Sulfur-bridged Chromophores: Polymers, Copolymers and Ligands for Metal Complexes

by

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Abstract

The impact of the incorporation of sulfur bridges and their oxidation on the electronic and photophysical properties of macromolecules was investigated through the synthesis of oligomers, short polymers and copolymers. In oligomers, the energies of the frontier orbitals and the band gap can be modulated with the oxidation state of the bridge along with the length of the molecule. The sulfone containing oligomers are emissive in solution and in a polymer matrix while the compounds with sulfide bridges are non-emissive. Polymers containing sulfide groups exhibit conjugated-like behavior where the length of the polymers influences the maximum absorption and emission wavelengths. The photophysical and electronic properties of the sulfone-bridged polymers do not depend on their molecular weight and behave like distinct chromophores. Incorporation of sulfur bridges in copolymers containing electron rich or electron poor comonomers influences the energies of the frontier orbitals and the photophysical behavior. Sulfide containing copolymers have smaller band gaps while the sulfone containing copolymers are more emissive. Incorporating monomers containing a N^N bidentate motif, the copolymers coordinate metal ions and the emission of the polymer decreases.

Sulfur-bridged thiazoles containing a N^N bidentate motif are used as ligands for metal complexes. Homoleptic and heteroleptic complexes incorporating sulfide or sulfone N^N ligands were obtained with ruthenium(II) and copper(I) metal centers. Their structures were elucidated using NMR spectroscopy and single crystal X-ray diffraction. The ruthenium(II) heteroleptic complexes were found to undergo photoejection when irradiated in coordinating solvent with UV light. The complexes were found to be non-emissive in fluid solution at room temperature and are emissive in the solid state and at low temperature.
Lay Summary

The ever-increasing demand in energy along with the growth of the population has led to an all-time low of the non-renewable resources on the planet. These issues have motivated the scientific community to develop more efficient ways to harvest energy, especially from sunlight. Materials that interact with light from the sun is at the center of this research. The use of plastics (polymeric materials) has been attractive as they are easily processed and can be coated on many surfaces. The first two research chapters are focused on the interaction of novel polymeric materials with light and the impact of small chemical changes on the properties. In the fourth chapter, the investigation is focused on the combination of small organic molecules with metals ions and their properties when light is shined on them.
Preface

Prof. Michael O. Wolf acted in a supervisory role in all Chapters. Chapters 2 has been published in Macromolecules, Chapter 3 will be submitted for publication and I am the principle author and carried out all of the work in these chapters (2 and 3).

Chapter 4 will be submitted for publication and I am the principal author of the work in Chapter 4. The crystal structures of proligands 13-S and 13-SO$_2$ and complexes 18-S, 19-SO$_2$, 20-S and 20-SO$_2$ were determined by MSc. Duane Hean at the University of British Columbia.
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<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>a. u.</td>
<td>Arbitrary Units</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical Shift (ppm)</td>
</tr>
<tr>
<td>D</td>
<td>Polydispersity</td>
</tr>
<tr>
<td>Da</td>
<td>Dalton</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volts</td>
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<td>g</td>
<td>Gram</td>
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<td>Hz</td>
<td>Hertz</td>
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<td>h</td>
<td>Hour</td>
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<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Average number molecular weight</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>mol%</td>
<td>Mole Percent</td>
</tr>
<tr>
<td>µM</td>
<td>Micromolar</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of Rings</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of repeating units</td>
</tr>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>W</td>
<td>Watts</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight Percent</td>
</tr>
<tr>
<td>[ ]</td>
<td>Concentration</td>
</tr>
<tr>
<td>{ }</td>
<td>Decoupled</td>
</tr>
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### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>Anal.</td>
<td>Analysis</td>
</tr>
<tr>
<td>BDT</td>
<td>Benzo[1,2-(b):4,5-(b)']dithiophene</td>
</tr>
<tr>
<td>btz</td>
<td>2,2'-Bithiazole</td>
</tr>
<tr>
<td>&quot;BuLi</td>
<td>(n)-Butyllithium</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2’-Bipyridine</td>
</tr>
<tr>
<td>btz</td>
<td>2,2’-Bithiazole</td>
</tr>
<tr>
<td>ca.</td>
<td>Approximately</td>
</tr>
<tr>
<td>Calcd.</td>
<td>Calculated</td>
</tr>
<tr>
<td>CDCl(_3)</td>
<td>Chloroform-(d3)</td>
</tr>
<tr>
<td>CD(_2)Cl(_2)</td>
<td>Dichloromethane-(d2)</td>
</tr>
<tr>
<td>CD(_3)CN</td>
<td>Acetonitrile-(d3)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>CIS</td>
<td>Chemical Induced Shift</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation Spectroscopy</td>
</tr>
<tr>
<td>&quot;CPBA</td>
<td>(meta)-Chloroperbenzoic acid</td>
</tr>
<tr>
<td>D-A</td>
<td>Donor-Acceptor</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>DCTB</td>
<td>trans-2-[3-(4-(tert)-Butylphenyl)-2-methyl-2-propenylidene]malononitrile</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of Doublet</td>
</tr>
<tr>
<td>ddd</td>
<td>Doublet of Double of Doublet</td>
</tr>
<tr>
<td>DHAP</td>
<td>Direct Heretoarylation Polymerization</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl formamide</td>
</tr>
</tbody>
</table>
dmp 2,9-Dimethyl-1,10-phenanthroline
DSC Differential Scanning Calorimetry
$E_g$ Energy Gap, Band Gap
$E_{\text{HOMO}}$ Energy of the Highest Occupied Molecular Orbital
$E_{\text{LUMO}}$ Energy of the Lowest Unoccupied Molecular Orbital
em. Emission
$E_{\text{onset}}$ Energy of the intersection of the tangents of the slope and the baseline
$E_{\text{ox}}$ Oxidation Potential
$E_{\text{red}}$ Reduction Potential
eq Equivalents
ESI Electron Spray Ionization
Et$_2$O Diethyl ether
EtOH Ethanol
Fe Ferrocene
Fe$^+$ Ferrocenium cation
GPC Gel Permeation Chromatography
hbtz 4,4’-Hexyl 2,2’-bithiazole
HRMS High-Resolution Mass Spectrometry
H$_2$O$_2$ Hydrogen peroxide
HCl Hydrochloric acid
HOMO Highest Occupied Molecular Orbital
IR Infrared
ISC Intersystem Crossing
$J$ Coupling Constant
LC Ligand Centered
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDI</td>
<td>Laser Desorption Ionization</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand–Metal Charge Transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Energy</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
</tr>
<tr>
<td>(\lambda_{em})</td>
<td>Emission Wavelength</td>
</tr>
<tr>
<td>(\lambda_{ex})</td>
<td>Excitation Wavelength</td>
</tr>
<tr>
<td>(\lambda_{max})</td>
<td>Wavelength at peak maximum</td>
</tr>
<tr>
<td>(m)</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix Assisted Laser Desorption Ionization Time of Flight</td>
</tr>
<tr>
<td>MC</td>
<td>Metal Centered</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-Ligand Charge Transfer</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>NbC</td>
<td>Niobium carbide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NDA</td>
<td>neo-Decanoic acid</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser Effect Spectroscopy</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic Field Effect Transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light-Emitting Device</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>P3AT</td>
<td>Poly(3-alkylthiophene)</td>
</tr>
</tbody>
</table>
PA  Polyacetylene
PhCl  Chlorobenzene
phen  1,10-Phenanthroline
PivOH  Pivalic acid
PMMA  Poly(methyl methacrylate)
POP  (Oxydi-2,1-phenylene)bis(diphenylphosphine)
PPS  para-Polyphenyl sulfide
PT  Polythiophene
s  Singlet
S₁  lowest Singlet State
SiO₂  Silica
t  Triplet
T₁  Lowest Triplet State
Tc  Temperature of Crystallization
Tg  Glass Transition Temperature
Tm  Melting Temperature
THF  Tetrahydrofuran
TLC  Thin Layer Chromatography
Ts-Cl  4-Toluenesulfonyl chloride
tzS  2,2’-Bisthiazole sulfide
tzSO₂  2,2’-Bisthiazole sulfone
UHP  Urea Hydrogen Adduct
UV  Ultraviolet
vis  Visible
Acknowledgements

I acknowledge Dr. Michael O. Wolf for his guidance, his support, his help and his mentorship through these five grueling years. To NSERC and FRQNT for funding this Ph.D. work. To the NMR and MS facility for their help with problems that kept coming day after day.

To the past and present Wolf lab members for their insightful discussions, help in the lab and the fun times outside either on the slopes, in the trails or in the bar. Their daily help and support was a small joy that I could count on every day.

Thanks to the brave classmates that started with me for sharing this experience through joy and tears, to the old and wised chemistry grad students who have seen so much and helped me navigate the graduate student life, and to the fresh and young ones who have so much energy and kept reminding me why I started this in the first place.

To the friends I made through sports (all of them!), for providing me an outlet to let lose all the frustration of the day and allowing me to smile at the end of every day. To Vancouver for your summer beauty which makes us all forget about the dreadful rainy cold and dark winters.

À ma famille: la bibliothécaire madame Larouche, popa, philou, nous sommes loin mais nous sommes proche! Grâce à votre appui, je me suis rendue à Vancouver. To my new companion, Spencer you have been a breath of fresh air in the middle of a stressful period. Thank you for being so understanding and providing great feedback! You kept me sane with all the challenges that I faced throughout these last years.
To Penny
Chapter 1: Introduction

1.1 Overview

Since the coining of the concept of polymers in the 1830s and the preparation of the first synthetic polymer (Bakelite) in 1907 by Leo Hendrik Baekeland, polymers have been intensely researched. They are now essential commodities in modern society.\textsuperscript{1-3} The ubiquity of these materials is mainly due to their tunability where the physical, optical and electronical properties can be modulated based on their chemical structure. A selection of the most important synthetic polymers and dates pertinent to their development in the field of synthetic polymer are highlighted in Figure 1.1. Polymer development can be divided into four significant breakthroughs\textsuperscript{1, 4-5}: simple plastics (pink), plastics with improved properties for construction materials (orange), specialty polymers (green) and polymers with high electric conductivity (blue).

![Timeline of the development of the polymer field in chemistry from the first concept to the 2000s.](image)

**Figure 1.1** Timeline of the development of the polymer field in chemistry from the first concept to the 2000s.
Polymers were initially thought to only be electrical insulators; however organic conjugated polymers can exhibit semiconducting and conductor behavior. These are now commonly referred to as synthetic metals due to the pioneering work performed by Nobel laureates MacDiarmid, Heeger and Shiakawa. Conducting polymers are currently being investigated for a number of applications such as OLEDs (organic light-emitting devices), OPVs (organic photovoltaics), and OFETs (organic field effect transistors) to name a few. Traditionally, inorganic materials are used for these applications and require high temperature and pressure to make a device. They are further limited to a rigid substrate. Conjugated polymers lend themselves particularly well to optoelectronic applications due to their electronic and photophysical properties (absorption and emission) and will be discussed further in section 1.2.2. The use of polymers over tradition inorganic materials for these application is advantageous due to the synthetic versatility, low-cost, light-weight, flexibility, large-area, and processability (ie. roll-to-roll printing methods). Indeed these soluble organic conjugated polymers can be made into inks, which allows for ink jet printing of the material for production of devices.

1.2 Polymers

1.2.1 Polymer Fundamentals

Figure 1.2 depicts a simplified representation of a polymer, where each circle represents a monomer. As the number of monomers linked increases, the chain created is called a dimer (2), trimer (3) up to octamer (8). These macromolecules are referred to as oligomers. Once the chain has more than 8 monomers, it is called a polymer, with a degree of polymerization (DP). The repeat unit (n), between the brackets, is the microstructure repeated throughout the polymer chain. There are two main types of polymers: homopolymers and copolymers. Homopolymers are composed of a single monomer (single color) in the repeat unit. Copolymers are obtained by the polymerization of more than one monomer, most often two. Copolymers can be coupled in an alternating, statistical, or in a block fashion (Figure 1.2). The properties of the polymers are highly dependent on the microstructure, making each of the polymer types very different, even with the combination of the same monomers. These types of copolymers are obtained though
different synthetic routes; Pd-catalysed cross coupling is the most common polymerization of conjugated alternating polymers, block copolymers are often obtained with living polymerization and statistical copolymers can be obtained with either method.\textsuperscript{46} An average molecular weight for a conjugated copolymer is 10,000 to 100,000 g mol\textsuperscript{-1}, whereas much higher molecular weight can be achieved using living polymerizations.\textsuperscript{47-50} The scope of this thesis will focus on alternating copolymers and their synthesis will be further discussed in section 1.2.3.

![Figure 1.2 Schematic representation of polymers and the types of copolymers.](image)

Since alternating polymers are obtained through a series of reactions (step-growth), the resulting material is composed of many molecules that have different molecular weights. Since there is a distribution of molecular weights, the molecular weights are reported as averages based on the number of molecules ($M_n$) or the weight of the molecules ($M_w$). Furthermore, the molecules size distribution of the polymers chains is referred as the polydispersity index ($D$) and is the ratio of $M_w/M_n$. It can be calculated according to equation 1,

\[
D = \frac{M_w}{M_n} = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{\sum N_i}{\sum M_i}
\]

where $M_i$ is the molar mass and $N_i$ is the number of moles of each polymer. A small value ($D$) is representative of a narrow distribution. To put this concept in perspective, a sample with the following
molecules: $1 \times 10,000$ g mol$^{-1}$, $5 \times 20,000$ g mol$^{-1}$, $7 \times 30,000$ g mol$^{-1}$ and $4 \times 40,000$ g mol$^{-1}$ has a $M_n$ of 27,500 g mol$^{-1}$, $M_w$ of 29,990 g mol$^{-1}$ and a $Đ$ of 1.1. The physical and optical properties of polymers, especially conjugated polymers, differ from the monomer, and is caused by their large size, the polydispersity of the sample and the overlap of the molecular orbitals (see section below). $^{51,52}$

1.2.2 Conducting Polymers

Conductive polymers are mostly conjugated, meaning that their chemical structure is composed of an alternation of $σ$- (single) and $π$- (double or triple, unsaturated) bonds. These $π$-bonds lead to one free electron per atom/unsaturation ($π$ electron) that can be delocalized along the polymer chain. This is referred as $π$-conjugation. These electrons allow for conduction when the polymer is doped, where doping is the process of introducing charges on the polymer chain. $^{53}$ The charges can be positive (p-type) or negative (n-type) and they can be introduced chemically, electrochemically or photochemically. $^{1,54}$ As the length of the polymer increases, the energy of the frontier molecular orbitals is lowered and they go from being distinct levels to continuous energy levels, often referred to as bands (Figure 1.3). Semiconductors have a valence band filled with electrons and their conduction band is largely empty. Upon n-type doping, additional electrons are introduced in the conduction band, while p-type doping removes electrons from the valence band. The difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is referred to as the band gap ($E_g$). The energy of these levels is crucial for a number of optoelectronic applications as the absorption and emission of the material (active layer) is related to the $E_g$. Furthermore, as the active layer is only one of many layers in the device it needs to be carefully matched to other components to ensure high efficiency for a given physical process in a device. The optimization of the layers and their requirements for efficient device fabrication is beyond the scope of this thesis.
Organic conjugated polymers have been intensively investigated since the $\pi$-conjugation gives rise to many useful and interesting properties that are not achievable with other classes of synthetic polymers. Examples include high conductivity with oxidative or reductive doping, luminescence, and visible and near-IR light absorption. This generation of polymers is subdivided into three categories based on the complexity of the repeating unit. The first generation was marked by the discovery of the conductivity of polyacetylene (PA) the smallest possible repeat unit for a $\pi$-conjugated organic polymer (Figure 1.3). The main drawback of PA was environmental instability, the degeneracy of the ground state, and the lack of solubility in common organic solvents. This limited both their performances and practical applications. The second generation was marked by polyarenes and polyarene vinylene where the repeating unit increased in molecular weight compared to the first generation (Chart 1.1). A heteroatom in the aromatic ring (S or N) provide stabilization of the cis-diene, therefore removing the degeneracy of the ground state observed in PA. These aromatic rings are important as they allow tailoring of the energy levels (HOMO and LUMO) of the polymers. In addition, the possibility of chemically modifying the aryl groups with alkyl chains to increase the solubility of the polymers and the functionalization with electron

**Figure 1.3** Simplified band diagram for oligo- and polythiophenes adapted from reference [55].
donating/withdrawing groups to modify the frontier orbital energies rendered the conjugated polymers more suitable for solution processing of the semi-conductors. The most studied polymers of the second-generation polymers are poly(3-alkylthiophene) (P3AT) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), due to their simple synthesis, crystallinity, high molecular weights and ease of processability.

Chart 1.1 Polymers of the first and second generation of conjugated polymers.

The third generation of conjugated polymers are marked by an increase in complexity, a larger number of atoms in the repeating unit and typically copolymers (Chart 1.2). The aim of such large units is to tailor the energy levels to a specific application and to optimize the solid state morphology for efficient charge transport. Charge transport mainly happens along the single polymer chain. However, due to the finite nature of the molecules, chain ordering is important to allow for interchain charge hopping, therefore connecting different polymers. This is mainly due to the presence of crystalline regions within the bulk of the polymer film. Furthermore, the mobility of the charge carriers also depends on the coplanarity of the conjugated units, molecular weight, polydispersity, and regioregularity. Many members of the third generation of conjugated copolymers are composed of an electron rich and an electron poor monomer
(denoted donor-acceptor or D-A copolymer) which increases the internal charge transfer and allows control over the band gap. A donor monomer is considered to be an electron rich unit and it is often based on a thienyl moiety. In contrast, an acceptor is an electron deficient unit and it usually possesses a phenyl moiety. Polymers in Chart 1.2 are a selection of polymers used in OLEDs and OPVs.

![Diagram of polymers](image)

**Chart 1.2** Selection of conjugated copolymers of the third generation.

### 1.2.3 Conjugated Polymer Synthesis

Conjugated polymers can be obtained either by electro- or chemical polymerization. Although electropolymerization is effective and yields polymer films that are already doped, it leads to poorly defined structures. The molecular weight of the obtained molecules is difficult to control and the electropolymerization is limited to small amounts. The third generation is mainly obtained from the homocoupling of large monomers or by the copolymerization of two monomers to obtain an alternating polymer, typically through Suzuki-Miyaura, Stille or oxidative polymerization (Scheme 1.1). In the case of either a Suzuki-Miyaura or Stille polymerization, the required monomers that are synthetically challenging are often unstable and they yield a stoichiometric amount of by-product. In the case of the Stille reaction, toxic tin waste are generated which is not suitable for large scale manufacturing of the polymers.
As depicted in Scheme 1.1B, not all monomers can be functionalized with the required organometallic groups for Stille and Suzuki-Miyaura couplings. Alternatively, oxidative polymerization can be done with aromatic monomers. While this approach is one of the cleanest polymerization method, it is hard to control in terms of molecular weight. Additionally, the oxidative reaction conditions require the synthesis of large monomers (Scheme 1.1C) as it can only be applied to the synthesis of homopolymer or random copolymers.

Scheme 1.1

A.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*}
\]

\[ + \quad \text{N} \quad \text{S} \quad \text{N}\]

\[ \xrightarrow{\text{Pd(PPh}_3\text{)}_4 \text{SnMe}_3} \]

\[ \begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*} \]

B.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*}
\]

\[ + \quad \text{Me}_3\text{Sn} \quad \text{SnMe}_3 \quad \text{N} \quad \text{S} \quad \text{N} \]

\[ \xrightarrow{\text{Pd(PPh}_3\text{)}_4} \]

\[ \begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*} \]

C.

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[ \xrightarrow{\text{FeCl}_3} \]

\[ \begin{align*}
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N}
\end{align*} \]

D.

