1 in CH$_3$CN at room temperature. $\lambda_p$=488 nm; $\lambda_{probe}$=458 nm. Experimental data: red; single exponential fit: blue.](image)

**4.3.8 Photodegradation of the TTF-Containing Complex (1)**

The solid form of 1 can be stored in air for a prolonged period of time without any visible degradation, but when dark-red crystals of 1 were left under mother liquor (CH$_3$CN/Et$_2$O) saturated with O$_2$ for about a week, a complete transformation of this compound to a new orange crystalline solid was observed. The crystal structure determination revealed that the TTF fragment of 1 had undergone an oxidative cleavage of the central C=C bond, resulting in the complete transformation of 1 to 3.

To investigate the cause of this unexpected transformation, $^{13}$C NMR spectroscopy was utilized to monitor CD$_3$CN solutions of 1, as well as control CH$_2$Cl$_2$ solutions of L$_1$, kept under ambient light and in the dark (Figure 4.11). The experiment monitored solutions kept in both air-saturated and air-free environments. An analysis of the $^{13}$C NMR spectra showed that 1 remained intact in solutions kept in air-free or dark environments for 3 weeks, but converted to 3 in solutions exposed to air and light. Furthermore, upon conversion, the portion of L$_1$ cleaved from the Ru(II) complex precipitated as a light-orange solid. This solid was filtered prior to obtaining the final NMR, which explains the absence of peaks for the corresponding carbons (labeled r, s, and t in Figure 4.11). There is also a substantial change in the chemical shift of carbon q upon
conversion, from 115 ppm to 188 ppm, as expected for the formation of the carbonyl carbon upon transformation. The free ligand \( \text{L}_1 \) did not show decomposition in any of the solutions tested (i.e. its \(^{13}\text{C} \) NMR spectra remained unchanged after 3 weeks). These results indicate the need for the presence of the photoactive \( \text{Ru}^{\text{II}} \) ion for the transformation of \( \text{L}_1 \) to \( \text{L}_3 \).

![Figure 4.11: \(^{13}\text{C} \) NMR spectra of 1 in CDCl\(_3\) before (a) and after (b) being exposed to light for a period of 20 days.](image)

Taking into account the difference in the photophysical properties of 1 and 3 (Table 4.7), we recorded absorption and emission spectra of a CH\(_3\)CN solution of 1 before and after 4-hour irradiation with a 458 nm pulsed laser (Figure 4.12). The attenuation of both the low-energy tail of the MLCT band above 500 nm and the mixed ILCT/LLCT band (TTF → phen/bpy, Table 4.4) that appears as a shoulder at 340 nm, along with the hypsochromic shift of the emission maximum from 642 nm to 630 nm, is in accord with the conversion of 1 to 3. A control
experiment was also performed on a CH$_3$CN solution of 1 that was kept in a dark and O$_2$-free environment. The absorption and emission spectra of this solution remained essentially unchanged after the 4-hour period without irradiation (Figure S4.4), thus yet again confirming the necessity of irradiation for the oxidative cleavage of the C=C bond in the TTF unit of 1.

Given the difference in the luminescence lifetimes of 1 and 3 (1.77(4) µs and 2.08(4) µs, respectively), we monitored the change in this parameter for a deaerated CH$_3$CN solution of 1 under continuous irradiation with the 458 nm pulsed laser for 4 hours (Figure 4.13). During this period, the sample was kept in a capped cuvette. The initial measurement was performed immediately after degassing the solution and prior to turning on the laser. It resulted in $\tau_{\text{obs}} = 1.74(5)$ µs, as expected for the deaerated solution of 1 (Table 4.7). The continuous irradiation led to a gradual decrease in the luminescence lifetime until it reached a constant value of 0.353(3) µs after 4 h of irradiation.

**Figure 4.12:** Absorption (solid lines) and emission (dashed lines) spectra of 1 in a CH$_3$CN solution before (blue) and after (red) pulsed-laser irradiation at 458 nm for a period of 4 h. Inset shows the normalized $^3$MLCT absorption and emission spectra.
The substantial decrease in the luminescence lifetime points toward the incidental seepage of atmospheric oxygen into the cuvette, which results in substantial luminescence quenching. Thus, the luminescence decay of a freshly prepared and degassed CH$_3$CN solution of I was measured immediately after the solution was exposed to air under visible light, resulting in $\tau_{\text{obs}} = 0.279(4)$ µs. This value, however, is significantly shorter than 0.353(3) µs obtained for the solution kept in a capped cuvette under irradiation for 4 h. Since the presence of oxygen and irradiation can also result in the photodegradation of I to 3, the same measurement was performed on a degassed CH$_3$CN solution of 3 immediately after it was exposed to air. The measured $\tau_{\text{obs}} = 0.358(8)$ µs is substantially shorter than 2.08(4) µs obtained for a deaerated solution of 3 (Table 4.7). Nevertheless, it is in excellent agreement with the value observed after continuously irradiating the CH$_3$CN solution of 1 in a capped cuvette for 4 h. These results confirm our initial assumption about the slow photodegradation of 1 to 3 due to the seepage of air into the cuvette. They also indicate that the photodegradation process occurs quite fast once the solution is exposed to air under visible light.