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[ + \quad \text{Br} \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*}

\[ \xrightarrow{\text{Pd(OAc)}_2} \]

\[ \begin{align*}
\text{S} & \quad \text{S} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N}
\end{align*} \]

Recent work has shown that the polymerization can be done by the careful design of monomers using CH activation. This method is commonly referred as direct heteroarylation polymerization (DHAP) and is depicted in Scheme 1.1D and the catalytic cycles are depicted in Figure A6.1. DHAP can yield high molecular weight polymers, requires fewer synthetic steps in the preparation of the monomers and yields less by-products. However, this method generally requires optimization of the monomer structure and the polymerization condition (catalyst, solvent, base and additive). Indeed, in the case of some monomers, including thiophene, the β position of the brominated monomer can be easily activated. Therefore, the
presence of either an alkyl chain or a steric element is necessary to deactivate unwanted coupling products.\textsuperscript{109-112}

\subsection*{1.2.4 Heteroatom Containing Polymers}

As stated in section 1.2.3, the presence of main group elements in the conjugated polymer is common. P-block elements such as boron,\textsuperscript{113-116} nitrogen,\textsuperscript{117-119} phosphorous,\textsuperscript{120-122} and silicon\textsuperscript{123-125} can be incorporated into the main chain as pendant (A), comonomers (B) or incorporated into the monomer aromatic rings (C) (Figure 1.4). Each possesses a different electronic character that can further the applicability of the organic polymers by giving them unique electronic, optical, and physical properties that are not possible with all-organic polymers.\textsuperscript{126} Many examples of conjugated polymers containing sulfur have been reported, with many examples incorporating the sulfur atom into either the aromatic ring or side chains.\textsuperscript{127-131}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic_representation}
\caption{Schematic representation of incorporation of p-block elements (X) in A. side chain, B. main backbone and C. ring of conjugated polymers.}
\end{figure}

This thesis focuses on the placement of sulfur atoms in polymers either as thiophene and thiazole monomers or as a sulfur bridge in the main backbone. Thiophenes are structurally similar to \textit{cis}-polyacetylene that is confined with a highly polarizable sulfur atom. This configuration makes it an ideal candidate to study charge mobility.\textsuperscript{77,132} The stabilization of polythiophene (PT) arises from the formation of two non-equivalent ground states corresponding to the two resonance forms; aromatic and quinoidal. Only a few examples of sulfur being incorporated in the main polymer chain have been reported.\textsuperscript{133-135} When sulfur is a linker in the polymer backbone it can be oxidize. This alters its electronic properties by converting it to an electron accepting sulfone.\textsuperscript{136} Poly-\textit{para}-phenylene sulfide (PPS), containing thioethers linking two conjugated moiety, has been studied. While it is a good melt processable polymer and has good flame retardancy, its low solubility precludes characterization and ultimately its applications as luminescent
Despite the conjugation being interrupted by a sulfur atom, PPS still exhibits high conductivities when doped. Related polymers such as polyphenyl sulfone and polyphenyl sulfide sulfone are commonly used as engineering plastics, proton exchange membranes in fuel cells, and solid acid catalysts. However, the sulfone linkers hinders the conductivity of the polymer upon doping.

Incorporating sulfur into the polymer backbone can be done synthetically by two different strategies: making a carbon-sulfur (C-S) bond during polymerization and the polymerization of a monomer containing a thioether (Scheme 1.2). The C-S bond formation can occur during the polymerization by nucleophilic substitution of a sulfur source (Na$_2$S) with a dichloroarene (2,5-dichlorothiophene), as depicted in Scheme 1.2A. This method has been successful for preparing high molecular weight polymers. However it requires high reaction temperatures (260 °C) and it is done under pressure (2 atm). The sulfur link can be incorporated in the monomer and can undergo homo- and co- polymerization either electrochemically or chemically. Lower reaction temperatures are possible with these approaches. Also, in the case of the copolymerization (Scheme 1.2C), the repeat unit structure can be varied courtesy of the second monomer.

**Scheme 1.2**
Thiazole is a five-membered rings containing a sulfur and a nitrogen. It is structurally similar to thiophene with an imine. It is isoelectronic to thiophene and has a HOMO lower in energy.\textsuperscript{150-151} Introducing thiazole into polymers is of interest due to its similarity to thiophene, but having the advantage of an imine that can coordinate metals, especially when two rings are covalently linked through the 2 position to form a N\(^{\text{N}}\)N or N\(^{\text{S}}\)S bidentate ligand.\textsuperscript{152-153}

1.3 Metal-containing Polymers

Metallopolymers are a combination of metal complexes and polymers. They combine the physical and electronic properties of metal complexes and polymers, where the functionality of the metal center and the processability of the polymer can be exploited. The combination of conjugated polymers and metals has proven to be particularly interesting. It has found applications as conductive and semi conductive materials, luminescent and photovoltaic materials, photocatalysts, electrocatalysts, and stimuli responsive materials.\textsuperscript{154} The metal atom can be incorporated into polymers in three ways (Figure 1.5): tethered to the backbone via a linker (Type I), coordinated to the polymer (Type II), and into the main chain (Type III). The electronic interaction between the polymer and the metal is greatest in type II and III, whereas in the metallopolymers of type I the polymer is a support for the metal. Limited polymer/metal interaction exists with the latter.\textsuperscript{155-156}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.5.png}
\caption{Schematic representation of metal (M) incorporation into conjugated polymers of Type I-III.}
\end{figure}

Adapted from reference [155]

Integrating metals into conjugated polymers opens the possibility of coupling metal and polymer chemical, electronic and optical properties.\textsuperscript{153} To understand the extent of the coupling between the polymer
and the metal, the polymers without metal and their complexes should be independently evaluated. Model complexes therefore play a pivotal role for accurate structure-property studies.

1.3.1 Electronic Impact of Metal Coordination in Polymers

Transition metal complexes have many properties that are not achievable in organic molecules. This is in part owing to their d orbitals that are not available with organic counterparts. The metal center dictates the reactivity and geometry of a complex. However, the ligands surrounding the metal play a major role in modulating the electronics and steric of the metal. The photophysical properties of metal complexes depends on the metal center as well as the nature of the coordinating ligand. Moreover, the bite angle, steric and electron donor/acceptor capacity of the ligand influence the molecular energies. These in turn influence the optical properties. Since complexes have two components, metal and ligand, light absorption can be centered on either one of the two components or a transition between the two components. There are four main transitions possible: ligand-centered (LC), metal-centered (MC) or a charge transfer between the two, ligand-to-metal (LMCT), and metal-to-ligand (MLCT).

The intensity and energies of the optical transitions due to light absorption in organometallic and organic molecules are governed by two main selection rules. These result in spin allowed/forbidden transitions and they are as follows: absorption of light is allowed between states of the same multiplicity (same spin; s→s; T→T…). This must result in a change in the orbital and total angular momentum (cannot redistribute electrons between orbitals of the same geometry). Once a complex has absorbed a photon, it is considered to be in an excited state (C*). It can then undergo multiple deactivation pathways to the ground state (C): 1) inter- or intra- molecular reaction, 2) intramolecular radiative decay, or 3) non-radiative decay. The intramolecular radiative and non-radiative pathways are the most common and these are illustrated in a Jablonski diagram in Figure 1.6. From the lowest spin-allowed excited state (S1), the compound can relax to the ground state either by the emission of a photon (fluorescence) or not (internal conversion). In the presence of a heavy atom (i.e. metal) intersystem crossing (ISC to a triplet state (T1) is allowed due to spin orbit coupling. From the resulting triplet state, a photon can be either emitted (phosphorescence) or it can
relax without emission by intersystem crossing. Fluorescence has a shorter lifetime due to the spin allowed transition. In contrast phosphorescence requires the electron to undergo a spin flip, leading to a longer lifetime. Phosphorescence is rare in organic chromophores at room temperature or above. However, it is more common in metal complexes. This is due to orbital mixing between the ligand and the metal that creates a break in the symmetry. This renders the transition spin allowed. The energies of the states involved in the photophysical process of organic chromophores and metal complexes are intimately related to the orbital energies. These can be tuned to absorb/emit at desired wavelengths. A low energy MLCT is expected with a metal that can easily be oxidized and a ligand easy that can be reduced. Meanwhile, a LC transition is expected with aromatic ligands having extended π and π* orbitals.  

![Jablonski Diagram](image)

**Figure 1.6** Simplified Jablonski diagram showing light absorption (1), fluorescence (2), phosphorescence (3), internal conversion (IC) and intersystem crossing (ISC). Emissive events are depicted as undulating lines and non-radiative events as dashed arrows.

As previously mentioned, metal complexes can be incorporated into polymers for a variety of applications. Luminescent complexes are of particular interest in probing the excited states of photocatalysts and as emissive materials for light-emitting devices. The latter has gained much traction recently due to the possibility of harvesting both the singlet and triplet excited states to achieve emissions close to the theoretical quantum yield of 100%.  

In the scope of this thesis, complexes with
ruthenium(II) and copper(I) metal centers are primarily evaluated. These metals are highly studied due to their high luminescence, extended excited state lifetimes, redox chemistry, and ease of ligand modification. While both have a MLCT emissions and can coordinate with diimine ligands, their excited states behave quite differently. The next two sections will provide background information on well known ruthenium(II) and copper(I) complexes.

1.3.1.1 Ruthenium tri(2,2'-Bipyridine)

Ruthenium (II) complexes were the first examples of luminescent complexes. The tris(2,2'-bipyridine) ruthenium(II) dication ([Ru(bpy)₃]²⁺, 1) is a d⁶ polypyridyl species with D₃ symmetry that has played a key role in inorganic photochemistry. Complexes containing this cation and analogues are known for their long-lived metal-to-ligand charge transfer triplet state and their redox properties. The cation’s inherent stability allows for its easy modification of the ligands and the formation of mixed ligand complexes. The ruthenium polypyridyl system can be tuned by introducing up to three different bidentate ligands to form heteroleptic complexes [Ru(L)(L')(L'')]²⁺, or partial substitution to form [Ru(L)₂(L')]²⁺. The energy of the LUMO in these species can easily be varied as this orbital is ligand centered while the HOMO is metal based. The energy of the MC, MLCT and LC excited states depends on the ligand field strength, the redox properties of the metal and ligands and intrinsic electronic properties of the ligands respectively. This modular approach makes the ruthenium polypyridyl system applicable in many fields such as in solar antennae for light harvesting, water splitting for energy storage, and as photocatalysts for organic synthesis.

![Chart 1.3 Structure of tris(bipyridine) ruthenium (II) dication ([Ru(bpy)₃]²⁺).](chart.png)
1.3.1.2 Copper Complexes

Copper(I) complexes have been studied as cost effective replacements for ruthenium and iridium complexes. Rare transition metals are further cost prohibitive for large scale application and sustainability.\textsuperscript{164,170} The d\textsuperscript{10} copper(I) system adopts a tetrahedral elongated geometry when coordinated by four ligands. Homoleptic systems with two bidentate N\textsuperscript{N} ligands or mixed ligand system with one N\textsuperscript{N} and one P\textsuperscript{P} are the most common.\textsuperscript{162,170-171} In the ground state, the complex does not possess a dipole moment. However upon excitation, the system becomes polarized in the following fashion: Cu\textsuperscript{2+}-(NN)\textsuperscript{−}. This polarization results in copper(II) character and a flattening of the tetrahedral geometry towards square planar. This allows a fifth ligand to coordinate. This stabilizes the excited charge transfer state and destabilizes the ground state resulting in a quenching of the emission.\textsuperscript{172} To mitigate the copper(II) character issues, structural changes can be made such as increasing the steric bulk. This prevents geometry change and coordination by a fifth ligand. The donor ability of the solvent can also be decreased. The rigidity of the environment can be increased and/or coordination with a bulky π-acidic ligand (i.e. phosphines) to stabilize the copper(I) center.\textsuperscript{157,173-175} The first example of an emissive copper(I) complex in fluid solution was [Cu(dmp)\textsubscript{2}]\textsuperscript{+} (2) (dmp = 2,9-dimethyl-1,10-phenanthroline). This had a lifetime of 85 ns and the lifetime can be increased (14,300 ns) by using a mixed ligand system Cu(dmp)(POP)]\textsuperscript{+} (3) (POP = (oxydi-2,1-phenylene)bis(diphenylphosphine)), which surpassed commonly used Ru and Ir photocatalysts.\textsuperscript{170,176}

These improvements led to suitable copper(I) complexes for the replacement of expensive transition metals in many application such as OLEDs,\textsuperscript{162,177-180} photosensitizer in OPV,\textsuperscript{164,181} and as photoredox catalysts.\textsuperscript{165-166,170,182-183}
1.4 Sulfur-bridged Chromophores

Sulfur has an interesting chemistry that is often the center of debate and is not always well understood. Its many modes of coordination make sulfur quite attractive as ligands and chromophores. Indeed, the incorporation of a sulfur atom bridging two chromophores (Chart 1.5) leads to interesting photophysical behavior. As the oxidation of the sulfur atom increases from sulfide to sulfoxide to sulfone, the quantum yield of emission increases (4-SO₂), surpassing the quantum yield of the parent arene (terthiophene for 4) in some cases. The enhanced emission has been attributed to the relative rate of intersystem crossing, which in turn is dependent on the oxidation state of the sulfur-bridge. As the electron density moves away from the bridging sulfur, as the oxidation state increases, the charge transfer state is stabilized and the resulting compounds are more emissive (Figure 1.7A).

Furthermore, sulfur bridges have shown enhanced solubility of the dimer compared to the directly linked compounds (sexithiophene for 4) and the frontier molecular orbitals can be tuned with the oxidation state of the bridge (Figure 1.7B). Finally, the calculated geometry of the sulfur-bridged chromophores maintains a tetrahedral geometry with a 105° ± 3 C-S-C angle between the chromophores with increasing oxidation state between the chromophores.
Figure 1.7 A. Quantum yield of compounds 4 and B. The calculated energy of the frontier orbitals of compounds 4 contingent on the oxidation state of the sulfur bridge. Adapted from reference [184].

1.5 Goals and Scope

The goals of this thesis are to explore the impact of incorporating a bridging sulfur group of different oxidation states on the physical and photophysical properties of conjugated oligomers, polymers and metal complexes. The variations of the electronic behavior on the different oxidation states of sulfur while maintaining the same geometry is an interesting tool to exploit for tuning the electronic and photophysical behaviors. The initial goal of this study was to prepare a series of oligomers containing multiple sulfur bridges (5-7), to obtain the non-oxidized (-S) and fully-oxidized (-SO₂) versions, and to compared them to fully conjugated α-oligothiophenes. The second goal involved the synthesis of polymers via DHAP. Optimization of the polymerization conditions was carried out for homopolymers (both sulfide- and sulfone-containing) and the same conditions were used to obtained copolymers. The copolymerization with electron rich and electron poor comonomers was investigated to evaluate the compatibility of the sulfur-bridged monomer with other monomers in copolymers. Ultimately this was to modulate the electronic, physical and optical properties of the polymers. Incorporation a bithiazole comonomer allowed to investigate metal coordination within the main backbone and its impact on the photophysical properties based on the oxidation state and the presence of a coordinating N^N moiety. The final goal was to incorporate the thioethers in a N^N bidentate ligand to coordinate metals such as ruthenium(II) and
copper(I). The stability and the optical properties of complexes containing the sulfur bridge was monitored as a function of the oxidation state of the ligand.
Chapter 2: Soluble Oligo- and Poly- Thienyl Sulfides and Sulfones: Synthesis and Photophysics

2.1 Introduction

As introduced in Chapter 1, polymers incorporating p-block elements in the backbone give rise to properties that cannot be accomplished with all organic polymers. The insertion of sulfur atoms as bridging groups in the main backbone of conjugated polymers has been mainly focused on poly-para-phenylene sulfide (PPS, Chart 2.1), which has been shown to have high conductivity when doped.\textsuperscript{139-142} Although large number of studies have been performed on the conductivity of PPS, the photophysical properties of this material have not been thoroughly investigated. This is impart owing to its low solubility.\textsuperscript{138} Analogs of PPS containing different aryl groups have also been synthesized, for example the phenyl has been replaced with thienyls, vinyls, and benzodithienyls.\textsuperscript{133-135} Introducing longer conjugated segments between the sulfur bridges has been extended only to bithienyls.\textsuperscript{188} Polymers with longer conjugated segments are of interest as they are expected to behave more like the fully conjugated counter parts. They additional have the possibility of controlling their electronic properties by changing the oxidation state of the sulfur atom.

\[ \text{Chart 2.1} \]

As previously mentioned, sulfur-bridged chromophores 4 (Chart 2.1) exhibit increased solubility compared to the non-sulfur containing parent chromophores. They also have increased emission quantum yield. The emission enhancement is contingent on the oxidation state of the sulfur: it increases from sulfide...
(4-S) to sulfoxide (4-SO) to sulfone (4-SO$_2$).\textsuperscript{184-185, 187} Furthermore, the oxidation state of the sulfur bridge modulates the energy of the frontier orbitals, which is anticipated to affect the electronic states of their corresponding oligomers and polymers. Incorporation these tunable features into macromolecules and polymers would provide an additional mean to further modulate the electronic and photophysical properties of these materials.

![Chart 2.2](image)

Chart 2.2

We envisioned oligomers 5-7 (Chart 2.2) and polymers P1 and P2 (Chart 2.1), where structural elements of both PPS and PT are combined in one system. Herein, the impact of incorporating multiple sulfur bridges and their oxidation is probed in the oligomeric series and compared to fully conjugated $\alpha$-oligothiophenes ($n = 2, 3, 4$) 8-10. In the polymeric systems, the thiophene monomers are functionalized with alkyl chains to make them soluble. This is advantageous for enhancing their processability and providing additional characterization options that rely on homogenous solutions. Furthermore, the introduction of extended conjugated blocks between the bridges is expected to increase the electronic delocalization. Finally, altering the oxidation state of the bridging sulfur potentially allows control of the electronic properties. The synthesis of the model compounds (5-7) and its soluble polythienyl sulfide and sulfone (P1 and P2 respectively) counter parts prepared by direct heteroarylation polymerization (DHAP) is reported here along with electronic and photophysical properties of these materials.
2.2 Experimental

2.2.1 General

The following materials were purchased and they were used without further purification: thiophene, 4-para-toluensulfonyl chloride (Ts-Cl), N-bromosuccinimide (NBS), cesium carbonate (Cs$_2$CO$_3$) and 1-bromobutane from Alfa Aesar, 2-bromothiophene, 2,5-dibromothiophene, 2-thiophenethiol, poly(methyl methacrylate) (PMMA), n-butyllithium (1.6 M, n-BuLi), magnesium turnings and 1-bromo-octane from Sigma-Aldrich, tri-o-tolyl phosphine (P(o-MePh)$_3$) from Oakwood Chemicals, 3,4-dibromothiophene from AKSci, pivalic acid (PivOH) from Eastman, anhydrous diethyl ether (Et$_2$O) from Anachemia, [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl$_2$), trans-dichlorobis(triphenylphosphine)palladium(II) and neo-decanoic acid (NDA) from Strem, sublimed sulfur, hydrogen peroxide (H$_2$O$_2$), dichloromethane (CH$_2$Cl$_2$; HPLC grade), acetonitrile (MeCN; HPLC grade) and toluene (PhMe; HPLC grade) from Fisher, and N,N’-dimethylformamide (DMF) from Omnisolv. trans-Bis(acetato)bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II) (Herrmann-Beller catalyst),$^{189}$ tri(o-methoxyphenyl) phosphine (P(o-OMePh)$_3$),$^{190}$ tri(o-dimethylaminophenyl) phosphine (P(o-NMe$_2$Ph)$_3$),$^{191}$ 2,5-dibromo 3,4-dibutylthiophene,$^{192}$ 2,5-dibromo 3,4-dioctylthiophene,$^{193}$ 2,5-bis[(2-thienyl)thio]thiophene (6-S)$^{194}$ and 2,2’-thiobis[5-(2-thienyl)thio]thiophene (7-S)$^{194}$ were synthesized according to literature procedures. Tetrahydrofuran (THF) and 1,2-dioxane were dried over sodium and freshly distilled before use.

Polymer molecular weights were determined by gel permeation chromatography (GPC) using an Agilent liquid chromatograph equipped with an Agilent 1200 series isocratic pump, Agilent 1200 series standard autosampler, Phenomenex Phenogel 5 mm narrow bore columns (4.6 × 300 mm) 104 Å (5000-500,000 Da), 500 Å (1,000-15,000 Da), and 103 Å (1,000-75,000 Da), Wyatt Optilab T-rEx differential refractometer ($\lambda = 658$ nm, 40 °C). A flow-rate of 0.5 mL min$^{-1}$ was used and samples were dissolved in THF (ca. 1 mg mL$^{-1}$). Molecular weights were determined by comparison to polystyrene standards.
Thermal stability measurements were performed by thermogravimetric analysis (TGA) using a PerkinElmer Pyris 6 thermogravimetric Analyzer with a porcelain crucible. A differential scanning calorimeter (DSC) TA Instruments Q1000 was employed to determine the glass transition ($T_g$), crystallization ($T_c$) and melting ($T_m$) temperatures. The samples were subjected to 3 cycles of heating/cooling at 10 °C min$^{-1}$ from -10 °C to 180 °C. Only the last cycle was analyzed.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance 400 inverse broadband probe at 298 K using the residual protonated solvent peak for referencing.

MALDI-TOF mass spectra were obtained on Bruker Autoflex MALDI-TOF using a variety of matrices (DCTB, LDI, Dith) in linear and reflective modes.

UV-visible absorption spectroscopy was carried out on a Cary Varian 5000 UV-vis-Near-IR spectrophotometer using HPLC grade solvents. The optical bandgaps were estimated from the onset of absorption spectra in CH$_2$Cl$_2$. Photoluminescence spectra was measured on a Photon Technology International QuantaMaster 50 fluorimeter equipped with a double monochromator and using a 75 W Xe arc lamp as the source. Photoluminescence spectra were measured at 298 K. Solutions had absorbance bellow 0.1 and were normalized using their absolute absorbance. Solid state measurements were performed on VWR VistaVision™ White glass microscope slides and annealing was performed in a Hewlett Packard 5890 series II oven.

Electrochemical experiments were performed using a Pine AFCBP1 bipotentiostat in an airtight three-electrode cell with a 7 mm glassy carbon working electrode (Bioanalytical Systems, Inc.), platinum mesh counter electrode, and silver wire pseudoreference electrode in an electrolyte solution of 0.10 M triply recrystallized ($n$-Bu$_4$N)PF$_6$ in anhydrous MeCN sparged with nitrogen prior to use. The glassy carbon electrode was cleaned by successive polishing with 1, 0.3, and 0.05 μM alumina paste, followed by rinsing with deionized water. The polymer was deposited on the glassy carbon electrode from THF. Ferrocene was added at the end of the electrochemical experiments as an internal standard, and the HOMO energy level was calculated according to equation 1.\textsuperscript{195}
Furthermore, the LUMO energy was estimated from the spectroscopically determined band gap ($E_g$) according to equation 2. This method is commonly used since the reduction of polymers is typically outside the operating window of commonly used organic solvents. This overestimates the frontier orbital energies.

\begin{equation}
E_{LUMO} = E_g + E_{HOMO}
\end{equation}

### 2.2.2 Method

#### Scheme 2.1

2,2'-Dithienyl sulfide (5-S). $n$-BuLi (160 mmol, 100 mL, 1.6 M) was added drop-wise to a solution of thiophene (12.8 mL, 160 mmol) in dry Et$_2$O (120 mL) at -78 °C and stirred at 0 °C for 1 h. Sulfur (5.13 g, 160 mmol) was added at -78 °C and stirred for 30 min at this temperature followed by 30 min stirring at 0 °C. 4-Toluenesulfonyl chloride was then added at 0 °C and the mixture was heated at reflux for 4 h. A second solution of lithiated thiophene (200 mmol, 125 mL, 1.6 M) prepared in the same way in dry Et$_2$O was added drop-wise to the first solution at -78 °C and stirred for 16 h at room temperature. The mixture was then diluted with Et$_2$O, concentrated, purified by flash chromatography (SiO$_2$, petroleum ether) and distilled (108 °C at 0.1 Torr) to give a pale-yellow oil. Yield 10.50 g (33 %). $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.34 (dd, $J = 5.4$, 1.3 Hz, 2H), 7.21 (dd, $J = 3.6$, 1.3 Hz, 2H), 6.96 (dd, $J = 5.3$, 3.6 Hz, 2H). $^{13}$C{$^1$H} (100 MHz, CDCl$_3$, 298 K) δ: 135.6, 132.9, 129.8, 127.6. HRMS (ESI) for C$_8$H$_6$S$_3$ [M$^+$]: calcd. 197.9632; found 197.9625. Anal. calcd. for C$_8$H$_6$S$_3$: C 48.45, H 3.05, S 48.50; found: C 49.03, H 3.13, S 50.17.

2,2'-Dithienyl sulfone (5-SO$_2$). Hydrogen peroxide (30 wt%, 15 mL) was added to 5-S (7.7 g, 38.8 mmol) in EtOH (70 mL) with niobium carbide (0.40 g, 3.9 mmol) at 60 °C. The reaction was stirred for 3
h, quenched with a saturated solution of sodium thiosulfate and extracted with EtOAc. The organic layer was washed with water and brine, dried with MgSO₄ and concentrated. The white solid was recrystallized from EtOH to give white needles. Yield 6.88 g (77 %). 

$^1$H NMR (400 MHz, CDCl₃, 298 K) δ: 7.73 (dd, $J = 3.8, 1.4$ Hz, 2H), 7.65 (dd, $J = 5.0, 1.4$ Hz, 2H), 7.09 (dd, $J = 5.0, 3.8$ Hz, 2H). 

$^{13}$C{$^1$H} NMR (100 MHz, CDCl₃, 298 K) δ: 143.7, 134.0, 133.4, 128.0.

HRMS (ESI) for C₈H₆O₂S₃ [M⁺]: calcd. 229.9530; found 229.9532.

Anal. calcd. for C₈H₆O₂S₃: C 41.72, H 2.63, S 41.76; found: C 41.76, H 2.78, S 41.84.

Scheme 2.2

5,5'-[(2-Thienyl)sulfonyl-(2,2'-dithienyl sulfone) (6-SO₂). This compound was prepared analogously to 5-SO₂ using 0.3 mmol of niobium carbide and 14.6 mmol of hydrogen peroxide. Recrystallization from MeOH gave colorless needles. Yield 0.36 g (77 %). 

$^1$H NMR (400 MHz, CDCl₃, 298 K) δ: 7.76 (m, 4H), 7.61 (s, 2H), 7.14 (dd, $J = 4$ Hz, $J = 4.8$ Hz, 2H). 

$^{13}$C{$^1$H} NMR (100 MHz, CDCl₃, 298 K) δ: 150.9, 141.7, 135.5, 134.8, 132.3, 128.5.

HRMS (ESI) for C₁₂H₈S₄O₄ [M⁺]: calcd. 375.9026; found 375.9028. Anal. calcd. for C₁₂H₈S₄O₄: C 38.28, H 2.14, S 42.58; found: C 38.34, H 2.39, S 42.76.

5,5'-[(2-Thienyl)sulfonyl-(2,2'-dithienyl sulfone) (7-SO₂). Prepared analogously to 5-SO₂ where 0.45 mmol of niobium carbide and 21.9 mmol of hydrogen peroxide were used. Recrystallization from pentane gave a white solid. Yield 0.17 g (26 %). 

$^1$H NMR (400 MHz, CDCl₃, 298 K) δ: 7.78 (m, 4H), 7.64 (m, 4H), 7.16 (m, 2H). 

$^{13}$C{$^1$H} NMR (100 MHz, CDCl₃, 298 K) δ: 152.5, 148.6, 141.3, 135.9, 135.0, 133.7, 132.5, 128.6.

HRMS (ESI) for C₁₆H₁₀S₇O₆ [M⁺]: calcd. 521.8522; found 521.8523. Anal. calcd. for C₁₆H₁₀S₇O₆: C 36.77, H 1.93, S 42.94; found: C 36.70, H 2.16, S 39.44.
5-Methylthio(2,2'-dithienyl sulfide) (11-S). n-BuLi (1.6 M, 1.4 mL, 2.3 mmol) was added dropwise to a solution of 5-S (0.50 g, 2.5 mmol) in anhydrous Et₂O (2.0 mL) at 0 °C under nitrogen. The solution was stirred at room temperature for 2 h and then cooled to -78 °C, after which dimethyl disulfide (0.2 mL, 2.5 mmol) was added dropwise. The mixture was then slowly brought to room temperature and stirred for 16 h. The solution was poured over water, extracted with EtOAc (3 × 20 mL), washed with brine, dried over anhydrous MgSO₄, and filtered. The solvent was removed in vacuo. Purification by column chromatography (SiO₂, hexanes) gave a colorless oil. Yield 0.21 g (34 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.36 (dd, J = 1.2 Hz, J = 5.2 Hz, 1H), 7.22 (dd, J = 1.2 Hz, J = 3.6 Hz, 1H), 7.03 (d, J = 3.6 Hz, 1H), 6.97 (dd, J = 3.6 Hz, J = 5.2 Hz, 1H), 6.88 (d, J = 3.6 Hz, 1H), 2.47 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 141.7, 136.9, 134.7, 133.3, 132.8, 130.4, 130.1, 127.7, 21.6. HRMS (ESI) for C₉H₈S₄ [M⁺]: calcd. 243.9509; found 243.9509. Anal. calcd. for C₉H₈S₄: C 44.23, H 3.30, S 52.47; found: C 44.16, H 3.50, S 52.57.

5,5'- (Methylthio)-2,2'-dithienyl sulfide (12-S). Compound 12-S was prepared similarly to 11-S where 4.8 mmol of n-BuLi and 5.3 mmol of dimethyl disulfide were used. Purification by column chromatography (SiO₂, hexanes) gave a colorless oil. Yield 0.40 g (55%). ¹H NMR (400 MHz, CDCl₃) δ: 7.03 (d, J = 4 Hz, 2H), 6.88 (d, J = 4 Hz, 2H), 2.48 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 142.2, 136.1, 133.2, 130.3, 21.6. HRMS (ESI) for C₁₀H₁₀S₅ [M⁺]: calcd. 289.9386; found 289.9388. Anal. calcd. for C₁₀H₁₀S₅: C 41.31, H 3.47, S 55.18; found: C 41.39, H 3.53, S 55.24.
5-Methylsulfonyl-(2,2'-dithienyl sulfone) (11-SO$_2$). Prepared similarly to 5-SO$_2$ using 0.3 mmol of niobium carbide and 14.6 mmol of hydrogen peroxide. Recrystallization from MeOH gave a white solid. Yield 0.25 g (65 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.78 (dd, $J = 1.2$ Hz, $J = 4$ Hz, 1H), 7.76 (dd, $J = 1.2$ Hz, $J = 4.8$ Hz, 1H), 7.69 (d, $J = 4$ Hz, 1H), 7.63 (d, $J = 4$ Hz, 1H), 7.15 (dd, $J = 2.8$ Hz, $J = 4$ Hz, 1H), 3.21 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$: 151.3, 148.8, 141.5, 135.7, 134.8, 132.9, 132.4, 128.5, 46.0. HRMS (ESI) for C$_9$H$_8$S$_4$O$_4$ [M$^+$]: calcd. 307.9305; found 307.9303. Anal. calcd. for C$_9$H$_8$S$_4$O$_4$: C 35.05, H 2.61, S 41.58; found: C 35.38, H 2.93, S 41.45.

5,5'-(Methylsulfonyl)-2,2'-dithienyl sulfone (12-SO$_2$). Prepared similarly to 5-SO$_2$ where 0.45 mmol of niobium carbide and 21.9 mmol of hydrogen peroxide were used. Purification by column chromatography (SiO$_2$, EtOAc) gave a white solid. Yield 0.07 g (15%). $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$: 8.12 (d, $J = 4$ Hz, 2H), 7.97 (d, $J = 4$ Hz, 2H), 3.49 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, (CD$_3$)$_2$CO) $\delta$: 215.8, 145.3, 144.2, 55.2. HRMS (ESI) for C$_{10}$H$_{16}$S$_4$O$_6$ [M$^+$]: calcd. 385.9081; found 385.9080. Anal. calcd. for C$_{10}$H$_{16}$S$_4$O$_6$: C 31.08, H 2.61, S 41.48; found: C 31.37, H 2.74, S 41.65.
2.2.2.1 Polymerization

Scheme 2.5

General procedure for polymerization. 2,2'-dithenyl sulfide or sulfone (1 mmol), 3,4-dialkyl, 2,5-dibromothiophene (1 mmol), additive (NDA or PivOH; 0.5 mmol), phosphine (0.1 mmol), cesium carbonate (2.5 mmol) and Herrmann-Beller catalyst (2.5 mol%) were placed inside a Biotage microwave vial 2-5 mL with a magnetic stirring bar. The vial was sealed with a rubber septum and thoroughly purged with nitrogen. Degassed solvent was added and the reaction mixture stirred at 125 °C for 48 h, then the polymer was precipitated in MeOH:HCl (10 %) (9:1), and filtered through a 0.45 µm nylon membrane. The resulting polymer was dried at 60 °C in a vacuum oven for 16 h.
Table 2.1 Condition optimization of direct heteroarylation polymerization of P1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd, L</th>
<th>Base, Additive</th>
<th>Solvent</th>
<th>([\text{M}]^a)</th>
<th>Yield (%)</th>
<th>(M_n^d) (g mol(^{-1}))</th>
<th>D</th>
<th>Name(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{PdCl}_2(\text{PPh}_3)_2, \text{P}(\text{o-MePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3, \text{PivOH})</td>
<td>Toluene</td>
<td>0.2</td>
<td>25</td>
<td>1000</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Herrmann, (\text{P}(\text{o-OMePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>THF</td>
<td>0.1</td>
<td>86</td>
<td>8700</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Herrmann, (\text{P}(\text{o-OMePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>THF</td>
<td>0.08</td>
<td>85</td>
<td>2700</td>
<td>2.8</td>
<td>P1-C</td>
</tr>
<tr>
<td>4</td>
<td>Herrmann, (\text{P}(\text{o-MePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>THF</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Herrmann, (\text{P}(\text{o-NMe}_2\text{Ph})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>THF</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Herrmann, (\text{P}(\text{o-MePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>Dioxane(^c)</td>
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<td>4</td>
<td>530</td>
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<tr>
<td>7</td>
<td>Herrmann, (\text{P}(\text{o-NMe}_2\text{Ph})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>Dioxane(^c)</td>
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<td>740</td>
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<td>8</td>
<td>Herrmann, (\text{P}(\text{o-OMePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3, \text{NDA})</td>
<td>THF</td>
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<td>95</td>
<td>2100</td>
<td>4.5</td>
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<td>9</td>
<td>Herrmann, (\text{P}(\text{o-OMePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3, \text{PivOH})</td>
<td>THF</td>
<td>0.2</td>
<td>28</td>
<td>1000</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Herrmann, (\text{P}(\text{o-OMePh})_3)</td>
<td>(\text{Cs}_2\text{CO}_3)</td>
<td>Dioxane(^c)</td>
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<td>11</td>
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<td>(\text{Cs}_2\text{CO}_3)</td>
<td>Dioxane(^c)</td>
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<td>59</td>
<td>1300</td>
<td>3</td>
<td>P1-B</td>
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\(a\). Concentration of monomers in solvent; \(b\). Name given to the polymer in the paper; \(c\). 1,4-dioxane; \(d\). determined by GPC methods.
Table 2.2 Condition optimization of direct heteroarylation polymerization for P2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd, L</th>
<th>Base, Additive</th>
<th>Solvent</th>
<th>$[\text{L}]^a$ (M)</th>
<th>Yield (%)</th>
<th>$M_n^d$ (g mol$^{-1}$)</th>
<th>D</th>
<th>Name$^b$</th>
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<td>12</td>
<td>PdCl$_2$(PPh$_3$)$_2$, P(o-MePh)$_3$</td>
<td>Cs$_2$CO$_3$, PivOH</td>
<td>Toluene</td>
<td>0.2</td>
<td>64</td>
<td>1090</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Herrmann, P(o-OMePh)$_3$</td>
<td>Cs$_2$CO$_3$</td>
<td>THF</td>
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<tr>
<td>14</td>
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<td>Cs$_2$CO$_3$</td>
<td>THF</td>
<td>0.2</td>
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<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Herrmann, P(o-NMe$_2$Ph)$_3$</td>
<td>Cs$_2$CO$_3$</td>
<td>THF</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Herrmann, P(o-MePh)$_3$</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane$^c$</td>
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<tr>
<td>17</td>
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<tr>
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<td>8300</td>
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<td>19</td>
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<td>THF</td>
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<td>93</td>
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<td>Cs$_2$CO$_3$, PivOH</td>
<td>THF</td>
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<td>65</td>
<td>3700</td>
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<td></td>
</tr>
<tr>
<td>23</td>
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<td>Dioxane$^c$</td>
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<td>5-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>24</td>
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<td>Cs$_2$CO$_3$, PivOH</td>
<td>Dioxane$^c$</td>
<td>0.2</td>
<td>44</td>
<td>4200</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

*a.* Concentration of monomers in solvent; *b.* Name given to the polymer in the paper; *c.* 1,4-dioxane; *d.* determined by GPC methods.

### 2.3 Results and Discussion

#### 2.3.1 Synthesis

##### 2.3.1.1 Oligomers

Compound 5-S was prepared via lithiation and nucleophilic substitution of 2-bromothiophene with sulfur. The oligomeric sulfides (6-7) were synthesized according to previously reported methods.$^{194}$ The conversion of the sulfide to a sulfone bridge for compounds 5-7 was achieved by oxidation with hydrogen peroxide in the presence of niobium carbide in ethanol.$^{196}$ All compounds were characterized by $^1$H and
$^{13}$C{1H} NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. Only the UV-visible absorption spectra of compounds 5-S and 5-SO$_2$ have been previously reported.$^{197}$

2.3.1.2 Polymers

The synthesis of polythienyl sulfides and sulfones was carried out using DHAP, starting from 2,5-dibromo-3,4-dialkylthiophene and either 2,2'-thienyl sulfide or sulfone (Scheme 2.5). The length of the alkyl chain was selected to obtain a solid polymer; longer chains on P1 yielded oils which are undesirable for studies in the solid state. The use of DHAP for the preparation of conjugated polymers has expanded over the last decade. This is impart because it is atom economic, requires fewer synthetic steps, and eliminates the stoichiometric production of toxic byproducts compared to conventional cross-coupling reactions.$^{94, 99-100, 198-200}$ This method has proven useful for the polymerization of a wide range of hetero(aryl) polymers, although careful monomer design and condition optimization are typically required.$^{101, 110, 112}$ Thus, multiple small-scale reactions were first carried out to monitor the polymerization as a function of conditions. As these sulfur-bridged monomers have not been investigated previously, we initially attempted polymerization using a commercially available palladium catalyst and with a phosphine ligand. Oligomeric materials were obtained from these attempts, which encouraged further investigation of this general approach. We focused our optimization on using the Herrmann-Beller catalyst (trans-bis(acetato)bis[o-(di-o-tolylphosphino)benzyl]-dipalladium(II)), since it has been previously shown to give high molecular weight polythiophenes using DHAP and it is relatively stable at high temperatures.$^{200}$

Scheme 2.6
A variety of polymerization conditions were explored where the solvent, ligand, additive and monomer concentration were systematically changed (Table 2.1 and Table 2.2). The reaction time was also varied from 12 to 48 h; however, no substantial differences were observed, although the reactions that were run for longer than 36 h resulted in polymers with slightly higher molecular weights. For poly(3',4'-dibutyl-2,2':5',2''-terthienyl sulfide) (P1) and poly(3',4'-dioctyl-2,2':5',2''-terthienyl sulfone) (P2) the polymerization using the Herrmann-Beller catalyst, tri(o-methoxyphenyl) phosphine and cesium carbonate in dioxane or THF led to the highest yield, and are highest molecular weight of soluble polymers (entry 2 in Table 2.1 and entry 19 in Table 2.2). We assigned letters after the polymer type (ie. P1-A) to identify the materials obtained using different reaction conditions for the photophysical characterization.