4.4 Conclusion and Outlook

A detailed study of Ru(II) complexes with redox-active TTF-annulated phenanthroline (edt-TTF-phen, L$_1$) and its analogues that contain only a half of the TTF unit (TTC-phen, L$_2$, and
DTC-phen, L3) reveals that [Ru(bpy)2(L1)](PF6)2 (1) exhibits behavior distinctly different from that observed for [Ru(bpy)2(L2)](PF6)2 (2) and [Ru(bpy)2(L3)](PF6)2 (3). This difference stems from the presence of an additional redox-active MO in 1 which is centered on the TTF unit, serving as the HOMO, and which is located at ~0.6 eV above the Ru-based d-orbitals. Such a high-energy ligand-centered HOMO is absent in 2 and 3. Consequently, 1 exhibits three reversible oxidations, of which the two occurring at lower potentials are TTF-based. A low-energy tail of the MLCT absorption band, observed only for 1, is assigned to the ILCT within the L1 ligand, according to TD-DFT calculations. Upon irradiation into the characteristic low-energy MLCT band, complexes 1-3 exhibit emission with the luminescence lifetimes of ~1-2 μs. The monoexponential rate of luminescence decay indicates that the MLCT state is the only one contributing to the observed emission. In contrast to 2 and 3, complex 1 also experiences intramolecular reductive excited-state electron transfer from the TTF moiety to the Ru center. This process is evident from the substantial decrease in the luminescence quantum yield of 1 (Φf = 0.012) when compared to those of 2 and 3 and the reference compounds [Ru(bpy)3](PF6)2 and [Ru(bpy)2(phen)](PF6)2 (Φf = 0.060-0.095). This finding is in agreement with the well-established electron-donating properties of TTF. Contrary to expectations from the previous reports on related Ru(II) complexes with TTF-containing ligands, the presence of the low-energy ILCT state (TTF → phen) is not accompanied by a long-lived charge-separated state (>10 ns) that is detectable as a transient species when probing the excited-state absorbance profile. Solutions of 1 exposed to air and visible light exhibit photodegradation that leads to the cleavage of the central C=C bond of the TTF unit and quantitative generation of 3.

The interesting photophysical behavior of complex 1 and the related previously reported complex, Ru(bpy)2(TTF-dppz)](PF6)2, 83 call for further studies of heteroleptic Ru(II) complexes with redox-active ligands. In particular, we are currently investigating the nature of excited states in these and related complexes by ultrafast spectroscopy and more thorough theoretical calculations. The results of these studies will be reported in due course.
4.5 Supporting Information

**Figure S4.1:** $^1$H and 2-D COSY NMR spectra of the complicated aromatic region of 2 in CD$_3$CN at room temperature.
Figure S4.2: $^1$H and 2-D COSY NMR spectra of the complicated aromatic region of 3 in CD$_3$CN at room temperature.
**Figure S4.3:** Kinetic profile of the difference absorbance spectrum of 1 in CH$_3$CN at room temperature. $\lambda_{\text{pump}}$=488 nm; $\lambda_{\text{probe}}$=370 nm. Experimental data: red; single exponential fit: blue.

**Figure S4.4:** Absorption (a) and emission (b) spectra of 1 recorded on a solution prepared with freshly degassed CH$_3$CN (red) and on the same solution after keeping it in the dark for 4 hours (blue). Note that there is almost no difference between the absorption and emission bands of the two samples.
CHAPTER FIVE
SPIN-CROSSOVER IN Fe(II) COMPLEXES OF TTF-ANNULATED PHENANTHROLINE AND OTHER FUNCTIONALIZED 1,10-PHENANTHROLINES

5.1 Introduction

Spin-crossover (SCO) complexes of first row transition metals have been the subject of extensive research for the last 50 years. The level of understanding of SCO has grown over this period, as an array of analytical and spectroscopic techniques has been used to monitor the chemical and physical changes that these complexes undergo during the spin transition. The switching between the high-spin (HS) and low-spin (LS) electronic configurations of the partially occupied 3d shell has been realized via external perturbations such as temperature, pressure, magnetic field, or photoexcitation. To date, Fe(II) complexes constitute the majority of the known SCO compounds. In the octahedrally coordinated, 3d⁶ Fe²⁺ ion the HS ↔ LS interconversion involves intersystem crossing between the HS state described as T₂g (t²g⁴ e⁸g⁰) and the LS state described as A¹g (t²g⁶ e⁸g⁰). The change in the spin state at the Fe²⁺ center is accompanied by pronounced changes in the structural, magnetic, and spectroscopic properties of the corresponding complex.

One of the most notable current trends in the field of SCO is the engineering of molecule-based functional materials in which the SCO properties are combined in a synergic fashion with other functions. Coupling the SCO to such properties as photoreactivity, host-guest interactions, liquid crystallinity, magnetic exchange, optical non-linearity, ligand isomerization, or in light of this dissertation, conductivity, promises to provide materials of great technological significance. As was already mentioned in the earlier chapters, TTF and its derivatives are commonly incorporated into transition metal complexes to produce multifunctional materials that combine the conductivity of the TTF substructure with magnetic, optical, or electrochemical properties of the transition metal ions. To date, however, there has been very little work on combining SCO and conductivity in a single material.

In 2005, Faulmann et. al. reported on the complexes [Fe³⁺(salten)Mepepy][M(dmit)₂] (M = Pd, Pt; H₂salten = 4-azaheptamethylene-1,7-bis(salicylideneiminate; Mepepy = 1-(pyridine-4-yl)-2-(N-methylpyrrol-2-yl)ethane, dmit²⁻ = 1,3-dithiole-2-thione-4,5-dithiolato) that demonstrate
SCO while containing conducting layers of [M(dmit)$_2$]$^{2-}$ anions.\textsuperscript{185} The synergy of the two properties, however, was negligible. Then, in 2009, the Real group reported a metal organic framework (MOF), [Fe(TTF-adpy)$_2$M(CN)$_4$] (M = Pd, Pt; TTF-adpy = 4-tetrathiofulvalenylcarboxamidopyridine).\textsuperscript{186} This material did exhibit a spin transition but did not show any appreciable conductivity.

It was not until 2011 that Oshio et al. reported the first example of an Fe$^{II}$ complex that exhibited both electrical conductivity and SCO.\textsuperscript{124} The complexes [Fe(dppTTF)$_2$](BPh$_4$)$_2$ and [Fe(dppTTF)$_2$][Ni(mnt)$_2$](BF$_4$)$_2$ (dppTTF = 1-(2-(1,3-dithiol-2-ylinene)-1,3-dithioyl)-2-(2,6-bis(1-pyrazolyl)pyridyl)-ethylene; mnt = maleonitriledithiolate) incorporate TTF-containing ligands in their neutral and oxidized forms, and the resulting analyses suggested some synergy between the spin transition and electrical conductivity. In 2013, the Hauser and Decurtins groups reported the coexistence of SCO and a charge separated state upon optical excitation of [Fe(phen)$_2$(TTF-dppz)](PF$_6$)$_2$.\textsuperscript{127}

It is with similar ambition that we embarked on the exploration of SCO in Fe(II) complexes prepared with the TTF-annulated phenanthroline ligands described in Chapter 3. In the present Chapter, we describe the synthesis and characterization of a family of Fe$^{II}$ complexes, Fe(R-phen)$_2$(NCS)$_2$, where R-phen represents a functionalized ligand derived from 1,10-phenanthroline. These complexes include [Fe(TTF-phen)$_2$(NCS)$_2$] and its more soluble alkylated analogue, [Fe(bht-TTF-phen)$_2$(NCS)$_2$] (Figure 5.1). All these complexes show a thermally induced switching of the Fe$^{2+}$ spin state and are of potential interest in the advancement of the field of multifunctional materials.