Attempts to use a Stille polycondensation using 2,5-bis(trimethylstannyl) thiophene and 5,5'-dibromo-2,2'-thienylsulfide/sulfone with bis(triphenylphosphine)palladium(II) dichloride and tri-o-toly phosphine in chlorobenzene were also carried out. In this case, only a red oligomeric material was obtained. The solubility of the material appeared to be the limiting factor since the residue did not completely dissolve in common organic solvents.

Efforts at direct oxidation of the bridging sulfur centers of P1 were unsuccessful. Three different sets of conditions for direct polymer oxidation were tested, two of which have been successful previously on other polymers: 1) m-chloroperbenzoic acid in CH₂Cl₂, stirred at room temperature for different lengths of times (from 30 min to 24 h), 2) hydrogen peroxide in the presence of niobium carbide at 60 °C, and 3) rhenium oxide in the presence of a urea-hydrogen peroxide adduct (UHP). In each case, no evidence for oxidation was found by ¹H NMR, UV-vis, IR or emission spectroscopy. Since the oxidation of compounds 4-7 is possible, the added steric hindrance of the alkyl chains and the folding of the polymer chain presumably prevent the oxidation; rather than an electronic effect causing this lack of reactivity.
Figure 2.1 A. $^1$H and B. $^1$H-$^1$H COSY NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of P1-C.
2.3.2 Molecular Weights

NMR characterization was performed on the polymers in dichloromethane-d$_2$. The $^1$H NMR spectrum of P1 exhibits one broad feature at $\delta$ 7.00 ppm and lower intensity signals at $\delta$ 7.40-7.45 ppm. Using $^1$H-$^1$H COSY NMR spectroscopy to assign the signals, a correlation between the peaks at $\delta$ 7.40-7.45 ppm and the broad feature at $\delta$ 7.00 ppm is observed indicating the $\delta$ 7.40-7.45 ppm peak corresponds to the thiophene protons at the end of the polymer chain (Figure 2.1). This correlation allows NMR to be used to estimate the molecular weight of the polymers obtained by deconvolution of the NMR spectrum (Figure 2.2).

**Figure 2.2** Deconvolution of the $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of P1-C using a non-linear curve fitting with 6 components.
Table 2.3 Area under the fit peaks of the \(^1\text{H}\) NMR spectrum of P1-C.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Area (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>168,757</td>
</tr>
<tr>
<td>2</td>
<td>220,089</td>
</tr>
<tr>
<td>3</td>
<td>206,350</td>
</tr>
<tr>
<td>4</td>
<td>386,654</td>
</tr>
<tr>
<td>5</td>
<td>1,730,289</td>
</tr>
<tr>
<td>6</td>
<td>851,680</td>
</tr>
</tbody>
</table>

The peaks 1, 2, and 3 in Table 2.3 have smaller integrations, have a correlation to the main peak and have been assigned to the terminal thiophene ring (assuming that there is only one with protons and the other is doubly alkylated and mono brominated). The main peak, composed of the fit peaks 4, 5 and 6, is attributed to \(H_a\) and \(H_b\) in the main polymer chain (Figure 2.3).

![Figure 2.3 Aromatic \(^1\text{H}\) assignment on P1.](image)

For each terminal thiophene signal there are four protons in the polymer chain. Taking the average of the three numbers, dividing by four and multiplying by the repeat unit molecular weight the molecular weight of the polymer (1,500 ± 200 g mol\(^{-1}\)) is obtained. These results show that the GPC data overestimates molecular weight (2,700 (GPC) vs 1,500 (NMR) g mol\(^{-1}\)).
Figure 2.4 A. $^1$H, B. $^1$H-$^1$H COSY and C. $^1$H aromatic region NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of P2-C.
The $^1$H NMR spectrum of **P2** contains two doublets at $\delta$ 7.66 and 7.11 ppm and two weaker intensity doublets at $\delta$ 7.22 and 7.07 ppm (Figure 2.4). The latter signals are attributed to protons on the terminal thiophene groups. In this case, a correlation is also observed between these signals and the protons on the main polymer chain by two-dimensional $^1$H-$^1$H NMR spectroscopy. The doublet at $\delta$ 7.22 ppm was used to calculate the molecular weight since the signal is resolved from the other proton resonances. The molecular weight obtained from this calculation is half the values obtained by GPC (4,288 (GPC) vs. 2,144 (NMR) g mol$^{-1}$). To enable direct comparison on the impact of the oxidation state of the sulfur bridge on the folding of the polymers, **P2** was synthesized with butyl chains as substituents. The NMR-determined molecular weight was 1,325 g mol$^{-1}$ and the GPC-determined $M_n$ was 4,800 g mol$^{-1}$. This polymer was not studied further, and the optical studies reported here were all conducted with the octyl chain substituted **P2**.

Comparisons between the molecular weights obtained by GPC and $^1$H NMR spectroscopy suggest that the folding of the polymer chains differs depending on the oxidation state of the sulfur bridge, where a polymer chain of the same length occupies a larger volume when the sulfur bridge is oxidized. Attempts to determine the Mark-Houwink constants of the polymers were carried out, but the molecular weights obtained did not range widely enough to allow extraction of any quantitative information on the folding of the polymer chains in THF. The molecular weights of the polymers were low, however differences in electronic properties as a function of molecular weight and polydispersity for the polymers were seen which were not observed in the oligomers **2-4**.
The polymers were also probed by MALDI-TOF mass spectrometry. Unfortunately, this ionization method proved too harsh for these polymers and only polymer fragments were observed. Furthermore, P1 and P2 were found to be stable to high temperatures (above 350 °C by TGA, Figure 2.5A) which is higher than for polythienyl sulfide (250 °C)\textsuperscript{145, 205} but appreciably lower than for PPS (500 °C)\textsuperscript{145, 205}. The as-synthesized polymers were also found to be electrically resistive, which is comparable to observations for undoped PPS\textsuperscript{142}.

### 2.3.3 Frontier Orbital Energies

The DFT calculated energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of compounds 5-S and 5-SO\textsubscript{2} were previously reported; the HOMO was relatively unchanged in energy however a decrease in the LUMO energy was observed as the oxidation state increased\textsuperscript{184}. In compounds 5-7, HOMO and LUMO energies are calculated from the experimental electrochemical data (oxidation and reduction potentials) and UV-vis absorption data (Figure 2.7). The oxidation and reduction potentials of 5-7 were measured using cyclic voltammetry (CV). No polymerization was observed since they have a stable radical cationic state (Figure A2.1 and Figure A2.2)\textsuperscript{206-207}. In 5-7, a decrease in energy is observed for both HOMO and LUMO when the sulfur bridge is oxidized, however only the LUMO energy decreases as \(n\) increases (Figure 2.7). The sulfur oxidation state affects the HOMO energy in 5-7 but not in 4; this may be due to the differences in how the data were acquired (DFT calculated for 4, experimentally determined for 5-7). It is also possible that the sulfur group has less involvement in the HOMO in 4 (localized more on the terthiophene group) than in 5-7 which incorporate only single thiophene bridges.

To compare with reported literature values for \(\alpha\)-oligothiophenes, the reported oxidation and reduction potentials for 8-10 were converted to HOMO and LUMO energies using the same treatment as for the experimental data for compounds 5-7. The HOMO energies were found to be lower in energy than those of the \(\alpha\)-oligothiophenes 8-10 (-5.70 eV for 8, -5.43 eV for 9 and -5.37 eV for 10)\textsuperscript{208}. Similarly, the LUMO
values (-2.37, -2.75 and -2.9 eV for \(\alpha\)-oligothiophenes 8-10 with \(n = 2, 3, 4\) respectively) are higher in energy than those of the sulfur-bridged analogs.\textsuperscript{209} It is well known that conjugated oligomers show a decrease in HOMO-LUMO gap with an increase in conjugation length. In both the sulfides and sulfones, the HOMO-LUMO gap decreases as the length of the oligomer increases (only the HOMO-LUMO gap for \(7\)-SO\(_2\) is greater than for \(6\)-SO\(_2\)).

**Figure 2.6** Frontier orbital calculated energy levels. \(a\). Values obtained from cyclic voltammetry measurements (see Figure A2.1 and Figure A2.2) and UV-vis absorption spectra, \(b\). Values calculated in reference [184]

In the polymers, the frontier energy levels were estimated from the onset potentials\textsuperscript{210} of oxidation and reduction using cyclic voltammetry (corresponding to HOMO and LUMO respectively, Figure A2.4).\textsuperscript{195} The calculated values of the band gaps obtained in this way were compared to the low energy onset of absorption, which is expected to correspond to the HOMO-LUMO transition. An increase of the band gap can be observed (2.39 eV (P1) and 2.68 eV (P2) for optical band gaps and 2.89 eV (P1) and 2.97 eV (P2) for electrochemical band gaps) as the oxidation state of the bridging sulfur increases (Figure 2.6). This is consistent with the results for compounds 5-7 –S and –SO\(_2\). Furthermore, P1 and P2 exhibit similar
behavior to 4-S and -SO₂, where the energy of the LUMO slightly decreases as the oxidation state increases (-3.43 eV and -3.54 eV for P1 and P2 respectively); and the decrease in the HOMO is more pronounced (-5.82 eV and -6.22 eV), consistent with what is observed in the oligomers 5-7.

Figure 2.7 UV-vis absorption spectra of compounds 5-7 (-S and -SO₂) in acetonitrile at 293 K (where A., B., and C. correspond to n = 2, 3, 4 respectively) and D. is a plot of wavelength of maximum absorbance (λ_max) for the lowest energy absorption band vs n .

2.3.4 Absorbance Spectroscopy

2.3.4.1 Oligomers

The bridging sulfur atoms formally break the conjugation in oligomers 5-7, however these are structurally analogous to α-oligothiophenes 8–10 in terms of the number of thiophenes (n) and the position of substitution on the thiophenes. The general absorption spectra of 5-7 show two characteristic absorptions (~240 nm and 260-500 nm) (Figure 2.7). The higher energy absorption is assigned to a localized transition on the thiophene, whereas the lower energy band is dependent on the number of thiophenes. It undergoes a bathochromic shift as n increases (Figure 2.7D), analogous to the trend in unsubstituted 8–10 (303, 354 and 392 nm). The lowest energy band is consistently broader for the sulfides relative to the corresponding sulfones; this is attributed to the contribution of multiple conformations with differing degrees of interaction between the thiophenes across the sulfide bridge, while the sulfone bridges prevent such interactions due to the lack of lone pairs on the sulfur. It has been previously shown by calculation that the sulfur atom facilitates interactions between rings in PPS despite the fact that they are perpendicular to each other as
observed by X-ray diffraction. The sulfur bridge accounts for delocalization; mainly through the 3pₓ orbital.¹³⁴,²¹³-²¹⁴ We use the low energy absorption onset as a measure of the HOMO-LUMO gap, this increases with increasing sulfur oxidation state consistent with the trends observed in the electrochemical data. The absorption maxima show an opposite trend, however this is attributed to the presence of multiple conformers with differing degrees of interaction between thiophenes in the sulfides, whereas in the sulfones all conformers presumably have a similar lack of interaction across the sulfone bridge.

![Chart 2.3](image)

**Chart 2.3**

**Chart 2.4** Methyl-containing oligomers 11 and 12 and their analogues 6 and 7.

![Figure 2.8](image)

**Figure 2.8** UV-vis absorption spectra of compounds with A. two or B. three sulfur-bridge linked with all thiophene (6 and 7) or methyl flanked (11 and 12) in MeCN at 298 K.

Model compounds where the terminal thiophene was replaced by a methyl group (11 and 12) were synthesised to measure the impact of the α,ω-substitution with a methyl sulfide or sulfone group (Chart 2.4). The observed shifts in the lowest energy absorption band in Figure 2.8 suggest that sulfide-bridged
thiophenes behave as α,ω-substituted thiophene rings, where the absorption transition involves the sulfur atom.\textsuperscript{215} In the case of the sulfone-bridged thiophenes, the absorption is only dependent on the number of thiophene rings and the sulfone substitution does not impact on the electronic transition, consistent with the results above.

2.3.4.2 Polymers

The polymers P1 and P2 have similar absorption spectra to the small molecules; and the absorption onset, which correlates to the optical band gap, also differs significantly between the two materials (ranges from 2.18-2.34 eV for P1 and 2.34-2.58 eV for P2) (Figure 2.9A and B). In the case of P1, the breadth of the peak increases and the absorption maximum red shifts as the molecular weight increases a consequence of the greater interaction between the terthiophene segments across the bridge, and consistent with the results for the oligomers.

![Figure 2.9](image)

\textit{Figure 2.9} A. UV-vis absorption spectra of P1(A-C) and B. P2(A-C) in CH\textsubscript{2}Cl\textsubscript{2} at 298 K.

In the case of P2(A-C), the spectra nearly overlap completely and only the onset is slightly shifted for the lower molecular weight polymer. Similar to the oligomers, the absorption bands of the sulfone bridged polymers are narrower than for the corresponding sulfides. Furthermore the absence of conductivity when PPS is oxidized suggests that the sulfone, bearing no lone pairs, also acts here as an insulating group preventing effective electron delocalization on the polymer chain.\textsuperscript{134}
The absorption spectra of the polymers show a slight red shift from solution to the solid state, indicating the possible presence of interchain interactions (Figure 2.10).\textsuperscript{216-218} Furthermore, when the polymer films are annealed at 120 °C, the absorption profile stays the same and the absorption intensity remains unchanged for P1 but slightly increases in P2. This change in absorption intensity is indicative of an increase in ordering of the polymer chains. The absence of changes in P1 could be due to the polymer already being in its lowest energy conformation or that the reorganization energy has not been reached.\textsuperscript{219-220} Utilizing differential scanning calorimetry phase changes of the polymers (Figure A3.2) were examined. P2 has a transition at 97 °C assigned as a glass transition (T\textsubscript{g}) and shows the possible onset of T\textsubscript{c} at 145 °C, which is lower than in PPS (T\textsubscript{c} = 208 °C);\textsuperscript{221} P1 did not exhibit any characteristic features. This explains the change in intensity of the absorption upon annealing of the polymers; P2 was heated above T\textsubscript{g} allowing for chain reorganization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.10}
\caption{A) UV-vis spectra of polymers cast from specified solvents; B) UV-vis spectra of polymer pre- and post-annealing at 120 °C for 10 min.}
\end{figure}
Figure 2.11 Emission spectra of the oligomers 5-7, 11 and 12 in A. MeCN and B. PMMA matrix at 298 K.

2.3.5 Photoluminescence

2.3.5.1 Oligomers

The photoluminescence properties of sulfur-bridged chromophores are highly dependent on the oxidation state of the sulfur bridge. Compounds 5-7 exhibit different emission behaviour in solution based on the oxidation state of the bridges (Table 2.4): the sulfones are emissive while the sulfides show only very weak emission. The quantum yields of (5-7)-SO₂ (0.0016, 0.032 and 0.036 for \( n = 2, 3, 4 \) respectively) are lower than for 8–10 (0.01, 0.056 and 0.16 for \( n = 2, 3, 4 \) respectively) and are not proportional to \( n \). The emission is also dependent on the amount of sulfone bridges contained in the molecule. Compound 11-SO₂ and 12-SO₂ are much less emissive, as seen in Figure 2.11A, but the emission intensity increases as the number of sulfone increases while keeping the number of thiophene ring constant. With this information, the presence of the sulfone on a compound increases the quantum yield but it remains much lower than when the thiophene rings are fully conjugated.
Table 2.4 Photophysical properties of compounds 5-7 (-S and -SO₂) in acetonitrile and in PMMA matrix.

<table>
<thead>
<tr>
<th></th>
<th>Solution</th>
<th>PMMA</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_{abs} (nm)</td>
<td>λ_{em} (nm)</td>
<td>Φ_f(^a)</td>
<td>λ_{abs} (nm)</td>
</tr>
<tr>
<td>5-S</td>
<td>263</td>
<td>-</td>
<td>-</td>
<td>268</td>
</tr>
<tr>
<td>5-SO₂</td>
<td>277</td>
<td>363</td>
<td>0.0016 ± 0.0008</td>
<td>278</td>
</tr>
<tr>
<td>6-S</td>
<td>286</td>
<td>-</td>
<td>-</td>
<td>286</td>
</tr>
<tr>
<td>6-SO₂</td>
<td>295</td>
<td>462</td>
<td>0.034 ± 0.004</td>
<td>295</td>
</tr>
<tr>
<td>7-S</td>
<td>294</td>
<td>-</td>
<td>-</td>
<td>294</td>
</tr>
<tr>
<td>7-SO₂</td>
<td>302</td>
<td>456</td>
<td>0.036 ± 0.005</td>
<td>302</td>
</tr>
</tbody>
</table>

\(^a\) obtained by comparative method against anthracene. \(^b\) obtained with an integrating sphere

Figure 2.12 Emission spectra of compound A. 6-SO₂, B. 7-SO₂, C. 11-SO₂ and D. 12-SO₂ in specified solvents at 298 K.

The emission of all the compounds red shifts as the solvent polarity increases (Figure 2.12). This indicates that the excited state is polarized and can be stabilized by polar solvents, therefore diminishing the energy of the emitting state.\(^2\) In the solid state, a matrix was used to allow measurement of emission of compound 5-S which is an oil. The emission is blue-shifted, which suggests the presence of a higher energy emitting
species. This is attributed to the limited reorganization potential of the molecule in the matrix (Figure 2.11B).

![Relative emission of the A. polythienyl sulfides P1 and B. polythienyl sulfones P2 in DCM at 298 K corrected for optical density at the excitation wavelengths of the solutions.](image)

**Figure 2.13** Relative emission of the A. polythienyl sulfides P1 and B. polythienyl sulfones P2 in DCM at 298 K corrected for optical density at the excitation wavelengths of the solutions.

### 2.3.5.2 Polymers

The emission spectra of the polymers are shown in Figure 2.13. The emission of P2(A-C) is shifted ~60 nm to the blue compared to P1(A-C) as shown in Figure 2.13. Furthermore, the emission of the sulfide-containing polymers is dependent on the polymer molecular weight with a bathochromic shift of 30 nm observed between polymers P1-B (1300 g mol$^{-1}$) and P1-C (2700 g mol$^{-1}$). The emission of P1 (539 nm) is found at much lower energy than what is observed from sulfide-bridged terthiophene 4-S (473 nm)$^{184}$ On the other hand, for P2 (460 nm) the emission energy is closer to that of the oligomers 6-SO$_2$ and 7-SO$_2$ (480 nm). The presence of a lower energy emitting state in P1 is consistent with a larger degree of interaction between terthiophenes moieties over the sulfide bridges, while in the sulfone-bridged P2 there is no evidence for long range interactions.
Figure 2.14 Emission of A. P1 and B. P2 pre- and post-annealing at 120 °C for 10 min.

P1 has similar emission intensity to P2 for solutions with comparable optical density, however P2 is relatively more emissive than P1 in the solid state (Figure 2.14). The annealing of the films at 120 °C for 10 min decrease the intensity of emission, but the emission spectra remains unchanged suggesting an increase in the amount of low energy non-emissive interchain species.70

Table 2.5 Photophysical properties of the P1(A-C) and P2(A-C).