5.2 Starting Materials and Syntheses

All reactions were performed in an inert N$_2$ atmosphere using standard Schlenk techniques, unless noted otherwise. Commercially available (Bu$_4$N)NCS (98%, Aldrich) and Fe(BF$_4$)$_2$·6H$_2$O (97%, Aldrich) were used as received. Additional purification of anhydrous commercial solvents used in anaerobic reactions was achieved by passing them through a double-stage drying/purification system (Glass Contour Inc.). Otherwise, ACS grade solvents were used.

[Fe(edt-TTF-phen)$_2$(NCS)$_2$] (4). A colorless solution of (Bu$_4$N)NCS (40 mg, 0.134 mmol) in 10 mL of acetonitrile was transferred via cannula into a 50-mL Schlenk tube containing 23 mg (0.067 mmol) of Fe(BF$_4$)$_2$·6H$_2$O. A clear purple solution formed almost instantaneously. The
solution was transferred via cannula to a solution of TTF-phen in 10 mL of dichloromethane, resulting in quick precipitation of a dark-purple solid. The reaction mixture was stirred at room temperature for 2 h. The product was isolated by filtration and washed with 3 × 10 mL portions of both reaction solvents (CH$_3$CN and CH$_2$Cl$_2$) to remove any unreacted starting materials. Yield = 85% (61 mg). *Elem. analysis:* calcd. (found) for FeC$_{40.1}$H$_{23.7}$N$_{6.5}$S$_{14}$Cl$_{2.2}$ (4·0.5CH$_3$CN·1.1CH$_2$Cl$_2$), %: C, 40.84 (40.96); H, 2.03 (1.85); N, 7.72 (7.56); S, 38.06 (37.77). *IR:* $\nu$, cm$^{-1}$: 2058, 2006, 1589, 1575, 1477, 1415, 931, 801, 770, 724. X-ray quality crystals of 4 were obtained by layering the solution obtained by mixing (Bu$_4$N)NCS and Fe(BF$_4$)$_2$·6H$_2$O in CH$_3$CN on the top of the solution of TTF-phen in CH$_2$Cl$_2$ in a 4 mm I.D. glass tube. Dark-purple needle-like crystals were obtained after 1 month.

Compounds 5-8 were prepared in a manner analogous to that described for 4.

**[Fe(NCS)$_2$(L$_4$)$_2$]** (5). Yield = 56%. *Elem. analysis:* calcd. (found) for FeC$_{59.8}$H$_{66.7}$N$_{6.5}$S$_{14}$Cl$_{1.2}$ (5·0.5CH$_3$CN·0.6CH$_2$Cl$_2$), %: C, 50.36 (49.99); H, 4.73 (4.50); N, 6.41 (6.70); S, 31.58 (31.87). *IR:* $\nu$, cm$^{-1}$: 2955, 2923, 2853, 2058, 1590, 1576, 1418, 932, 798, 770, 723, 635.

**[Fe(NCS)$_2$(Br$_2$phen)$_2$]** (6). Yield = 89%. *IR:* $\nu$, cm$^{-1}$: 2066, 2044, 1705, 1657, 1576, 1480, 1423, 925, 796, 726.
[Fe(NCS)$_2$(L)$_2$] (7). Yield = 64%. IR: $\nu$, cm$^{-1}$: 2068, 2049, 1523, 1424, 1386, 1267, 1244, 885, 813, 724, 619.

[Fe(NCS)$_2$(L)$_3$] (8). Yield = 76%. IR: $\nu$, cm$^{-1}$: 2069, 2041, 1570, 1496, 1479, 1417, 1067, 935, 805, 734, 726, 637.

5.3 Results and Discussion

5.3.1 Synthetic Procedures

All the reactions between the Fe(II) starting material and phen-containing ligands were carried out under inert atmosphere to avoid oxidation of the Fe(II) ions. The metal salt was initially reacted with the thiocyanate salt to avoid the possible formation of the tris-phenanthroline complex which is expected to be more thermodynamically stable than the desired Fe(R-phen)$_2$(NCS)$_2$ complexes. The dark purple solution obtained was stirred for $\sim$15 min to ensure complete homogeneity of the precursor solution. The solution was then transferred via cannula to a vessel containing a stoichiometric amount of the respective ligand. A dark precipitate formed almost immediately upon mixing of the two solutions. Although we suspected that the reaction goes to completion in a few minutes, it was allowed to stir at room temperature under nitrogen atmosphere for $\sim$2 hours before the product was isolated by filtration.

Complexes 4-8 are insoluble in most common organic solvents, with the exception of DMF and DMSO. The dissolution in these solvents, however, was shown to stem from a ligand displacement reaction, in which DMF or DMSO molecules substitute for the NCS$^-$ ligands, as was confirmed by $^1$H NMR spectroscopy on the resulting DMSO solution. A singlet at 3.50 ppm was observed and assigned to the CH$_3$ groups of the coordinated DMSO molecules. As expected, the signal is shifted downfield from the normal solvent peak of free DMSO (2.50 ppm) due to the coordination to the Fe(II) ion which withdraws electron density from DMSO and, as a result, deshields the methyl protons.