<table>
<thead>
<tr>
<th></th>
<th>M_n (g mol⁻¹)</th>
<th>PDI</th>
<th>λ_max (nm)</th>
<th>Onset (nm)</th>
<th>λ_max (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-A</td>
<td>2,400</td>
<td>2.8</td>
<td>374</td>
<td>535</td>
<td>539</td>
</tr>
<tr>
<td>P1-B</td>
<td>1,300</td>
<td>3.0</td>
<td>369</td>
<td>516</td>
<td>526</td>
</tr>
<tr>
<td>P1-C</td>
<td>2,700</td>
<td>2.8</td>
<td>392</td>
<td>575</td>
<td>558</td>
</tr>
<tr>
<td>P2-A</td>
<td>8,300</td>
<td>1.6</td>
<td>385</td>
<td>475</td>
<td>481;501</td>
</tr>
<tr>
<td>P2-B</td>
<td>8,500</td>
<td>1.7</td>
<td>386</td>
<td>478</td>
<td>480;501</td>
</tr>
<tr>
<td>P2-C</td>
<td>2,100</td>
<td>3.2</td>
<td>387</td>
<td>487</td>
<td>507;484</td>
</tr>
</tbody>
</table>
2.4 Conclusions

The polymerization of thienyl sulfide and sulfone with 2,5-dibromo, 3,4-dialkyl thiophene was carried out using DHAP. The molecular weights of the resulting materials were obtained through GPC and $^1$H NMR where the chain end signals were identified and they were found to be overestimated by GPC. The resulting polymers were found to have relatively low molecular weights and show a polydispersity that ranges from 1.5 to 3. The electronic and photophysical properties of the oligomers and polymers were compared to those of model compounds containing no sulfur bridged ($\alpha$-oligothiophene 8-10) and to sulfur-bridged terthiophene 4 respectively. The oligomers were found to 1) have a lower HOMO and LUMO energy when the sulfur bridge is a sulfone, 2) have a higher emission when bridged by sulfones and 3) behave similarly to conjugated $\alpha$-oligothiophene when bridged by sulfides. The polymeric materials were found to have 1) a lower HOMO and a larger bandgap upon oxidation of the sulfur bridge, 2) a more intense emission with sulfone containing polymer and 3) a dependence of the optical behavior on the molecular weight in the presence of the sulfide only. These results suggest that there is orbital overlap between the terthiophene segments and the bridging sulfur; which allows for delocalization on the polymer chain.
Chapter 3: Copolymerization of Aryl –Sulfides and –Sulfone

3.1 Introduction

The incorporation of p-block elements into the backbone of polymers furthers the potential applications of these materials. A wide array of elements have been incorporated into such polymers, including boron, phosphorous and silicon. Sulfur-containing polymers have been studied and this element has been mainly incorporated into aromatics (thiophene), as pendant groups, and as disulfides. The incorporation of p-block elements into polymer backbones between conjugated units is also of interest, with poly-para-phenylene sulfide being a relatively well-studied example.

As previously discussed, sulfur-bridged chromophores show enhanced emission upon changing the oxidation state of the sulfur atom. Their incorporation into conjugated polymers leads to polythienyl sulfide and sulfone, which have distinct emissive properties and electronic structure. Properties of conjugated polymers can be tailored for different electronic applications by changing the electron density on the co-monomer to achieve the desired properties. We envisioned utilizing this approach along with varying the oxidation state of the sulfur bridge (sulfide moiety being more electron rich than sulfone) for further tuning of the properties of copolymers containing both sulfur bridges and conjugated units.

In this chapter, sulfur-bridged (sulfide or sulfone) monomers are copolymerized with known organic comonomers, which are either electron-rich or electron-deficient (Chart 3.1). The resulting materials are characterized using \(^1\)H and COSY NMR, UV-vis absorption and emission spectrosopies, cyclic voltammetry, thermal gravimetric analysis, and differential scanning calorimetry. Furthermore, by incorporating a bithiazole moiety (ie P5 and P6), one can envision complexation of metals to further tune the photophysical and electronic properties of the polymers. The effect of copper(I), silver(I) and palladium(II) ions on the emission properties of these materials is investigated here.
3.2 Experimental

3.2.1 General

Cesium carbonate was purchased from Alfa Aesar. 9,9-Dioctyl-2,7-dibromofluorene, tetrakis(acetonitrile)copper(I) tetrafluoroborate, copper(I) acetate, silver(I) triflate, silver(I) trifluoroacetate, palladium(II) acetate, palladium(II) trifluoroacetate, and tetrabutylammonium tetrafluoroborate were purchased from Sigma. Dichloro(1,5-cyclooctadiene)palladium(II),\textsuperscript{226} 4,7-dibromo-2-n-hexylbenzotriazole,\textsuperscript{227} 5,5’-dibromo-4,4’-dihexy-2,2’-bithiazole,\textsuperscript{228} tri-o-methoxyphenyl phosphine,\textsuperscript{190} trans-bis(acetato)bis[o-(di-o-toly)phosphino]benzyl]dipalladium(II) (Herrmann-Beller catalyst),\textsuperscript{189}
2,2-dibromo-4,8-bis(octyloxy)-benzo[1,2-b:4,5-b’]dithiophene\textsuperscript{229} were prepared according to reported procedures. Chemicals were used as received and THF was distilled and degassed with N\textsubscript{2} for 20 min before use.

Polymer molecular weights were determined by gel permeation chromatography (GPC) using an Agilent liquid chromatograph equipped with an Agilent 1200 series isocratic pump, Agilent 1200 series standard auto sampler, Phenomenex Phenogel 5 mm narrow bore columns (4.6 × 300 mm) 104 Å (5,000–500,000 Da), 500 Å (1,000–15,000 Da), and 103 Å (1,000–75,000 Da), and a Wyatt Optilab T-rEx differential refractometer (λ = 658 nm, 40 °C). A flow-rate of 0.5 mL min\textsuperscript{-1} was used and samples were dissolved in THF (ca. 1 mg mL\textsuperscript{-1}). Molecular weights were determined by comparison to polystyrene standards.

Thermal stability measurements were performed by thermogravimetric analysis (TGA) using a PerkinElmer Pyris 6 thermogravimetric Analyzer with a porcelain crucible. A TA Instruments Q1000 differential scanning calorimeter (DSC) was employed to examine phase transitions. The samples were cycled from 0 °C to 250 °C at 10 °C min\textsuperscript{-1}.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance 400 inverse broadband probe at 298 K using the residual protonated solvent peak for referencing.

UV-visible absorption spectroscopy was carried out on a Cary Varian 5000 UV-vis-near-IR spectrophotometer using HPLC grade solvents. The optical band gap was estimated from the onset of absorption spectra in CH\textsubscript{2}Cl\textsubscript{2}. Photoluminescence spectra was measured on a Photon Technology International QuantaMaster 50 fluorimeter equipped with a double monochromator using a 75 W Xe arc lamp as the source. Photoluminescence spectra were measured at room temperature. Solutions had absorbance bellow 0.1 and were normalized using their absolute absorbance. Solid state measurements were performed on VWR VistaVision\textsuperscript{™} White glass microscope slides and annealing was performed in a Hewlett Packard 5890 series II oven. Quantification of the emission quenching by the metals ions was performed by making solutions in triplicate and letting them stand to equilibrate for 16 h for the
palladium(II) ions, 1 h for copper(I), and 10 h for the silver(I) solutions. The solutions were prepared by the addition of 100 µL of a 10⁻⁵ M solution of the polymer in a 10 mL volumetric flask. Aliquots of a fresh stock solution metal complexes were added to the flask and they were completed to the graduation mark with HPLC grade non-UV stabilized THF. Measurements were performed after the above mention time.

Electrochemical measurement were performed using a Pine AFCBP1 bipotentiostat in an airtight three-electrode cell with a 7 mm glassy carbon working electrode (Bioanalytical Systems, Inc.), platinum mesh counter electrode, and silver wire pseudoreference electrode in an electrolyte solution of 0.10 M triply recrystallized (n-Bu₄N)PF₆ in anhydrous MeCN sparged with nitrogen prior to use. The glassy carbon electrode was cleaned by successive polishing with 1, 0.3, and 0.05 µM alumina paste, followed by rinsing and sonicating in deionized water. The polymer was deposited on the glassy carbon electrode from THF. Ferrocene was added at the end of the electrochemical experiments as an internal standard, and the HOMO energy level was calculated according to equation 1.¹⁹⁵

\[
E_{\text{HOMO}} = -(E_{\text{onset,ox}} + 5.1)(eV)
\]

where the \(E_{\text{onset}}\) is versus the Fe⁺/Fc couple.

Furthermore, the LUMO energy can be estimated by the addition of the band gap (\(E_g\)) obtained by UV-vis absorption to the HOMO energy obtained by equation 1. This method is commonly used since the reduction of polymers can be difficult to measure and this approach reduces the overestimation of the frontier orbitals.

\[
E_{\text{LUMO}} = E_g + E_{\text{HOMO}}
\]

### 3.2.2 Methods

**2,2'-Bisthiazole sulfide (13-S, tzS).** This compound was prepared according to the reported procedure.²³⁰

\(^1\text{H} \text{NMR (400 MHz, CD}_3\text{CN)} \delta: 7.84 \text{ (d, } J = 3.4 \text{ Hz, 2H)}, 7.64 \text{ (d, } J = 3.4 \text{ Hz, 2H)}\). \(^{13}\text{C}^{\text{\{1\text{H}\}} \text{ NMR (100 MHz, CD}_3\text{CN)} \delta: 164.8, 146.9, 130.2. HRMS (EI) [M]+ calcd. 199.9537; found 199.9537. Anal. calcd. for C₆H₄N₂S₃: C 35.98, H 2.01, N 13.99, S 48.02; found: C 36.16, H 1.99, N 14.01, S 47.64.
2,2’-Bisthiazole sulfone (13-SO₂, tzSO₂). Compound was prepared according to the reported procedure.¹⁹⁶ ¹H NMR (400 MHz, CD₂CN) δ 8.08 (d, J = 3.0 Hz, 2H), 8.05 (d, J = 3.0 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CD₂CN) δ: 164.5, 146.3, 128.5. Anal. Calcd. for C₆H₄N₂O₂S₃: C 31.02, H 1.74, N 12.06, S 41.41; found: C 11.95, H 1.60, N 11.95, S 41.20. * undergoes reaction upon ionization, MS ESI [M]+ not observed.

**General polymerization method.** 2,2’-Dithienyl sulfide or sulfone (1 mmol), the appropriate dibrominated comonomer (1 mmol), tri-o-methoxyphenyl phosphine (0.1 mmol), cesium carbonate (2.5 mmol) and Herrmann-Beller catalyst (2.5 mol%) were placed inside a 2-5 mL Biotage microwave vial with a magnetic stirring bar. The vial was sealed with a rubber septum and thoroughly purged with nitrogen. Degassed anhydrous THF was added and the reaction mixture stirred at 125 °C for 48 h, then the polymer was precipitated in MeOH:HCl (10 %) (9:1), and filtered through a 0.45 µm nylon membrane. The resulting polymer was dried at 60 °C in a vacuum oven for 16 h.

3.3 Results and Discussion

3.4 Synthesis

The copolymers were synthesis according to the optimized conditions from Chapter 2. Attempts to copolymerize the sulfur-bridged thiazole (13, tzS and tzSO₂) were unsuccessful with a sulfide (P11), while a sulfone (P12) yielded polymeric material (Scheme 3.1). This difference in reactivity was attributed to the chelating ability of tzS and it was further explored in Chapter 4.
Scheme 3.1

\[
\begin{align*}
\text{Scheme 3.1} & \\
\text{Reaction 1} & : \quad \text{Scheme 3.1} \\
\text{Reaction 2} & : \quad \text{Scheme 3.1}
\end{align*}
\]
3.4.1 NMR

NMR spectroscopy was used to confirm the structure of the copolymers repeating unit. Complete assignment of the protons signals was not always possible, however the integration of the aromatic protons relative to a specific alkyl CH$_2$ unit gave the expected ratio for an alternating copolymer. Assignment of the NMR spectrum has been previously reported in Chapter 2 for polymer P1 and P2. The 1D and 2D proton NMR spectra ($^1$H and COSY) and their assignment (when available) are shown in Figure A1.1 - Figure A1.8.

2-$n$-Hexylbenzotriazole copolymers (P3 - P4). The spectrum of the sulfide-containing polymer (P3) has many overlapping peaks and the assignment of the protons and the end-chain signal was not possible. However, the structure of the repeat unit is confirmed as the integration ratio of the 4.77 ppm CH$_2$ alkyl peak (on the hexyl chain) versus the aromatic region is 6:2 (CH$_2$:Aromatic). The sulfone-containing polymer (P4) has an aromatic region composed of 6 multiplets centered at 8.02, 7.99, 7.81, 7.77, 7.72 and 7.12 ppm. The three protons on the terminal thiophene were identified as the signal at $\delta$ 7.12 ppm along with two shoulders at $\delta$ 7.78 and 7.70 ppm. With this information, a calculation of the molecular weight was possible and the resulting value is significantly lower than the value obtained by GPC (GPC: $M_n = 1,800$ g mol$^{-1}$, NMR: $M_n = 860$ g mol$^{-1}$).

4,4’-Dihexyl 2,2’-bithiazole copolymer (P5 - P6). The $^1$H NMR spectra of these polymers are simpler to interpret due to the two set of two equivalent protons and both polymers show a ratio of 4:4 (alkyl CH$_2$: aromatic region). In the sulfide containing polymer (P5), a broad signal is observer from $\delta$ 7.21-7.07 ppm and corresponds to the aromatic protons (H1 and H2) in the main chain. There are three smaller features at $\delta$ 7.42, 7.29 and 7.01 ppm that are slightly more resolved and show COSY correlation. The latter peaks can be assigned as the three protons on the terminal thiophene of the chain. Using the integration of these signals (especially the peak at $\delta$ 7.42 ppm which is fully resolved) the molecular weight is calculated to be 1,590 g mol$^{-1}$, which is much lower than the value obtained by GPC ($M_n = 4,800$ g mol$^{-1}$). In the sulfone-containing polymer (P6) the two aromatic protons are resolved at $\delta$ 7.73 and 7.20 ppm. Two smaller signals at $\delta$ 7.77
and 7.67 ppm were attributed to the protons on the thiophene at the end of the chain and these were confirmed by 2D proton NMR. A molecular weight of 1,700 g mol\(^{-1}\) (lower than the GPC value of 3,400 g mol\(^{-1}\)) was calculated when these signals were integrated against the main chain protons.

**9,9’-Dioctyfluorene copolymers (P7 - P8).** The NMR analysis of these polymers was performed with limited success since the five protons are overlapping. Despite this, the integration of the aromatic region relative to a resolved CH\(_2\) alkyl signal (\(\delta 1.88\) ppm for P7 and \(\delta 2.03\) ppm for P8) gave the expected ratio of 4:10 (CH\(_2\): aromatic protons), confirming the chemical structure of the polymer.

**4,8-Bis(octyloxy) benzo[1,2-b:4,5-b’]dithiophene copolymers (P9 - P10).** Identification of the end chain proton was not possible for the sulfide-containing polymer (P9). The structure of the repeating unit was confirmed with the ratio of the integration of CH\(_2\) protons (\(\delta 4.24\) ppm) versus the protons in the aromatic region of 4:6. While the sulfone-containing polymer (P10) has a crowded aromatic region, no correlation with the signal at \(\delta 7.46\) ppm were observed by 2D COSY NMR. This signal is attributed to the proton on the benzo[1,2-b:4,5-b’]dithiophene (BDT) at terminus near the bromine (H3’). Using the integration of the \(\delta 7.46\) ppm signal relative to the integration of the remainder of the aromatic region, a molecular weight of 2,000 g mol\(^{-1}\) was calculated. This is also lower than the value obtained by GPC (3,500 g mol\(^{-1}\)).

In all cases where the polymer molecular weight was determined by both GPC and NMR spectroscopy, the value obtained by NMR was lower than the GPC value. This is attributed to chain folding and the required method to calculate the molecular weight using GPC. As the polymers are emissive, the use of dynamic light scattering is not possible due to over estimation of the size with the emission of the polymer. Furthermore, the use of the polystyrene calibration curve leads to overestimation of the molecular weight as the polymers structures are quite different and adopt different effective radius and morphologies in THF, leading to different elution times for similar molecular weight polymers.
These materials exhibit low degrees of polymerization and they are consistent with oligomers (Table 3.1). Optimization of the polymerization condition would have to be performed to increase the molecular weights.

**Table 3.1** Molecular weight, polydispersity and degree of polymerization of sulfur-containing copolymers (P3-P10).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$D^b$</th>
<th>DP$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3</td>
<td>2300</td>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>P4</td>
<td>1800</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>P5</td>
<td>5200</td>
<td>3.9</td>
<td>9</td>
</tr>
<tr>
<td>P6</td>
<td>6200</td>
<td>1.6</td>
<td>11</td>
</tr>
<tr>
<td>P7</td>
<td>3400</td>
<td>2.3</td>
<td>5</td>
</tr>
<tr>
<td>P8</td>
<td>4200</td>
<td>1.9</td>
<td>6</td>
</tr>
<tr>
<td>P9</td>
<td>2200</td>
<td>1.6</td>
<td>3</td>
</tr>
<tr>
<td>P10</td>
<td>3500</td>
<td>2.0</td>
<td>5</td>
</tr>
</tbody>
</table>

a. Molecular weight calculated by GPC; b. polydispersity; and c. degree of polymerization.

### 3.4.2 Estimation of Frontier Orbitals Energies

The impact of the oxidation state and the nature of the co-monomer on the frontier orbitals was established by using cyclic voltammetry and UV-vis spectroscopy (Figure 3.1). The HOMO energy can be calculated using equation 1, assuming that the electrochemical event involves the HOMO.$^{195}$ The energy of the LUMO was calculated using equation 2, where the optical band gap is calculated from the onset of the absorption spectra of the polymer, assuming the lowest energy transition corresponds to the HOMO-LUMO gap (Figure A2.4 - Figure A2.8). The comonomers are considered having increased electron-donating capacity in the following order: triazole < bithiazole < thiophene < fluorene < benzodithiophene.$^{53,231}$
In the case of the electron rich sulfide-containing polymers, the LUMO energy is lower in energy when polymerized with electron rich co-monomer. The HOMO decreases in energy with highly electron rich or poor comonomers. The formation of an electronic push-pull (electron poor – electron rich) copolymer in P3 leads to an intrachain charge transfer, lowering the HOMO. Meanwhile P9 is a highly electron rich and it has a lower energy HOMO.\textsuperscript{63,232-233}

The LUMO of the sulfone-containing polymers increase in energy as the electron density increases on the co-monomer. The exception is fluorene-containing polymer (P8). The energy of the HOMO remains relatively constant throughout the polymer series, except for the BDT copolymers (P10) where it is much higher in energy. A high energy HOMO is typical of BDT containing polymers, which can be attributed to the high electron density making the oxidation more facile at this site.\textsuperscript{234-235}

The nature of the co-monomer does not appear to a specific impact on the magnitude of the band gap of the polymers. However, the oxidation state of the sulfur bridge leads to higher energy transitions for the analogous polymer containing the same co-monomer.
3.4.3 Physical Properties

Differential scanning calorimetry was performed on the copolymers, only P2, P6 and P8 exhibit an observable phase transition (Figure A3.2). The melting temperature (T_m) was observed to be 97 °C for P2, and 89 °C for P6. In the case of P6, crystallization was also observed at 60 °C. P8 exhibit a small transition at approximately 97 °C which could also be a crystallization event.

The thermal stability was measured using TGA and the sulfone containing polymers were found to be stable to higher temperatures (Figure A3.3 and Figure A3.4). In all cases, the decomposition temperature was between 350-400 °C which is typical for conjugated polymers. This information was used to attempt to improve the optical properties of thin films by thermal annealing.

3.4.4 UV-vis Absorption Spectroscopy

The absorbance maximum of the polymers depends on the co-monomer used (Figure 3.2). In the case of the sulfide-containing polymers, the absorption maximum increases with increasingly electron rich co-monomers. A similar trend is observed with the sulfone-containing polymers, despite the sulfone monomer being more electron-poor than the sulfide.

![Absorbance Spectra](image)

Figure 3.2 UV-vis absorbance spectra of A. sulfide containing and B. sulfone containing copolymer in dichloromethane.

The absorption spectra all consist of a single Gaussian band except for the fluorene (P7 and P8) and benzodithiophene (P9 and P10) containing copolymers. The second feature in the absorption spectrum of
**P7** is attributed to a fluorene-centered absorption in the copolymer (expected at ~370 nm) while in **P8** the transition is only present as a shoulder.\(^{240}\) The copolymers **P9** and **P10** both show a feature at ~430 nm that can be attributed to a transition on the BDT.\(^{235,241}\)

The absorbance of the polymers does not shift significantly with solvent polarity \((E_T(30))^{242}\) (Figure A4.1). The polymer film absorbance exhibited a small red shift relative to the absorbance in solution, indicating the presence of interchain interaction. The magnitude of the shift depends on the solvent from which the polymer was cast; where a film cast from a less polar solvent (THF) favors interchain interactions compared to a more polar solvent \((\text{CH}_2\text{Cl}_2)\) (Figure A4.2). Attempts at increasing the crystallinity of the polymer films by annealing at 120 °C was sensitive to thickness of the films; thin films did not show a decrease in absorbance upon annealing, while thicker films were visibly more opaque.
Table 3.2 Photophysical properties of the polymers in different solvents and in the solid state where the films were cast from different solvents.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solution*</th>
<th>Solid state</th>
<th>Solid state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption (nm)</td>
<td>Emission (nm)</td>
<td>Absorption (nm)</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>PhCl</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>P1</td>
<td>400</td>
<td>550</td>
<td>386</td>
</tr>
<tr>
<td>P2</td>
<td>385</td>
<td>485</td>
<td>397</td>
</tr>
<tr>
<td>P3</td>
<td>440</td>
<td>556</td>
<td>491</td>
</tr>
<tr>
<td>P4</td>
<td>407</td>
<td>465</td>
<td>469</td>
</tr>
<tr>
<td>P5</td>
<td>409</td>
<td>555</td>
<td>432</td>
</tr>
<tr>
<td>P6</td>
<td>403</td>
<td>522</td>
<td>462</td>
</tr>
<tr>
<td>P7</td>
<td>353</td>
<td>544</td>
<td>518</td>
</tr>
<tr>
<td>P8</td>
<td>382</td>
<td>431</td>
<td>427</td>
</tr>
<tr>
<td>P9</td>
<td>407</td>
<td>530</td>
<td>412</td>
</tr>
<tr>
<td>P10</td>
<td>375</td>
<td>570</td>
<td>374; 457</td>
</tr>
</tbody>
</table>

* in dichloromethane

3.4.5 Photoluminescence

All the polymers reported here are emissive in solution and in the solid state. The emission was found to be dependent on the oxidation state of the sulfur bridge. The emission of the sulfone containing polymers is up to five times more intense than the sulfide in solution (Figure 3.3). These results are consistent with previous work on small molecules, where the sulfone-bridged chromophores show enhanced emission.¹⁸⁴
Figure 3.3 Emission spectra of the copolymers containing A. sulfides and B. sulfones in dichloromethane at 293 K.

In the case of the sulfur-containing polymers, the emission intensity is relatively similar for all polymers studied. The emission wavelength can be modulated using different co-monomers; the energy of emission decreases with comonomers of increasing electron deficiency.

When the polymers contain sulfones, the emission can be tuned over a wider range, but there is no relationship between the emission energy and the nature of the co-monomer. The intensity of emission varies depending on the polymer, where P4 and P8 show more intense photoluminescence. This is to be expected for benzotriazole (P3 and P4) and fluorene (P7 and P8) containing polymers as they are known to be highly efficient emitters. In the case of P10, much weaker emission is observed and it is red shifted from the counterpart without a sulfur bridge (495 nm). BDT is known to form π-π stacked aggregates in solution due to its increased planarity, explaining the lower emission observed.

The emission of some of the polymers (P1, P2, P3, P7, P9 and P10) was found to be slightly dependent on the polarity of the solvent (Figure A4.3). In all cases, the shift is no more than 20 nm and the emission energy increases as the polarity of the solvent decreases. However, the energy difference is not significant to suggest a pronounced charge transfer behavior.

In the solid state, the emission spectra are also dependent on the solvent used to cast the films (Figure A4.4). The chains adopt different conformations to minimize enthalpy contingent on solvent. A good
solvent will favor an unraveled chain while a poor solvent will have highly folded chains. Therefore, casting the polymers from chlorobenzene (PhCl) leads to more interchain interactions and a decrease in emission intensity, while a film cast from chloroform leads to a more disordered chains and more intense emission.

3.4.6 Effect of Metal Cations on Emission

Measurements of the photophysical properties in the presence of metal ions was performed on P5 and P6 to determine whether the bithiazole moiety could chelate metals, resulting in a change in emission. The following metals and ligands were used for these measurements: Pd(COOCH₃)₂, Pd(COOCF₃)₂, Pd[cod]Cl₂, CuCOOCH₃, Cu(MeCN)₄(BF₄), Ag(OTf) or AgCOOCF₃. Different ligands were used to assess the impact of stronger/weaker metal coordination interaction with the polymers. Qualitative measurements were performed by UV-vis and NMR with solid metal complexes being added to the polymers in solution. Quantitative measurements were performed by adding different amounts of a stock solution of metal complexes in THF to the polymer in solution. The resulting solutions were left to stand (between 1 h to 16 h) to equilibrate and the emission were afterwards measured. Treatment of the intensity of emission of the polymer without metal addition divided by the intensity of the emission with metal against the concentration of the metal ion gave a Stern-Volmer like plot (Figure A4.7 - Figure A4.16). Quantification of the quenching was carried out for polymers P1, P2, P5 and P6 to monitor the impact of the sulfur bridge and the bithiazole moiety (Figure 3.4 and Table 3.3). A linear regression was fitted to all the curves, even when the data deviate from linearity to allow comparison between the different polymers and metals. The deviation could be due to the range of concentration of the quencher being outside the linearity regime of the Stern-Volmer relationship and/or the quenching being a static phenomenon rather than dynamic.
Figure 3.4 Emission quenching upon addition of Pd(COOCF$_3$)$_2$ to a solution of P5 in THF at 293 K.

Upon qualitative addition of metal, the $^1$H NMR chemical shifts are shifted for polymers P5 and P6, however no shift is noticed for polymers P1 and P2 (Figure A1.9 - Figure A1.12). Furthermore, only the UV-vis absorption spectra of P5 and P6 show differences upon addition of metals (Figure A4.5 and Figure A4.6). A MLCT-like transition was observed only in the case of P1 with the addition of copper(I) acetate. However further investigation is needed to unequivocally identify the nature of this transition.

Table 3.3 Linear correlation slope value between the $I_0/I$ ($x 10^3$) and the concentration of metals.

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P5</th>
<th>P6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(COOCF$_3$)</td>
<td>340 ± 40</td>
<td>1.5 ± 0.5</td>
<td>2100 ± 200</td>
<td>410 ± 20</td>
</tr>
<tr>
<td>Pd(COOCH$_3$)</td>
<td>6 ± 2</td>
<td>0.9 ± 0.3</td>
<td>46 ± 3</td>
<td>34 ± 2</td>
</tr>
<tr>
<td>Pd[cod]Cl$_2$</td>
<td>4 ± 1</td>
<td>14.0 ± 0.3</td>
<td>17 ± 3</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>Cu(COOCH$_3$)</td>
<td>0.63 ± 0.03</td>
<td>0.720 ± 0.008</td>
<td>0.6 ± 0.2</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>Ag(COOCF$_3$)</td>
<td>-0.01 ± 0.004</td>
<td>0.01 ± 0.01</td>
<td>0.20 ± 0.05</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Ag(OTf)</td>
<td>0.02 ± 0.06</td>
<td>0.02 ± 0.01</td>
<td>1.1 ± 0.2</td>
<td>0.25 ± 0.04</td>
</tr>
</tbody>
</table>

When copper(I) is added in the form of [Cu(MeCN)$_4$][BF$_4$], an initial large quenching is observed, but the emission intensity is restored upon standing 1 hours (Figure 3.5). When copper(I) acetate is used, the emission decrease stabilized after 1 h; however, the difference in emission intensity between P1, P2, P5 and
**P6** for the same amount of copper is small and overlaps with the error on the emission intensity (Figure A4.7). Furthermore, as small blue shift is observed in the quenched emission, further supporting the complexation of copper(I) by the polymer. This indicates that [Cu(MeCN)₄][BF₄] leads to a quick complexation of the polymer but the complexes are not stable in solution over a short period of time. This could also be explained by the copper(I) being oxidized to copper(II) in the presence of air since the direct addition of copper(II) acetate did not have any impact on the emission.

![Emission intensity of P5 in the presence of [Cu(MeCN)₄][BF₄] as a function of time.](image)

**Figure 3.5** Emission intensity of **P5** in the presence of [Cu(MeCN)₄][BF₄] as a function of time.

In the case of silver(I) triflate and silver(I) trifluoroacetate, the quenching was minimal for **P1**, **P2** and **P6**, however **P5**, showed a more pronounced emission quenching (Figure A4.8 and Figure A4.9). Surprisingly, silver(I) trifluoroacetate led to a small enhancement of the emission for **P1** (slope of -11.79). The use of silver(I) acetate was not possible due to poor solubility in THF.

The addition of palladium(II) gave rise to the most pronounced emission quenching. The effect on the emission was dependent on the nature of the polymer and the counter anion. The presence of the bithiazole moiety (**P5** and **P6**) led to the strongest quenching of emission (Figure A4.10 - Figure A4.12). Furthermore, the presence of the sulfide over a sulfone bridge resulted in a stronger quenching. When comparing different sources of palladium (II), the presence of fluorine on the ligand lead to larger quenching, most likely due
to the inductive effect making the ligand easier to displace and interact with the polymer (especially the bithiazole moiety).

Since the polymers are organic and are showing emission at room temperature, the emitting state is most likely singlet in nature. There are four phenomena that can explain quenching of the singlet excited states: 1) the heavy atom effect, 2) a complete/partial charge transfer, 3) an energy transfer or 4) the formation of a ground/excited state complex. The heavy atom effect can be excluded since the presence of different sources of palladium(II) leads to different responses, even with the metal being the same. Charge transfer quenching can also be ruled out as the polymer emission is not dependent on the polarity of the solvent. The presence of energy transfer between the polymer and the metal would require an overlap of the metal absorption spectra and the emission of the polymers; which is not the case (Figure 3.2, Figure A4.5 and Figure A4.6). The final option is the complexation of the polymers with metals, which can be observed by a shift in the absorption wavelength in the UV-vis spectrum. This is plausible since the strongest response comes from the polymer that contains a bidentate coordinating moiety (P6) and a metal with the most easily displaced ligand (Pd(II)COOCF₃). This proposed interaction is depicted in Figure 3.6. However, a contribution from the other factors can still play a role in the emission quenching of the polymers in the presence of metals in solution.

![Figure 3.6 Proposed interaction of the polymer with metal](image-url)
3.5 Conclusions

A series of copolymers incorporating a sulfur-bridged thienyl moiety was synthesized. The nature of the comonomer and the oxidation state of the sulfur bridge were found to influence the photophysical, electronic and physical properties of these materials. The sulfide-containing polymer were less emissive and had a smaller optical band gap than the sulfone-containing polymers. The nature of the comonomers influenced the properties, but no clear trends were established in relation to the electron-rich/poor characters. Finally, the presence of a bithiazole moiety resulted in a shift in the absorbance and a diminished emission intensity in the presence of metals (Pd(II), Cu(I) and Ag(I)). The presence of a bithiazole and sulfide bridge led to the highest quenching and is believed to be due to the complexation of the metals by the polymer. The incorporation of a sulfur-bridged thiazole in the polymers was possible in the case of the sulfone, but not the sulfide. This is probably due to the complexation of the palladium(II) center, shutting down the catalytic cycle. Investigation of the sulfur-bridged thiazole as a metal ligand is explored in Chapter 4.
Chapter 4: Synthesis and Characterization of Sulfur-Bridged Thiazole

Ruthenium Homo- and Hetero-leptic Complexes

4.1 Introduction

Ruthenium(II) polypyridyl complexes have been intensively studied due to their stability, ease of ligand modification and their interesting photophysical and electrochemical properties.\(^{168-169, 250}\) The energy of the frontier orbitals in these species can easily be varied since the LUMO is ligand-centered, while the HOMO is metal-based. Furthermore, the energy of the excited states depends on the ligand field strength, the redox properties of the metal and ligands, and the intrinsic electronic properties of the ligands.\(^{168-169}\) While many 6-membered pyridine ligands have been made, only a limited amount of 5-membered aromatic ligands has been investigated, especially those with more than one heteroatom. The synthesis of ruthenium(II) complexes containing bithiazole (btz) ligands has been limited to [Ru(bpy)\(_2\)(btz)]\(^{2+}\) (14) and [Ru(btz)\(_3\)]\(^{2+}\) (15) (Chart 4.1). While the homoleptic cation (15) is well characterized, only limited electrochemical information is available for the heteroleptic cation (14).\(^{250-253}\)

![Chart 4.1 Structure of ruthenium(II) complexes containing bithiazole (btz) ligands.](image)

While [Ru(bpy)\(_3\)]\(^{2+}\) finds application in many fields, the inherent high cost of the ruthenium metal has motivated the exploration of other, less expensive metals with similar polypyridyl ligands. Copper(I) complexes, [Cu(N^N)\(_2\)]\(^+\) usually have weaker and shorter-lived emission then ruthenium(II) due to the \(^3\)MLCT state involving a low-lying d\(\sigma^*\) component. The excited state is charge-separated (Cu\(^{2+}\)-N^N),
where the copper(II) character forces the initial $D_{2d}$ geometry to flatten towards $C_{4v}$. \textsuperscript{172} This distortion decreases the energy gap and increases the non-radiative decay rate. \textsuperscript{165-166, 254-255} Furthermore, the excited state can expand its coordination sphere in coordinating solvents, which gives rise to efficient exciplex quenching. The addition of steric bulk close to the coordinating nitrogen atoms has proven to be effective in restricting the flattening distortion. Moreover, the use of mixed ligand systems such as in $[\text{Cu}(\text{P}^\text{3} \text{P})(\text{N}^\text{N})]^+$, have also been shown to emit at ambient conditions. This is because of the bulky $\pi$-acidic phosphine ligands that inhibit the deactivating distortion by stabilizing the copper(I) center. \textsuperscript{171, 173, 176, 256} Such copper(I) complexes can be emissive, even at high temperatures in fluid solutions. \textsuperscript{257} These copper(I) complexes could be useful in applications such as luminescence-based chemical sensors, emissive layers in OLEDs, \textsuperscript{162, 258-259} sensitizers for solar cells, \textsuperscript{164} and photocatalysts. \textsuperscript{170}

The incorporation of 2,2'- or 4,4'-bithiazole ligands in $[\text{Cu(N}^\text{N})_2]^{+}$ (16) or $[\text{Cu(PPh}_3)_2(\text{N}^\text{N})]^+$ (17) cations has been carried out by Krause et al.\textsuperscript{260} (Chart 4.2). These complexes showed no $^1$MLCT transitions in their absorption spectra and they were non-emissive unless the ligands were 4,4' substituted with phenyl rings.

![Chart 4.2 Structure of copper(I) complexes containing bithiazole (btz) ligand.](image)

As explored in Chapter 3, the bithiazole moiety can be used to coordinate metals. Further investigation of the complexation of metals by bithiazole and sulfur-bridged thiazole ligands is presented in this Chapter. The capacity to alter the electronic properties of the ligands, while maintaining the same coordination motif is a classic approach to tune the photophysical, and electrochemical properties of complexes. \textsuperscript{164, 169-170, 261}
However the incorporation of a non-coordinating sulfur atom in the ligand to modify the electron density of the ligand is not common, while it is an ideal substituent to allow changes from a less electron-poor (sulfide, 13-S) to a more electron-poor (sulfone 13-SO2) ligand.262-264

Compound 13 was used as a ligand for two different metals: ruthenium(II) and copper(I) (Chart 4.3). The syntheses of ruthenium(II) [Ru(L)3]2+ and [Ru(L)2(L')]2+ complexes and copper(I) P^P and N^N mixed ligand systems, [Cu(POP)(N^N)]+, were performed and these complexes were spectroscopically characterized. The photophysical and electrochemical behaviors of these new complexes were compared to analogous complexes containing 2,2'-bithiazole ligands.

![Chart 4.3 Proposed structure of sulfur-bridged thiazole as ligand for ruthenium(II) and copper(I) complexes.](image-url)
4.2 Experimental

4.2.1 General

The following materials were purchased and they were used without further purification: 2-bromothiazole from Matrix scientific, thiourea and 2-octanone from TCI, ethanol, methanol, dithioaxamide, 1,10-phenanthroline, tetrabutylammonium hexafluorophosphate (n-Bu4N)PF6, RuCl3, and Cu(MeCN)4BF4 from Sigma, niobium carbide from Alfa Aesar, 2,2'-bipyridine from Lancaster, bromine, dichloromethane (CH2Cl2, HPLC grade), acetonitrile (MeCN, HPLC grade) from Fisher, and (oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEPhos) from Strem. 4,4'-Dihexyl 2,2'-bithiazole (hbzt),228 Ru(DMSO)4Cl2,265 Ru(bpy)2Cl2,266 and Ru(phen)2Cl2267 were prepared according to previously reported methods. Distilled water was used when required.

NMR spectroscopy was performed on a Bruker Avance 400 inverse broadband probe for 1D and 2D 1H experiments, a Bruker Avance 400 direct spectrometer was used for 1D 13C experiments. The residual protonated solvent peaks were used for referencing. Measurements were performed at 298 K.

UV-visible absorption spectroscopy was carried out on a Cary Varian 5000 UV-vis-Near-IR spectrophotometer using HPLC grade solvents. The optical band gaps were estimated from the onset of absorption spectra in CH2Cl2. Photoluminescence was measured on a Photon Technology International QuantaMaster 50 fluorimeter equipped with a double monochromator and using a 75 W Xe arc lamp as the source. Photoluminescence spectra were measured at 293 K unless otherwise indicated. Solid state emission measurements were performed on VWR VistaVision™ White glass microscope slides. Low temperature measurements were performed in the solid state on quartz slides using an Oxford Optistat DN cryostat.

Electrochemical experiments were performed using a Pine AFCBP1 bipotentiostat in an airtight three-electrode cell with a platinum working electrode, platinum mesh counter electrode, and silver wire pseudoreference electrode in an electrolyte solution consisting of 0.10 M triply recrystallized (n-Bu4N)PF6 in anhydrous MeCN sparged with nitrogen prior to use. The platinum electrode was cleaned by cycling from -0.23 to 1.1 V twenty times in aqueous 0.5 M H2SO4 against a Ag+/AgCl reference electrode until
well resolved peaks reduction peaks were observed at -0.05, -0.143 and 0.5 V, followed by rinsing with deionized water.\textsuperscript{268} Ferrocene was added at the end of the electrochemical experiments as an internal standard and the values were referenced against NHE. Conversion of literature values to the NHE reference were made according to Pavlishchuk and Addison conversion values.\textsuperscript{269} Electrochemical band gaps were calculated using the lowest oxidation potential and the first reduction potential.

Single crystal X-ray data were collected using a Bruker APEX DUO diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 90 K. Raw frame data were processed using APEX2.\textsuperscript{270} The program SAINT+, version 6.02\textsuperscript{271} was used to reduce the data and the program SADABS was used to make corrections to the empirical absorptions. Space group assignments were made using XPREP\textsuperscript{271} on all compounds. In all cases, the structures were solved in the WinGX\textsuperscript{272} Suite of programs by direct methods using SHELXS-97\textsuperscript{273} and refined using full-matrix least-squares/difference Fourier techniques on F\textsuperscript{2} using SHELXL-97.\textsuperscript{274} All non-hydrogen atoms were refined anisotropically. Diagrams and publication material were generated using OLEX2\textsuperscript{275} Crystal data collection and refinement were performed by Duane Hean.