5.3.2 Crystal Structure

Single crystals of 4 were grown by slow diffusion of reactant solutions in sealed 4 mm i.d. glass tubes. An acetonitrile solution containing (Bu$_4$N)NCS and Fe(BF$_4$)$_2$·6H$_2$O was carefully layered atop a dichloromethane solution of a stoichiometric amount of L$_1$. After about a month, purple crystals were observed along the walls of the tube. A summary of pertinent information relating to unit cell parameters, data collection, and crystal structure refinement is provided in Table 1.
Table 5.1: Data collection and structure refinement parameters for $4\cdot2\text{CH}_2\text{Cl}_2$.a

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\text{C}<em>{40}\text{H}</em>{24}\text{Cl}_4\text{FeN}<em>6\text{S}</em>{14}$ (1a $2\text{CH}_2\text{Cl}_2$)</th>
</tr>
</thead>
<tbody>
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<td>Crystal description</td>
<td>purple plates</td>
</tr>
<tr>
<td>Space group</td>
<td>Aba2</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>13.165(6)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>36.65(2)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>10.232(5)</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma$, deg</td>
<td>90</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>4937(4)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{calc}$, g cm$^{-3}$</td>
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</tr>
<tr>
<td>Temperature, K</td>
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</tr>
<tr>
<td>$\lambda$, Å</td>
<td>MoKα, 0.71073</td>
</tr>
<tr>
<td>$\mu$, mm$^{-1}$</td>
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</tr>
<tr>
<td>$2\theta_{max}$, deg</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$R_{int}$</td>
<td>0.1196</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>4358</td>
</tr>
<tr>
<td>Parameters/Restraints</td>
<td>294/1</td>
</tr>
<tr>
<td>$R_1$, w$R_2$, $[F_o &gt; 4\sigma F_o]$</td>
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</tr>
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<td>Goodness-of-fit</td>
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</tr>
<tr>
<td>Diff. peak and hole, e/Å$^3$</td>
<td>0.598 and -0.413</td>
</tr>
</tbody>
</table>

$^a$ Attempts to crystallize complexes 5-8 are still ongoing. Crystallization of [Fe(R-phen)$_2$(NCS)$_2$] complexes, in general, represents a significant challenge due to their insolubility.

Complex 4 crystalizes in the orthorhombic space group Aba2. The dark purple crystals exhibit plate-shaped morphology. The crystal structure determination revealed that the structure also includes interstitial solvent molecules situated in large voids that propagate along the c axis (Figure 5.2b). The crystal structure of the compound thus corresponds to the formula $4\cdot2\text{CH}_2\text{Cl}_2$. The TTF subunits of the $\text{L}_1$ ligands from neighboring complexes align in a staggered manner suggesting the presence of weak S-S contacts. The packing also reveals weak non-covalent interactions between the N-containing ring of the phenanthroline subunit of the ligand, and one of the electronegative Cl atoms of $\text{CH}_2\text{Cl}_2$ (Figure 5.2a). Such interaction can be rationalized by attractive forces between the electronegative Cl atom and the electropositive $\pi$-system in the phen moiety of $\text{L}_1$ that is coordinated to the Fe(II) ion. Such anion-$\pi$ interactions have been shown to be important intermolecular forces in the crystal packing of molecular solids.187
5.3.3 Room Temperature Infrared Spectroscopy

The infrared spectrum of 4 is shown in Figure 5.3 and plotted against the [Fe(NCS)$_2$(phen)$_2$] benchmark for comparison. IR spectroscopy was shown to be a useful tool for following the SCO in [Fe(NCS)$_2$(phen)$_2$], which undergoes a spin transition with $T_{1/2} = 178$ K. In the HS state, the CN stretch of the SCN$^-$ ligand appears at 2087 cm$^{-1}$. Upon transition to the LS state, this stretch is shifted to higher energy, 2135 cm$^{-1}$\cite{122}. The room-temperature IR spectrum of complex 4 reveals a broad peak with the maximum at 2057 cm$^{-1}$ corresponding to the CN stretch of the HS state. The low-energy shoulder of this peak cannot be taken as the signature of the LS state, because the latter should manifest itself by a higher-energy CN stretch, according to the behavior of [Fe(NCS)$_2$(phen)$_2$]. Therefore, we attribute this broadening to low crystallinity of the sample that might result in inhomogeneous molecular packing and thus a range of CN stretches for the HS state. Thus, IR spectroscopy suggests that complex 4 exists predominantly in the HS state at room temperature.

5.3.4 Magnetic Properties

The magnetic properties were studied on polycrystalline samples of 4-8. All complexes exhibit similar magnetic behavior manifested in a gradual temperature-driven spin transition. In measuring the magnetic data of 4 (Figure 5.4a), the compound was initially cooled rapidly from room temperature down to 30 K by lowering the sample into the SQUID chamber maintained at that temperature. The sample chamber heated up slightly, to $\sim$48 K, and then returned to 30 K. Subsequently, the sample was cooled down to 1.8 K, and the thermal variation of the magnetic susceptibility was measured in heating mode (red curve in Figure 5.4a). After reaching 300 K,
the measurement was repeated from 300 to 1.8 K, now in cooling mode, at 1 K/min (blue curve in Figure 5.4a).

The temperature dependence of $\chi_T$ observed allows us to draw the following conclusions about the magnetic behavior of 4. The room-temperature $\chi_T$ value is $\sim$3.3 emu K mol$^{-1}$, characteristic of the HS Fe(II) ion. Upon slow cooling, the complex exhibits a gradual and incomplete transition to the LS state (blue curve). By comparing the $\chi_T$ values at 300 K and 50 K, we establish that $\sim$40% of the HS molecules have been converted to the LS state after cooling to low temperatures. The HS state, however, can be “frozen” by rapid cooling of the material below the temperature of the spin transition. Upon heating the sample to $\sim$80 K, the metastable HS state relaxes back to the LS state which transforms to the stable HS state at higher temperatures (red curve). Therefore, the observed loop in Figure 5.4a is not a result of thermal hysteresis, but an indication of the metastable HS state. The presence of the metastable HS state at low temperatures indicates that this complex might exhibit a photoinduced LS $\rightarrow$ HS transition (so called LIESST, or light-induced excited spin state trapping).
Given the limited solubility of 4, we prepared its analogue with the more soluble alkylated version of L1, namely bht-TTF-phen (L4, Figure 5.1). This allowed further characterization of the complex as discussed in more detail in the following sections. The magnetic behavior of 5 is similar to that of 4, in that there is a gradual spin transition starting with the complex in the HS state at room temperature. The gradual SCO to the LS state is observed upon cooling below ~200K (Figure 5.4b). Similar to 4, the SCO in 5 is incomplete and constitutes ~50% according to the $\chi T$ value observed below 50 K.

![Figure 5.4](image)

**Figure 5.4.** (a) The temperature dependences of $\chi T$ for [Fe(NCS)$_2$(L$_1$)$_2$]·2CH$_2$Cl$_2$. The red and blue lines represent heating (after the sample was quenched directly to 30 K, then cooled down to 1.8 K) and cooling processes respectively. (b) The temperature dependences of $\chi T$ for [Fe(NCS)$_2$(L$_4$)$_2$].

### 5.3.5 Mössbauer Spectroscopy

The Mössbauer spectra of 4 and 5 were collected in collaboration with Dr. Catalina Achim of Carnegie Mellon University. The spectra were collected at 4 K and clearly shows the existence of two different spin states for Fe(II). In the spectrum of both 4 and 5, there are two doublets present, one that exhibits large quadrupole splitting, and one with small quadrupole splitting, indicative of HS Fe(II) and LS Fe(II), respectively (Figure 5.5). The observed spectra clearly indicate that there are only two species of Fe present, as it consists of only two doublets for each complex as seen. More importantly it shows that the oxidized Fe(III) species is not present given the absence of its characteristic feature. Thus, we can discard a suspicion that certain Fe-containing impurities can be present in this largely amorphous material.
The Mössbauer spectra can also provide a degree of quantitative information in the determination of the percent conversion realized upon the lowering of the temperature through the spin transition (i.e. what fraction of the material has undergone the HS → LS transition upon arriving at 4 K).

Upon quantifying the results from the experiment, it is possible to determine the exact fraction of each spin state present. At 4 K, the sample of 4 contains 62% of HS Fe(II) and 38% of LS Fe(II), thus indicating a partial SCO. At the same temperature in complex 5, the amount of the HS Fe(II) and LS Fe(II) are 40% and 60%, respectively. These data are in agreement with our findings from the magnetic measurements in that there exists slightly more HS complex at 4K in 4 than in 5, upon gradual cooling below the spin transition region (Figure 5.4). The room-temperature Mössbauer spectra of these complexes are still to be recorded. They should be helpful in confirming the SCO behavior as established by magnetic measurements.

5.3.6 Variable Temperature Infrared Spectroscopy

Shown in Figure 5.6. are infrared spectra recorded for compound 4 (blue lines) and for the [Fe(NCS)₃(phen)₂] benchmark (red lines) at 100 K and 300 K. As mentioned above, the spin
transition can be conveniently monitored via vibrational spectroscopy, specifically by the location and strength of the NC stretch from the isothiocyanate ligands. At 300 K, the standard \([\text{Fe(NCS)}_2(\text{phen})_2]\) exhibits a fairly sharp and strong doublet at 2087 \(\text{cm}^{-1}\). In a similar fashion, the 300-K spectrum of 4 consists of a broader singlet that appears at 2057 \(\text{cm}^{-1}\). Both high temperature spectra are in agreement with the findings from the magnetic studies that indicate that both complexes are in the HS state at 300 K. Considering the spectrum of the standard the \([\text{Fe(NCS)}_2(\text{phen})_2]\) at 100 K, the spin transition is evidenced in the appearance of a sharp and strong LS Fe(II) doublet at slightly higher energy (2135 \(\text{cm}^{-1}\)) with a small remnant signal from the original HS Fe(II) doublet. The IR spectrum of 4, however, does not experience such a drastic change as the temperature is lowered to 100 K. The broad and strong CN stretch corresponding to HS Fe(II) remains, but also observed is a small peak at slightly higher energy showing the partial conversion of the complex to the LS state. The position of this stretch coincides with the CN stretch observed for the LS state of \([\text{Fe(NCS)}_2(\text{phen})_2]\), thus confirming the validity of our assignment. It is expected that the LS feature would be enhanced if the sample were cooled at a slower rate (~4 K/min was used in this experiment), thus preventing the more pronounced freezing of the HS state at low temperature.

![Figure 5.6](image)

**Figure 5.6**: The CN stretching region of the IR spectra of 4 (blue) and \([\text{Fe(phen)}_2(\text{NCS})_2]\) (red) recorded at 100 K (a) and 300 K (b).
Another factor that might be at play here is the large difference in mass between the molecules of \([\text{Fe(phen)}_{2}(\text{NCS})_{2}]\) and 4. The addition of the edt-TTF moieties onto the phen units in 4 effectively doubles the molar mass of the complex from 532 g/mol to 1065 g/mol. Since the spin transition relies heavily on elastic effects propagating throughout the lattice, it occurs more readily in materials that are lighter and exhibit more efficient packing in the crystal structure. If this were the case in 4 and 5, a sharper spin transition would be realized. It is also expected that the \(\pi\)-donating ability of TTF ultimately weakens the ligand field strength of phen and thus destabilizes the LS state, shifting the SCO to lower temperatures.

5.3.7 Spin Crossover in Fe(II) Complexes Related to 4 and 5

We also synthesized complexes 6-8 that can be considered as parent structures with respect to complexes 4 and 5 (Figure 5.1). Preliminary magnetic data collected for these \([\text{Fe(R-phen)}_{2}(\text{NCS})_{2}]\)-type complexes suggest that each of them exhibits a complete temperature-induced spin transition from the HS to LS state. Depicted in Figure 5.7 are the temperature dependence plots of \(\chi T\) for 6-8. In comparison to 4 and 5 (Figure 5.4), it is obvious that the SCO in 6-8 is less gradual and shifted to higher temperatures, due to the lack of the \(\pi\)-donating TTF moiety and smaller mass of the molecules. Mössbauer and IR spectroscopic studies are also necessary to explore the SCO behavior of 6-8 in greater detail.