4.2.2 Methods

\[ \text{[Ru(bpy)\textsubscript{2}(tzS)][PF\textsubscript{6}]_{2} (18-S)} \] Ru(bpy)\textsubscript{2}Cl\textsubscript{2} (0.10 g, 0.21 mmol) was added to a solution of 13-S (0.05 g, 0.23 mmol) in 20 mL of EtOH:H\textsubscript{2}O (1:1) that had been purged with N\textsubscript{2} for 30 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and precipitated with the addition of a minimal amount of saturated aqueous NH\textsubscript{4}PF\textsubscript{6}. The solid was filtered, then washed with small amounts of H\textsubscript{2}O and EtOH. No further purification was required. Yield: 73 mg (38%). \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \( \delta \): 8.5 – 8.4 (m, 4H), 8.4 (d, \( J = 8.1 \) Hz, 2H), 8.2 (d, \( J = 1.5 \) Hz, 2H), 8.0 (d, \( J = 1.4 \) Hz, 2H), 7.8 – 7.7 (m, 2H), 7.7 – 7.6 (m, 4H), 7.4 (s, 2H), 6.9 (d, \( J = 3.7 \) Hz, 2H). \textsuperscript{13}C (\textsuperscript{1}H) NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \( \delta \): 158.1, 157.7, 156.5, 154.1, 152.6, 145.6, 139.2, 138.8, 128.6, 128.3, 126.1, 124.9, 124.8. HRMS (TOF-MS) [M-PF\textsubscript{6}]\textsuperscript{2+} calcd. 306.9978; found 306.9818. Anal. Calcd. for C\textsubscript{26}H\textsubscript{20}F\textsubscript{12}N\textsubscript{6}P\textsubscript{2}RuS\textsubscript{3}: C 34.56, H 2.23, N 9.30, S 10.64; found C 34.93, H 1.96, N 8.99, S 10.56.
[Ru(bpy)₂(tzSO₂)][PF₆]₂ (18-SO₂). Ru(bpy)₂Cl₂ (0.10 g, 0.21 mmol) was added to a solution of 13-SO₂ (0.05 g, 0.23 mmol) in 20 mL of EtOH:HO (1:1) that had been purged with N₂ for 30 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and precipitated using a minimal amount of saturated aqueous NH₄PF₆ solution. The microcrystals were filtered and washed with a small amount of H₂O and Et₂O. Yield: 0.11 g (56%). ¹H NMR (400 MHz, CD₂Cl₂) δ: 8.5 – 8.4 (m, 4H), 8.2 – 8.1 (m, 4H), 8.1 (td, 5.7 Hz, 2H), 8.0 (d, 5.6 Hz, 2H), 7.7 – 7.6 (m, 2H), 7.6 (ddd, 7.4, 5.7, 1.4 Hz, 2H), 7.5 (ddd, 7.4, 5.7, 1.4 Hz, 2H), 7.2 (d, 3.5 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CD₃CN) δ: 159.0, 155.7, 153.1, 148.1, 139.6, 131.2, 128.8, 128.1, 125.6, 125.3. HRMS (TOF-MS) [M-PF₆]²⁺ calcd. 322.9927; found 322.9881. Anal. calcd. for C₂₆H₂₀F₁₂N₆O₂PF₂RuS₃: C 33.38, H 2.15, N 8.98, S 10.28; found C 33.45, H 1.94, N 8.54, S 9.92.

[Ru(phen)₂(tzS)][PF₆]₂ (19-S). Ru(phen)₂Cl₂ (0.10 g, 0.19 mmol), was added to a solution of 13-S (0.04 g, 0.21 mmol) in 20 mL of EtOH:HO (4:1) that had been purged with N₂ for 15 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and precipitated using a minimal amount of saturated aqueous NH₄PF₆ solution. The precipitate was filtered and washed using small amounts of H₂O and Et₂O. The product was used without further purification. Yield: 0.10 g (54%). ¹H NMR (400 MHz, CD₂Cl₂) δ: 9.0 (d, 5.2 Hz, 2H), 8.7 (d, 8.3 Hz, 2H), 8.4 (d, 8.3 Hz, 2H), 8.2 (d, 8.8 Hz, 2H), 8.2 – 8.0 (m, 4H), 7.8 (d, 5.4 Hz, 2H), 7.6 – 7.5 (m, 4H), 6.9 (d, 3.8 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂) δ: 155.6, 153.6, 146.0, 138.2, 137.5, 131.6, 129.0, 128.6, 126.9, 125.9. HRMS (TOF-MS) [M-PF₆]²⁺ calcd. 330.9978; found 331.0071. Anal. calcd. for C₃₀H₂₀F₁₂N₆O₂PF₂RuS₃: C 37.85, H 2.21, N 8.83, S 10.11; found C 37.75, H 2.06, N 8.15, S 8.85.

[Ru(phen)₂(tzSO₂)][PF₆]₂ (19-SO₂). Ru(phen)₂Cl₂ (0.11 g, 0.20 mmol) was added to a solution of 13-SO₂ (0.06 g, 0.27 mmol) in 20 mL of EtOH:HO (1:1) that had been purged with N₂ for 30 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and precipitated using a minimal amount of saturated aqueous NH₄PF₆ solution. The precipitate was filtered and washed with small amounts of H₂O and Et₂O. The compound was used without further purification. Yield: 94 mg (47%). ¹H NMR (400
MHz, CD$_2$Cl$_2$) $\delta$: 8.7 (dd, $J = 8.3$, 1.2 Hz, 2H), 8.5 (dd, $J = 5.3$, 1.2 Hz, 2H), 8.5 (dd, $J = 8.3$, 1.2 Hz, 2H), 8.2 (d, $J = 8.8$ Hz, 2H), 8.2 (d, $J = 8.9$ Hz, 2H), 8.1 (d, $J = 3.5$ Hz, 2H), 8.0 (dd, $J = 8.3$, 5.2 Hz, 2H), 7.8 (dd, $J = 5.3$, 1.2 Hz, 2H), 7.7 (dd, $J = 8.2$, 5.3 Hz, 2H), 7.1 (d, $J = 3.5$ Hz, 2H). $^{13}$C($^1$H) NMR (100 MHz, CD$_2$Cl$_2$) $\delta$: 164.1, 156.0, 153.6, 148.6, 148.2, 138.6, 138.5, 131.7, 131.6, 130.4, 129.1, 128.7, 127.1, 127.1. HRMS (TOF-MS) [M-PF$_6$]$^{2+}$ calcd. 346.9927; found 346.9816. Anal. calcd. for C$_{30}$H$_{20}$F$_{12}$N$_6$O$_2$P$_2$RuS$_3$: C 36.63, H 2.05, N 8.54, S 9.78; found C 36.25, H 1.92, N 8.24, S 9.87.

[Ru(tzS)$_3$][PF$_6$]$_2$ (20-S). Ru(DMSO)$_4$Cl$_2$ (0.14 g, 0.28 mmol) was added to 13-S (0.26 g, 1.3 mmol) in H$_2$O:EtOH (1:1) that had been purged with N$_2$ for 30 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and precipitated using a minimal amount of saturated aqueous solution of NH$_4$PF$_6$. The solid was filtered and washed using H$_2$O, EtOH and Et$_2$O. The compound was used without further purification. Yield: 0.21 g (77%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 7.73 (d, $J = 4$ Hz, 6H), 7.32 (d, $J = 4$ Hz, 6H). $^{13}$C($^1$H) NMR (100 MHz, CD$_3$CN) $\delta$: 157.4, 149.1, 125.5. HRMS (TOF-MS) [M-PF$_6$]$^{2+}$ calcd. 350.8827; found 350.8826. Anal. calcd. for C$_{18}$H$_{12}$F$_{12}$N$_6$P$_2$RuS$_9$: C 21.80, H 1.22, N 8.47, S 29.09; found C 21.92, H 1.58, N 8.40, S 30.23.

Ru(tzSO$_2$)$_2$Cl$_2$ (23-SO$_2$). Ru(DMSO)$_4$Cl$_2$ (0.12 g, 0.25 mmol) was added to 13-SO$_2$ (0.12 g, 0.51 mmol) and LiCl (0.06 g, 1.5 mmol) in H$_2$O:EtOH (1:1) that has been purged with N$_2$ for 15 min. The reaction mixture was heated at reflux for 16 h, concentrated until a precipitate appeared, filtered, washed with H$_2$O and Et$_2$O, and used without further purification. Yield: 72 mg (45%);

[Ru(tzSO$_2$)$_2$(MeCN)$_2$][PF$_6$]$_2$ (20-SO$_2$). 23-SO$_2$ (50 mg, 0.08 mmol) was added to 13-SO$_2$ (0.02 mg, 0.11 mmol) in H$_2$O:EtOH (1:1) that has been purged with N$_2$ for 30 min. The reaction mixture was heated at reflux for 16 h, filtered hot through glass wool and a small amount of saturated aqueous NH$_4$PF$_6$ solution was added. The solution was concentrated and redissolved in a small amount of MeCN and precipitated with H$_2$O. The solid was filtered and the solution was left standing for a week from which a small amount of material was obtained and filtered. Limited characterization was possible due to the small amount of product. Yield 20 mg (26%) $^1$H NMR (400 MHz, CD$_3$CN 3) $\delta$: 8.37 (d, $J = 4$ Hz, 2H), 7.97 (d, $J = 4$ Hz,
2H) $^{13}$C{H} NMR (100 MHz, CD$_3$CN) $\delta$:151.4, 130.9 HRMS (TOF-MS) [M-L]$^{2+}$ calcd. 282.8957; found 282.8956

[Cu(POP)(tzS)][BF$_4$] (21-S). This complex was synthesized according to previously reported methods.$^{176}$ [Cu(MeCN)$_4$][BF$_4$] (78.5 mg, 0.3 mmol) was stirred in CH$_2$Cl$_2$ in the presence of DPEPhos (134.4 mg, 0.3 mmol) at room temperature for 1 h. Compound tzS (13-S) (50 mg, 0.3 mmol) was then added and stirred for 2 h at room temperature. The reaction mixture was poured into Et$_2$O, the precipitate was filtered and washed with Et$_2$O. Yield: 88.4 mg (40 %). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 7.8 (d, $J = 3.4$ Hz, 1H), 7.6 (d, $J = 3.4$ Hz, 1H), 7.4 (dt, $J = 14.7$, 7.2 Hz, 7H), 7.3 – 7.2 (m, 6H), 7.0 (d, $J = 13.8$ Hz, 1H), 6.7 (td, $J = 3.7$, 1.5 Hz, 1H). $^{13}$C{H} NMR (100 MHz, CD$_3$CN) $\delta$: 144.9, 135.1, 134.6, 134.5, 134.4, 133.0, 131.2, 129.8, 129.8, 125.7, 125.2, 121.1, 118.3, 100.9. $^{31}$P{H} NMR (160 MHz, CD$_3$CN) $\delta$: -13.7. HRMS (TOF-MS) [M]$^{2+}$ calcd. 801.0448; found 801.0446. Anal calcd. for C$_{42}$H$_{32}$CuF$_4$N$_2$OP$_2$S$_3$: C 56.73, H 3.63, N 3.15, S 10.82; found C 56.54, H 3.87, N 3.08, S 10.20.

[Cu(POP)(tzSO$_2$)][BF$_4$] (21-SO$_2$). This complex was synthesized according to a previously reported method$^{176}$ using the same method as for [Cu(POP)(tzS)][BF$_4$] (21-S) where [Cu(MeCN)$_4$][BF$_4$] (67.7 mg, 0.2 mmol), DPEPhos (115.9 mg, 0.2 mmol) and tzSO$_2$ (13-SO$_2$) (50.0 mg, 0.2 mmol) were used.$^{176}$ Yield: 0.15 g (74 %). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 8.1 (d, $J = 3.0$ Hz, 1H), 8.0 (d, $J = 3.0$ Hz, 1H), 7.4 (dt, $J = 14.4$, 7.1 Hz, 8H), 7.4 – 7.2 (m, 7H), 7.0 – 6.9 (m, 3H), 6.7 (dtd, $J = 7.8$, 4.0, 1.7 Hz, 1H). $^{13}$C{H} NMR (101 MHz, CD$_3$CN) $\delta$: 146.9, 135.1, 134.6, 134.5, 134.4, 132.9, 131.2, 130.2, 129.9, 129.8, 125.7, 121.1. $^{31}$P{H} NMR (160 MHz, CD$_3$CN) $\delta$: -14.6. HRMS (TOF-MS) [M]$^{2+}$ calcd. 833.0346; found 833.0345. Anal. calcd. for C$_{42}$H$_{32}$BCuF$_4$N$_2$OP$_2$S$_3$: C 54.76, H 3.50, N 3.04, S 10.45; found C 52.57, H 3.55, N 2.71, S 9.29.

[Cu(POP)(hbtz)][BF$_4$] (22). This complex was synthesized according to a previously reported method$^{176}$ and using the same method as for [Cu(POP)(tzS)][BF$_4$] (21-S) where [Cu(MeCN)$_4$][BF$_4$] (67.7 mg, 0.2 mmol), DPEPhos (115.9 mg, 0.2 mmol) and hbtz (72.4 mg, 0.2 mmol) were used.$^{176}$ Yield: 0.13 g (60 %). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 7.4 (dt, $J = 14.8$, 7.2 Hz, 7H), 7.4 – 7.3 (m, 5H), 7.3 (d, $J = 1.7$ Hz, 6H),
7.2 (s, 1H), 7.0 – 7.0 (m, 1H), 7.0 (dd, J = 7.1, 4.0 Hz, 1H), 6.8 – 6.7 (m, 1H), 2.8 (t, J = 7.6 Hz, 2H), 1.7 – 1.6 (m, 2H), 1.3 (dd, J = 4.5, 2.0 Hz, 4H), 0.9 – 0.8 (m, 2H). $^{13}$C{\text{\textsuperscript{1}H}} NMR (10 MHz, CD$_3$CN) δ: 134.2, 133.7, 133.6, 130.4, 129.0, 120.2, 31.4, 31.1, 28.7, 22.4, 13.5. $^{31}$P{\text{\textsuperscript{1}H}} NMR (160 MHz, CD$_3$CN) δ: -14.0. HRMS (TOF-MS) [M]$^+$ calcld. 937.2605; found 937.2587.

C$_{54}$H$_{56}$BCuF$_4$N$_2$OP$_2$S$_2$: C 63.25, H 5.50, N 2.73, S 6.25; found C 61.92, H 5.42, N 2.68, S 5.96.

4.3 Results and Discussion

4.3.1 Synthesis and Characterization

The proligand tzS (13-S) was prepared by the condensation of 2-bromothiazole with thiourea. The oxidized proligand tzSO$_2$ (13-SO$_2$) was obtained through the oxidation of tzS with hydrogen peroxide catalyzed by niobium carbide (Scheme 4.1). Both compounds are colorless and color changes enabled monitoring the complexation of metals.

![Scheme 4.1](image)

The homoleptic complex [Ru(tzS)$_3$][PF$_6$]$_2$ (20-S) was synthesized by reacting Ru(DMSO)$_4$Cl$_2$ with tzS (13-S). The yellow ruthenium precursor became orange upon complexation with the ligand. The $^1$H NMR spectrum of 20-S contains ligand-based proton signals indicative of $D_3$ symmetry and the assignment of the peaks was carried out by comparison with literature values of related compounds (proligand btz δ 8.07 ppm and δ 7.96 ppm, 15 δ 7.34 ppm and δ 8.33 ppm for H4 and H5 respectively in DMSO-$d_6$).$^{252,276}$ Similarly to 15, a coordination-induced shift (CIS = δ$_{\text{complexed}}$ - δ$_{\text{free}}$) is observed from the free ligand 13-S to the homoleptic complex 20-S in acetonitrile-$d_3$. The proton located next to the coordinating nitrogen (H4) undergoes an upfield CIS (-0.53 ppm) while the other proton (H5) has a downfield CIS of 0.09 ppm (Figure 4.1). The nature of the CIS is different depending on the position of the proton, H4 is subjected to the shielding effect of the ring current from the neighboring ring. However, H5 has a positive CIS, which
suggest that it is deshielded by σ-donation from the nitrogen to the ruthenium center.\textsuperscript{252} The $^1$H NMR spectrum for compound $20\text{-SO}_2$ is ambiguous as it suggests a species with either $D_3$ or $D_{2h}$ symmetry. The absence of a [M - 2PF$_6$]$^{2+}$ peak in the high-resolution MS of complex $20\text{-SO}_2$ was the first indication along with the crystal structure (see Section 4.3.2.1) that the bis-solvento complex [Ru(tzSO$_2$)$_2$(MeCN)$_2$]$^{2+}$ was formed instead of complex $20\text{-SO}_2$. Furthermore, the CISs are in good agreement as H4 undergoes a much smaller shift (-0.11 ppm) due to the absence of the neighboring aromatic, while H5 has a larger CIS (0.32 ppm) due to the stronger σ-donation from the acetonitrile to the ruthenium center. Elemental analysis of [Ru(tzS)$_3$][PF$_6$]$_2$ (20-S) was done due to the low yield of the [Ru(tzSO$_2$)$_2$(MeCN)$_2$][PF$_6$]$_2$ (20-SO$_2$) complex. It was in good agreement with the calculated values.

**Figure 4.1** 400 MHz $^1$H NMR spectra of the free ligand and complex A. 13-S and 20-S and B. 13-SO$_2$ and 20-SO$_2$ in CD$_3$CN at 298 K.
The heteroleptic complexes (18 and 19) were prepared by reacting either tzS (13-S) or tzSO₂ (13-SO₂) with either Ru(bpy)₂Cl₂ or Ru(phen)₂Cl₂, respectively. The solutions of the ruthenium precursors (dark purple) became either deep red or orange upon the addition of the ligand (13). The ¹H NMR spectra of the bpy 2,2'-bipyridine) and phen (1,10-phenanthroline) ligands on the heteroleptic complexes reflect both the expected splitting patterns for these ligands and the chemical shifts reported for related complexes in the literature (Figure 4.2 and Figure 4.3). A large CIS is expected from the free ligand 13-S and 13-SO₂ to the heteroleptic complexes with bpy (18) or phen (19); especially for the proton next to the coordinating nitrogen (H4). This is because they are positioned over the shielding plane of another aromatic ring.

A large CIS is observed in all cases between the free ligand and the complexed ligand for proton H4 due to its proximity to the other coordinating rings. A shift in the resonance due to the protons of the bipyridine rings can also be observed, however this analysis of the CIS is focused on the thiazole H4 and H5 protons (assigned through 2D COSY NMR, Figure A1.15 - Figure A1.18). A positive CIS is observed for all H5 protons, while protons H4 have negative CISs. The magnitude and direction of the shifts are caused by a combination of four factors: a positive shift (downfield) caused by the i) σ-donation and ii) van der Waals forces, while a negative shift (upfield) is caused by iii) π-back donation and iv) ring current anisotropy. In the case of H4, the main factor contributing to the CIS in the complexes is the ring current anisotropy (-0.92, -0.89, -0.96, -0.92 for 18-S, 18-SO₂, 19-S and 19-SO₂ respectively). For H5, the σ-donation from the metal is the most significant effect at the proton and a positive CIS is measured (0.2, 0.32, 0.11 and 0.22 for 18-S, 18-SO₂, 19-S and 19-SO₂ respectively). The difference between the CIS of H4 for 18-S and 19-S can be attributed to the difference in π-back-donation due to the different bite angles of the bipyridyl ligands. Elemental analysis was done on all the heteroleptic complexes and it was in good agreement with the calculated values.
Figure 4.2 400 MHz $^1$H NMR spectra of the free ligand and complexes A. 13-S and 18-S, and B. 13-SO$_2$ and 18-SO$_2$ in CD$_2$Cl$_2$ at 298 K.
Figure 4.3 400 MHz $^1$H NMR spectra of the free ligand and complexes A. 13-S and 19-S, and B. 13-SO$_2$ and 19-SO$_2$ in CD$_2$Cl$_2$ at 298 K.