![Figure 5.7: Temperature dependence of \(\chi T\) for complexes \([\text{Fe(NCS)}_{2}(\text{L}_{2})_{2}]\) (6; dark blue line), \([\text{Fe(NCS)}_{2}(\text{L}_{3})_{2}]\) (7; red line), and \([\text{Fe(NCS)}_{2}(\text{Br}_{2}\text{phen})_{2}]\) (8; light blue line).]
These complexes also exhibit similar differences in their IR spectra. The NC stretching band (\(\sim 2100 \text{ cm}^{-1}\)) seems to be sharper in their appearance in comparison to that of complex 4. This makes them appear more like the spectrum of \([\text{Fe(NCS)}_2(\text{phen})_2]\) as seen in Figure 5.3. In a similar fashion, all three complexes 6-8 do not exhibit such a pronounced shoulder on the low energy side of the band at 2100 cm\(^{-1}\) as exists in the spectrum of 4. This also reinforces the completeness of their transition in that there exists little or no portion of the complex in the LS state at high temperature. It is of future interest to probe the vibrational spectra of this family of complexes at low temperature to gain a better understanding of the spin transition that occurs.

5.4 Conclusion and Outlook

The use of molecules or molecular assemblies for the processing of information is one of the most captivating destinations in modern molecular chemistry. Regardless of the ultimate industrial application, the intrinsic underlying concept is that of bistability, which may be defined as the ability of a molecular system to be observed in two different electronic states in a certain range of external perturbations.\(^{188}\) The most spectacular example of molecular bistability is the SCO phenomenon. However, it remains a challenge of universal interest, to realize materials that exhibit this phenomenon under ambient conditions (i.e. room temperature and
The ability to display SCO at elevated temperatures (i.e. at or above room temperature) has only been displayed by a few complexes and is one of the main interests in this area of chemistry. The ability to achieve room temperature spin transition would allow the utilization of these materials in molecular electronic devices intended for the purpose of information recording and processing.

The systems discussed herein all display gradual transitions occurring at or around ~200 K. The electron donating ability of the TTF moiety in the title complexes 4 and 5 offers the suggestion that it should be possible to oxidize TTF in these complexes. Oxidation should render TTF a weaker π-donor and as a result shift the observed transition to higher temperatures. The preparation of the singly and doubly oxidized versions of these complexes will be pursued in the immediate progression of this research project.

In an effort to shed light on the possibility of preparing the +1 and +2 versions of these complexes, the electrochemical properties of ligand L4 and its corresponding Fe(II) complex, [Fe(NCS)2(L4)2] (5), were investigated in a CH2Cl2 solution, and the results of these studies are collected in Table 5.2. Ligand L4 exhibits two reversible one-electron redox processes that are associated with the successive oxidations of the TTF subunit to the radical cation TTF+ and the dication TTF2+ (Figure 5.9). The half-wave potentials of L4 (0.15 and 0.51 V vs. Fc+/Fc) are positively shifted relative to those observed for unsubstituted TTF (–0.10 and 0.27 V), as expected from the π-accepting nature of the phenanthroline moiety. These potentials furthermore, are in correlation with those previously reported for L1, the less soluble and un-alkylated sister compound of L4 (Table 5.2).

**Figure 5.9:** Cyclic voltammograms of L4 (red line) and [Fe(NCS)2(L4)2] (blue line) recorded in a 0.100 M solution of (Bu4N)PF6 in CH2Cl2. Potentials are given vs. Fc+/Fc.
The corresponding Fe(II) complex 5 exhibits two reversible two-electron oxidations as well (Figure 5.9), also associated with the successive oxidations of the TTF subunits, although at slightly higher potentials (Table 5.2). The positive shift in the potentials of the TTF oxidations in 5 relative to the free ligand L₄ is because of the electrostatic inductive effect of the Fe(II) ion bound to L₄. Similar behavior was seen in the analogous Ru(II) complex [Ru(bpy)₂(L₁)]²⁺ and the Fe(II) complex [Fe(phen)₂(TTF-dppz)]²⁺ reported earlier (Table 5.2).

Table 5.2: Redox potentials (V vs Fe⁺/Fe) of ligand L₄ and complex 5, and of reference compounds, TTF,¹⁴⁶ L₁,¹⁸⁵ [Fe(phen)₂(TTF-dppz)]²⁺,¹²⁷ and [Ru(bpy)₂(L₄)]²⁺. Both samples and the reference compounds were collected in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₁/₂(1)</td>
<td>E₁/₂(2)</td>
</tr>
<tr>
<td>L₄</td>
<td>0.15</td>
<td>0.51</td>
</tr>
<tr>
<td>[Fe(NCS)₂(L₄)]₂⁻</td>
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<td>0.59</td>
</tr>
<tr>
<td>TTF</td>
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<td>0.27</td>
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<tr>
<td>L₁</td>
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<td>0.52</td>
</tr>
<tr>
<td>[Ru(bpy)₂(L₁)]²⁺</td>
<td>0.26</td>
<td>0.58</td>
</tr>
<tr>
<td>[Fe(phen)₂(TTF-dppz)]²⁺</td>
<td>-0.07</td>
<td>0.29</td>
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</table>
CHAPTER SIX
CLOSING STATEMENTS

Multifunctionality remains one of the central themes of modern-day materials science. Such research involves the rational assembly of specifically chosen building blocks into molecular assemblies that exhibit a combination of the individual component’s properties, or an enhancement thereof. It is the tunability of the molecular components through various synthetic schemes that makes this area of science such an interesting avenue to pursue from a chemical standpoint. A diverse toolbox of synthetic chemistry allows incorporation of an almost endless list of functionalities into these systems. More specifically, materials involving heterocyclic sulfurous compounds, such as TTF, can impart redox activity as one of the properties desired in the final multifunctional assembly. Furthermore, the use of coordination chemistry allows the formation of metal complexes that combine a specific metal center with a judiciously designed ligand, both of which provide the desired combination of properties.

In this thesis, some photophysical and photochemical properties of molecules incorporating TTF units have been studied. The incorporation of the redox-active TTF into molecular assemblies relies on the functionalization of TTF with a metal binding moiety. Described herein, via two different synthetic routes, is the attachment of the redox-active TTF directly to the backbone of the common metal-binding chelator, 1,10-phenanthroline. This synthesis led to the stable redox-active ligand edt-TTF-phen (L1). Ligand L1 can be used for the direct attachment of the TTF moiety to virtually any metal center. We have shown that this ligand itself crystallizes in the chiral orthorhombic space group P212121 and exhibits two reversible one-electron redox processes that are readily assigned to successive oxidations of the TTF moiety to the radical cation TTF\(^{+}\) and the dication TTF\(^{2+}\). A separate synthetic route was discovered affording another version of the ligand, bht-TTF-phen (L4), that exhibits increased solubility due to the replacement of the original ethylenedithio bridge in L1 with two long hexylthio alkyl chains in L4. This increased solubility allows for further characterization of the ligand and resulting complexes that is not possible in certain analogues prepared with L1.

The combination of TTF-containing materials with photoactive metal centers such as Ru(II) has been of particular interest during the development of a variety of multifunctional systems including charge separation systems, photoredox switches, and light harvesting antennae for
photovoltaic devices. In this thesis, we carried out a detailed study of Ru(II) complexes with the redox-active ligand L₁ and its analogues that contain only a half of the TTF unit (TTC-phen, L₂, and DTC-phen, L₃). Such study revealed that [Ru(bpy)₂(L₁)](PF₆)₂ (1) exhibits behavior distinctly different from that observed for [Ru(bpy)₂(L₂)](PF₆)₂ (2) and [Ru(bpy)₂(L₃)](PF₆)₂ (3), illustrating the drastic effect that the presence of the redox-active TTF has on the properties of the resulting material. This difference stems from the presence of an additional redox-active MO in 1 which is centered on the TTF unit, which is located at ~0.6 eV above the Ru-based d-orbitals and serves as the HOMO. Such a high-energy ligand-centered HOMO is absent in 2 and 3.

Consequently, 1 exhibits three reversible oxidations, of which the two occurring at lower potentials are TTF-based. A low-energy tail of the MLCT absorption band, observed only for 1, is assigned to the ILCT within the L₁ ligand, according to TD-DFT calculations. Upon irradiation into the characteristic low-energy MLCT band, complexes 1-3 exhibit emission with the luminescence lifetimes of ~1-2 µs. The monoexponential rate of luminescence decay indicates that the MLCT state is the only one contributing to the observed emission. In contrast to 2 and 3, complex 1 also experiences intramolecular reductive excited-state electron transfer from the TTF moiety to the Ru center. This process is evident from the substantial decrease in the luminescence quantum yield of 1 (Φᵣ = 0.012) when compared to those of 2 and 3 and the reference compounds [Ru(bpy)₃](PF₆)₂ and [Ru(bpy)₂(phen)](PF₆)₂ (Φᵣ = 0.060-0.095). This finding is in agreement with the well-established electron-donating properties of TTF. Contrary to expectations from the previous reports on related Ru(II) complexes with TTF-containing ligands, the presence of the low-energy ILCT state (TTF → phen) is not accompanied by a long-lived charge-separated state (>10 ns) that is detectable as a transient species when probing the excited-state absorbance profile. Interestingly, solutions of 1 exposed to air and visible light exhibit photodegradation that leads to the oxidative cleavage of the central C=C bond of the TTF unit and quantitative generation of 3.

The interesting photophysical behavior of complex 1 calls for further studies of heteroleptic Ru(II) complexes with redox-active ligands. In particular, the extension of the project described in this dissertation will focus on the investigation of excited states in 1-3 and related complexes by ultrafast spectroscopy and more thorough theoretical calculations. Also of interest is the formation of the Ru(II) complexes containing oxidized TTF, either through oxidation of the ligand prior to coordination, or oxidation of the Ru(II) complex itself. This will enable studies of
the conductivity of the resulting materials, imparted by the oxidation of the TTF substructure, an
effect shown to be possible from the results of the research presented herein. The measurements
of conductivity in these materials will constitute a collaborative effort with Dr. James Brooks at
the FSU Physics Department and National High Magnetic Field Laboratory.

The use of molecules or molecular assemblies for the processing of information is one of the
most captivating destinations in modern molecular chemistry. Regardless of the ultimate
industrial application, the intrinsic underlying concept is that of bistability, which may be
defined as the ability of a molecular system to be observed in two different electronic states in a
certain range of external perturbations. One of the most spectacular example of molecular
magnetic bistability is the spin crossover phenomenon. It remains a challenge, however, to
realize conducting materials that exhibit SCO under ambient conditions (i.e. room temperature
and pressure). The ability to display SCO at elevated temperatures (i.e. at or above room
temperature) has only been displayed by a few complexes and is one of the main interests in this
area of chemistry. The ability to achieve room temperature spin transition combined with
conductivity could lead to new paradigms in device engineering for the purpose of information
recording and processing.

Combined with the Fe(II) ion, the donor-acceptor properties of the TTF-phen ligands can be
associated with the SCO properties of the metal center. In these systems, the light induced charge
transfer states, whether sufficiently long-lived or not, can be realized in conjunction with the
light-induced population of the HS or LS states of Fe(II). The systems described in this thesis all
display gradual SCO occurring at or around 100-200 K. The electron donating ability of the TTF
moiety in complexes Fe(edt-TTF-phen)$_2$(NCS)$_2$ (4) and Fe(bht-TTF-phen)$_2$(NCS)$_2$ (5) shifts the
SCO to lower temperatures by weakening the ligand field provided by phen. Nevertheless, the π-
accepting nature of phen stabilizes the Fe$^{II}$ oxidation state, and the oxidation of the TTF units
precedes by several hundred millivolts the oxidation of the Fe$^{II}$ center. This observation suggests
that it should be possible to oxidize the TTF fragment in these complexes while preserving the
oxidation state of Fe. The oxidation should render TTF a weaker π-donor and as a result shift the
observed transition to higher temperatures. The electrochemical data presented herein provide
proof of the formation of these complexes in solution, and thus obtaining the complexes in the
solid state is of immediate interest. The preparation of the singly and doubly oxidized versions of
these complexes will be pursued in the immediate progression of this research project.
REFERENCES


25. Superconductivity has only been realized in a material at low temperatures, near absolute zero. Above the material's critical temperature (Tc), it may display conventional metallic conductivity or could possibly exist as an insulator. When brought below the material's Tc,
reisitivity rapidly drops to zero in superconductive materials. By definition, current can then flow through the material freely, in the absence of any resistance whatsoever.


29. The superconductivity was originally found for the (TMTSF)$_2$PF$_6$ salt under pressure at 1 K. A year later, the same lab reported superconductivity in the (TMTSF)$_2$ClO$_4$ salt at ambient pressure and 1.2 K.


75. Fourmigue, M.; Batail, P. Synthesis, Structure, Redox Properties, P-31 NMR of P(TTF)$_3$, PPh(TTF)$_2$, PPh$_2$(TTF), 3,4-Dimethyl-3',4'-Bis(Diphenylphosphino)-Tetrathiafulvalene and


132. Sheldrick, G. M. *SADABS*, Revision 2.03; University of Gottingen: Gottingen, Germany, 1996.


152. The study herein was performed in collaboration with Nathalie Dupont, formerly of the research group of Prof. Andreas Hauser at the University of Geneva, Geneva, Switzerland.


166. *cis*-dichloro-bis(2,2'-bipyridine)ruthenium(II) was obtained from Dr. Kenneth A. Goldsby who prepared the complex according to Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.


CURRICULUM VITAE

LAWRENCE K. KENILEY, JR.

EDUCATION
Ph.D., Chemistry, Florida State University, Tallahassee, FL (GPA: 4.0/4.0). 2007 – 2013
Thesis title: “Tetrathiafulvalene-Annulated Phenanthroline and Its Complexes with Transition Metals”
Advisor: Prof. Michael Shatruk

RESEARCH INTERESTS
Inorganic and materials chemistry; organic and inorganic synthesis; multifunctional inorganic-organic hybrid materials; intra- and intermolecular energy transfer; photochemistry and photophysics; coordination chemistry; alternate energy; dye sensitized solar cells; spin crossover; molecular magnetism; photoconductivity.

RESEARCH EXPERIENCE
Graduate Assistant  Aug 2007 – present
Department of Chemistry & Biochemistry, Florida State University, with Prof. Michael Shatruk

- Developed a synthetic route affording an asymmetric tetrathiafulvalene-annulated phenanthroline ligand requiring practice with air- and moisture-sensitive compounds, and usage of glove-box and Schlenk techniques.
- Investigated coordination compounds of transition metals including the optical, electrical, and photophysical properties of Ru$^{II}$ complexes, and the magnetic, structural, and spectroscopic properties of novel Fe$^{II}$ spin crossover complexes in search of multifunctional molecular materials.
- Augmented my comprehension of theoretical methods in chemistry including DFT and TD-DFT (job submission and data processing), through utilization of theoretical calculation software including Gaussian 98W5.4, GaussView 2.1, ChemCraft 1.6, AOMix 6.80f, SWizard 5.0, and SSH Secure Shell 3.2.9.
- Experienced in characterization methods including $^1$H and $^{13}$C NMR (1-D and 2-D), electrochemistry, UV-Vis, photoluminescence spectroscopy, FT-IR, elemental analysis, SQUID, mass spectrometry, TGA/DSC, and single crystal XRD.
Familiarized with IGOR Pro 6, Origin 9, CSD System software including Mercury 3.0.1 and Conquest 1.14, X-Seed 2.0, Bruker TopSpin 2.1, MNova 8.1.1, UV WinLab 1.00, and ChemBioDraw Ultra 13.0.

**Visiting Scientist**  
*Nov 2010 – Dec 2010*

Department of Physical Chemistry, University of Geneva, Switzerland with **Prof. Andreas Hauser**

- Initiated an international and interdisciplinary collaboration with Prof. Hauser who is one of the pioneers in the study of photoinduced spin transitions in metal complexes.
- Analyzed the existence of a charge-separated state using techniques involving transient absorption spectroscopy, quantum yield determination, and luminescence decay lifetime analysis.
- Studied the evolution of the optical spectrum through the spin transition of a Fe**II** spin crossover complex prepared in Prof. Shatruk’s lab at FSU.

**Undergraduate Studies**  
*Aug 2004 – Jul 2006*

Department of Chemistry, Eastern Illinois University, with **Prof. Rebecca Peebles** and **Prof. Howard Black**

- Participated in research, acquisition, and construction of Eastern Illinois University’s cavity ring-down spectrometer for investigating weak interactions among atmospheric chemicals at low concentrations.
- Investigated the reaction pathway followed by various substituted cycloketones upon butenolide annulations in order to determine both region- and stereospecificity associated with the conversion.

**Research Experience**

**Teaching Assistant**  
*Aug 2007 – Aug 2013*

Department of Chemistry & Biochemistry, Florida State University

- Supervised the research of six undergraduate students, two of which appear as author/co-author on manuscripts published in peer-reviewed journals.
- Accumulated 11 semesters of teaching experience in undergraduate chemistry courses including General Chemistry I & II, Introduction to Analytical Chemistry, and Inorganic Chemistry laboratories.
Publications


Presentations


AWARDS

Travel Fellowship Award, International Center for Materials Research at Santa Barbara and Easy Lab, International School and Symposium on Multifunctional Molecule-Based Materials, Argonne National Lab, Chicago, IL. 2011

Dissertation Research Grant Award, Florida State University Graduate School. 2010

ACS DIC Student Travel Award, ACS Division of Inorganic Chemistry, 238th ACS National Meeting in Washington D.C. 2009

East Asia and Pacific Summer Institute for U.S. Graduate Students, National Science Foundation, alternate selection. 2009

AFFILIATIONS

Chemistry Outreach Program, Florida State University, volunteer. 2011 – present

The Honor Society of Phi Kappa Phi, Florida State University Chapter, member. 2009 – present

The National Scholars Honor Society, member. 2008 – present

American Chemical Society, member. 2006 – present