The stability of the heteroleptic complexes in coordinating solvents such as acetonitrile was tested by NMR measurements on the complexes of 18. The sulfone containing complex 18-SO$_2$ was dissolved in non-coordinating solvent (dichloromethane-<em>d</em>2) and the proton NMR spectrum was acquired. The proton NMR spectra were taken after adding 10 equivalents of acetonitrile in the dark, with sunlight irradiation, with UV light, and with visible light, and proton NMR spectra were taken in each case. No changes were observed after the addition of the coordinating solvent in the dark. Only minor changes were observed with irradiation with visible light. However, with sunlight and UV light irradiation after 2 and 15 min,
respectively, significant changes in the $^1$H NMR spectrum were observed (Figure A1.13). The changes were attributed to the loss of the sulfur-bridged ligand by photoejection and coordination by two acetonitrile molecule.\textsuperscript{279} Exceptionally, complex $\textbf{18-S}$ were unchanged in acetonitrile, as shown by the NOESY correlation between H4 and one of the bipyridine protons ($\delta$ 6.84 ppm and $\delta$ 7.72 ppm, Figure A1.14). No photoejection was observed in the case of $\textbf{20-S}$, while $\textbf{20-SO}_2$ only formed the bis acetonitrile complex.

The mixed ligand copper(I) complexes ($\textbf{21}$ and $\textbf{22}$) were obtained by reacting one equivalent of the POP ligand (DPEPhos) with [Cu(MeCN)$_4$][BF$_4$] in DCM at room temperature, followed by the addition of the N$^N$N ligand (either tzS ($\textbf{13-S}$), tzSO$_2$ ($\textbf{13-SO}_2$) or hbtz = 4,4'$\prime$-dihexyl 2,2'$\prime$-bithiazole). The $^1$H NMR spectrum collected in acetonitrile-$d3$ shows enhanced peak resolution compared to in dichloromethane-$d2$. However, complex $\textbf{21-SO}_2$ was not stable in acetonitrile; thus, its NMR spectrum was collected in dichloromethane-$d2$. Upon complexation, the proton chemical shift of the protons for the ligands on complex $\textbf{21}$ are slightly different than for the free ligand: $\delta$ 7.84 ppm and 7.64 ppm for $\textbf{13-S}$ and $\delta$ 7.80 ppm and 7.63 ppm for $\textbf{21-S}$ (Figure A1.19) and $\delta$ 8.09 ppm and 7.83 ppm for $\textbf{13-SO}_2$ and $\delta$ 7.69 ppm and 7.49 ppm for $\textbf{21-SO}_2$ (Figure A1.20). In the case of [Cu(POP)(hbtz)][BF$_4$] ($\textbf{22}$) only a small CIS (0.02) is observed (Figure A1.21). The $^{31}$P{$^1$H} chemical shifts are -13.7, -14.6 and -14.0 for $\textbf{21-S}$, $\textbf{21-SO}_2$ and $\textbf{22}$ respectively, consistent with POP copper(I) complexes of a similar nature.\textsuperscript{280-281} The molecular structures were confirmed by high-resolution mass spectrometry, elemental analysis, and X-ray diffraction. The difference between the calculated and measured elemental composition of $\textbf{21-SO}_2$ was attributed to partial salt metathesis.
Figure 4.4 400 MHz $^1$H NMR spectra of the free ligand and complexes A. 13-S and 21-S in CD$_3$CN, B. 13-SO$_2$ and 21-SO$_2$ in CD$_2$Cl$_2$, and C. hbtz and 22 in CD$_2$Cl$_2$ at 298 K.

4.3.2 Single Crystal X-Ray Diffraction

4.3.2.1 Ruthenium(II) Complexes

The solid state structures of some of the ruthenium complexes were determined using single X-ray diffraction. X-ray quality crystals were grown either by the slow evaporation of EtOH or the slow diffusion of Et$_2$O into CH$_2$Cl$_2$ at 293 K. The introduction of the sulfur bridge between the thiazole moieties (13) increases the bite angle of the ligand relative to 2,2'-bithiazole (btz) (in complexes 14 and 15). Comparison of the angles and bond lengths between the metal and the ligands 13-S and 13-SO$_2$ can give insight into the
strength and strain of the sulfur-bridged bithiazole as a ligand and the binding motif (N^N, N^O or N^S). Surprisingly, the crystal structures of bithiazole ruthenium(II) complexes [Ru(bpy)_2(btz)]^2+ (14) and [Ru(btz)_3]^2+ (15) have not been reported.

The complexation of ruthenium(II) using the tzS (13-S) ligand results in an octahedral complex (Figure 4.5 and Table 4.1). The average bond length between the tzS nitrogen and the ruthenium(II) center is 2.090 Å for 18-S and 2.096 Å for 20-S. The N-Ru-N angle involving the tzS ligand is 88.39º for 18-S and 90.63º (average) for 20-S. In the case of the heteroleptic complexes, the tzS ligand is slightly further away from the metal compared to the bipyridyl ligands while in the case of the homoleptic complex, one tzS is further than the others from the metal. Each of the sulfur-bridged ligands (13-S) takes up more space around the ruthenium center in complex 20-S compared to the bipyridine in complex 18-S and leads to an increased bond length to accommodate the ligands around the metal center. The C3-S2-C4 angle is larger when the ligand is further from the metal, meaning that the 6-membered ring formed upon coordination of the ruthenium (Ru-N-C-S-C-N-) center is strained, forcing the C-S-C to adopt a small angle.
**Figure 4.5** Solid state structures of ruthenium(II) complexes incorporating tzS ligand (18-S and 20-S). Thermal ellipsoids are drawn at 50% probability. Counter ions and occluded solvent molecules are omitted for clarity.

**Table 4.1.** Selected bond lengths and angles for [Ru(bpy)₂(tzS)][PF₆]₂ (18-S) and [Ru(tzS)₃][PF₆]₂ (20-S).

<table>
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<tr>
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<th>[Ru(bpy)₂(tzS)][PF₆]₂</th>
<th>[Ru(tzS)₃][PF₆]₂</th>
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<td>101.3(5)</td>
</tr>
<tr>
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<td>-</td>
<td>99.9(6)</td>
</tr>
<tr>
<td>C - S8 - C</td>
<td>-</td>
<td>104.8(6)</td>
</tr>
</tbody>
</table>

The heteroleptic complex [Ru(phen)₂(tzSO₂)][PF₆]₂ (19-SO₂) and the [Ru(tzSO₂)₂(MeCN)₂][PF₆]₂ (20-SO₂) yielded crystals suitable for X-ray characterization. A selection of bond length and angles for these complexes are highlighted in Table 4.2. The average Ru-N bond lengths of the tzSO₂ ligand are 2.104 Å and 2.079 Å for 19-SO₂ and 20-SO₂ respectively. The longer bond in 19-SO₂ is probably due to
the larger size of the phenanthroline ligand (compared to acetonitrile), forcing the ligand further away from
the metal center. The bite angle of the tzSO₂ (13-SO₂) ligand also reflects the strain induced by the
phenanthroline decreasing from 87.56° in 20-SO₂ to 79.739° in 19-SO₂. However, the C3-S2-C4 angle is
comparable for both complexes, 103.5° and 104.9° for 19-SO₂ and 20-SO₂ respectively, and is similar to
the proligand structure (101.68 ° and 104.46° for 13-S and 13-SO₂ respectively).

![Diagrams of ruthenium(II) complexes incorporating tzSO₂ ligands](image)

**Figure 4.6** Solid state structures of ruthenium(II) complexes incorporating tzSO₂ ligand (19-SO₂ and
20-SO₂). Thermal ellipsoids are drawn at 50% probability. Counter ions and occluded solvent molecules
are omitted for clarity.
Table 4.2 Selected of bond lengths and angles for \([\text{Ru(bpy)}_2(\text{tzSO}_2)][\text{PF}_6]_2\) (19-\text{SO}_2) and \([\text{Ru(tzSO}_2)_3][\text{PF}_6]_2\) (20-\text{SO}_2).

<table>
<thead>
<tr>
<th></th>
<th>([\text{Ru(phen)}_2(\text{tzSO}_2)][\text{PF}_6]_2)</th>
<th>([\text{Ru(tzSO}_2)_3(\text{MeCN})][\text{PF}_6]_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lengths (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru1 - N1</td>
<td>2.081(5)</td>
<td>2.0814(14)</td>
</tr>
<tr>
<td>Ru1 - N2</td>
<td>2.053(6)</td>
<td>2.0769(14)</td>
</tr>
<tr>
<td>Ru1 - N3</td>
<td>2.068(5)</td>
<td>2.0206(14)</td>
</tr>
<tr>
<td>Ru1 - N4</td>
<td>2.062(5)</td>
<td>-</td>
</tr>
<tr>
<td>Ru1 - N5</td>
<td>2.103(5)</td>
<td>-</td>
</tr>
<tr>
<td>Ru1 - N6</td>
<td>2.105(5)</td>
<td>-</td>
</tr>
<tr>
<td>Angles (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1 - Ru1 - N2</td>
<td>79.739</td>
<td>87.56(5)</td>
</tr>
<tr>
<td>N3 - Ru1 - N4</td>
<td>80.1(2)</td>
<td>-</td>
</tr>
<tr>
<td>N5 - Ru1 - N6</td>
<td>90.8(2)</td>
<td>-</td>
</tr>
<tr>
<td>N2 - Ru1 - N3</td>
<td>-</td>
<td>89.09(6)</td>
</tr>
<tr>
<td>C3 - S2 – C4</td>
<td>103.5(3)</td>
<td>104.8(6)</td>
</tr>
</tbody>
</table>

4.3.2.2 Copper(I) Complexes

Single crystal structures of all three of the copper(I) complexes were obtained by slow diffusion of \(\text{Et}_2\text{O}\) into a \(\text{CH}_2\text{Cl}_2\) solution. The complex with the sulfur-bridged thiazole exhibits a tetrahedral geometry where one 13 and POP ligand is bound to the copper(I). In the case of the bithiazole (hbtz), the alkyl chains at the 4- position prevent a strong interaction with both nitrogen atoms, and the obtained structure has the bithiazole bridging two copper centers through the nitrogen and a long dative bond to the sulfur. This bimetallic complex is further referred to as 22b.
The bite angle of ligand 13 is slightly different depending on the oxidation state of the sulfur bridge; 91.28° in 21-S and 93.2° in 21-SO₂. This is also reflected in the C1-S1-C4 angle where the angle is larger in 21-SO₂ than in 21-S (Table 4.3). The average N-Cu bond length is slightly longer for 21-SO₂ (2.105 Å) than for 21-S (2.092 Å). Comparisons to 22b are difficult since this involves a bimetallic structure. However, the length of the N1-Cu1 bond in 22b is slightly shorter (1.975 Å) than in the bidentate complex 21 while the S1-Cu1 bond is much longer (2.7911 Å).

The P-Cu bond lengths decrease as the N-Cu bond distances increase (from 21-SO₂ to 21-S to 22b). This can be attributed to the N^N ligand becoming more electron poor (Taft inductive substituent constant = 0.28 for -S vs 0.59 for -SO₂) and the POP ligand interacts more strongly with the copper(I) center.
**Figure 4.7** Solid state structure of copper(I) complexes (21 and 22b) grown from slow diffusion of Et$_2$O in CH$_2$Cl$_2$ at 298 K. Thermal ellipsoids are drawn at 50% probability. Phenyl rings, alkyl chains, counter ions and occluded solvent molecules have been omitted for clarity.
Table 4.3. Selected bond length and angles for copper(I) complexes 21 and 22.

<table>
<thead>
<tr>
<th></th>
<th>[Cu(POP)(tzS)][BF₄] (21-S)</th>
<th>[Cu(POP)(tzSO₂)][BF₄] (21-SO₂)</th>
<th>[Cu(POP)²(hbtz)][BF₄]² (22b)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lengths (Å)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1 - N1</td>
<td>2.088(5)</td>
<td>2.123(5)</td>
<td>1.975(2)</td>
</tr>
<tr>
<td>Cu1 - N2</td>
<td>2.096(5)</td>
<td>2.087(5)</td>
<td>-</td>
</tr>
<tr>
<td>Cu1 - S1</td>
<td>-</td>
<td>-</td>
<td>2.791 1(10)</td>
</tr>
<tr>
<td>Cu1 - P1</td>
<td>2.2831(15)</td>
<td>2.2729(17)</td>
<td>2.2248(7)</td>
</tr>
<tr>
<td>Cu1 - P2</td>
<td>2.2530(16)</td>
<td>2.2357(17)</td>
<td>2.2347(7)</td>
</tr>
<tr>
<td><strong>Angles (°)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1 - Cu1 - N2</td>
<td>91.28(19)</td>
<td>93.2(2)</td>
<td>-</td>
</tr>
<tr>
<td>P1 - Cu1 - P2</td>
<td>111.76(6)</td>
<td>112.00(6)</td>
<td>119.93(2)</td>
</tr>
<tr>
<td>C1 - S1 - C4</td>
<td>98.5(3)</td>
<td>101.1(3)</td>
<td>-</td>
</tr>
<tr>
<td>S1 - Cu1 - N1</td>
<td>-</td>
<td>-</td>
<td>79.20(8)</td>
</tr>
<tr>
<td>C9 - O1 - C10</td>
<td>115.9(4)</td>
<td>116.3(5)</td>
<td>118.83(18)</td>
</tr>
</tbody>
</table>

4.3.3 Ruthenium(II) Complexes

4.3.3.1 UV-vis Spectroscopy

The UV-vis absorbance spectra of the ligands 13-S and 13-SO₂ exhibit similar transition energies. However, they differ in their absorption intensities (λₓᵧ = 264 nm and 282 nm for 13-S and 13-SO₂, respectively). The transitions are assigned to a π→π* transition on the thiazole ring (233 nm).²⁸² Upon complexation, the absorbance spectra are typical for heteroleptic ruthenium(II) complexes (Figure 4.8A and B): a strong ligand-based π→π* transition centered at 230 nm and a metal-to-ligand charge-transfer band (¹MLCT) at lower energy (centered at 440 nm for 18 and 410 nm for 19). The ligand-based absorption is maintained even as the oxidation state of the sulfur bridge is increased (18-S to 18-SO₂ or 19-S to 19-SO₂). The absorption is also slightly blue-shifted contingent to the ancillary ligands from bpy (18) to phen.
(19). The $^1$MLCT bands of the heteroleptic complexes exhibit two features (shoulders) that have previously been assigned as a statistical combination of the homoleptic complexes; $\frac{1}{3}[\text{Ru}(13)_3]^{2+}$ and $\frac{2}{3}[\text{Ru(bpy/phen)}_3]^{2+}$ ($\lambda_{\text{max}} = 450 \text{ nm for } [\text{Ru(bpy)}_3]^{2+}$ and $\lambda_{\text{max}} = 445 \text{ nm for } [\text{Ru(phen)}_3]^{2+}$).\textsuperscript{277, 283} As the sulfur oxidation state is increased, the $^1$MLCT transition undergoes a slight blue shift, which suggests the involvement of the ligand 13 $\pi^*$ orbital in this transition. The 350 nm shoulder in the spectrum of $[\text{Ru(bpy)}_2(tzS)]^{2+}$ cannot be attributed to the ligand but may be due to a second $^1$MLCT transition from the $d\pi$ to the low-lying second lowest occupied molecular orbital;\textsuperscript{284} or to a $d$-$d$ transition.\textsuperscript{167}

The homoleptic complexes $[\text{Ru(tzS)}_3]^{2+}$ (20-S) and $[\text{Ru(tzSO}_2)_2(\text{MeCN})_2]^{2+}$ (20-SO$_2$) have a low energy $\pi\rightarrow\pi^*$ transition centered at 290 nm and $^1$MLCT transitions at 334 nm and 421 nm respectively. The large difference in MLCT energy from the homoleptic (20-S) to heteroleptic (18-S and 19-S) complexes is attributed to the larger energy gap between the metal $d$ and ligand $\pi^*$ orbitals mainly due to the lowering of the HOMO energy, which is also reflected in the redox chemistry (see section 4.3.3.3).\textsuperscript{277} The complex 20-SO$_2$ has an intense and sharp $^1$MLCT absorption at 421 nm which is comparable with the reported value for $[\text{Ru(bpy)}_2(\text{MeCN})_2]^{2+}$ ($^1$MLCT centered at 440 nm in acetone).\textsuperscript{285} Furthermore, measurement of the absorbance spectrum of all ruthenium complexes (18-20) in either acetonitrile or in dichloromethane leads to the same spectra, further supporting the conclusion that the complexes remain intact in coordinating solvent without exposure to UV-light (Figure A4.17).
**Figure 4.8** UV-vis absorbance spectra of the complexes (solid trace) and the ligands (dashed trace) A. 18 and 13 in CH$_2$Cl$_2$, B. 19 and 13 CH$_2$Cl$_2$, and C. 20 and 13 in MeCN at 293 K.

**Table 4.4** Absorbance maxima of the proligand (13) and the ruthenium(II) complexes (18-20) in solution, solid state and in a polymer matrix.

<table>
<thead>
<tr>
<th></th>
<th>Solution$^a$</th>
<th>Neat$^b$</th>
<th>PMMA$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>tzS (13-S)</td>
<td>266; (293)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>tzSO$_2$ (13-SO$_2$)</td>
<td>(260); 283</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(tzS)]$^{2+}$ (18-S)</td>
<td>245; 289; 339; 445</td>
<td>292; (341); 438</td>
<td>306; (339); 445</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$tzSO$_2$]$^{2+}$ (18-SO$_2$)</td>
<td>250; 286; 433</td>
<td>290; 438</td>
<td>295; 325; 438</td>
</tr>
<tr>
<td>[Ru(phen)$_2$(tzS)]$^{2+}$ (19-S)</td>
<td>265; (290); 404; (444)</td>
<td>296; 408</td>
<td>270; 291; 406; (447)</td>
</tr>
<tr>
<td>[Ru(phen)$_2$(tzSO$_2$)]$^{2+}$ (19-SO$_2$)</td>
<td>264; (292); (373); 428</td>
<td>297; (375); 431</td>
<td>290; (376); 432</td>
</tr>
<tr>
<td>[Ru(tzS)$_3$]$^{2+}$ (20-S)</td>
<td>292; 334</td>
<td>300; 351</td>
<td>299; 351</td>
</tr>
<tr>
<td>[Ru(tzSO$_2$)$_2$(MeCN)$_2$]$^{2+}$ (20-SO$_2$)</td>
<td>292; 421</td>
<td>290; 395</td>
<td>295; 433</td>
</tr>
</tbody>
</table>

$^a$ in CH$_2$Cl$_2$; $^b$ cast from CH$_2$Cl$_2$; ( ) shoulders.

**4.3.3.2 Photoluminescence**

All the complexes show little to no emission in solution. They are very weakly emissive in the solid state and in polymer matrices at 293 K (Figure A4.18 and Figure A4.19). However, all complexes (18-20) show intense emission in the solid state when cooled to 77 K (Figure 4.9). Only the heteroleptic complexes (18 and 19) remain emissive in dichloromethane solution at 77 K (assessed qualitatively). This is common in ruthenium(II) complexes of this type. Their absence of emission at room temperature in fluid solution has been attributed to a deactivation of the $^3$MLCT state by thermal population of the non-emissive metal centered ($^3$MC) state due to a lower $^3$MLCT-$^3$MC energy gap compared to [Ru(bpy)$_3$]$^{2+}$.$^{169,251}$ The lowering of the $^3$MC state is attributed to the decrease of the ligand field strength caused by the change in the N$^N$N bite angle.$^{251}$ Upon ligand substitution from six-membered pyridyl rings to five-membered thiazoles, the bite angle increases and causes a shift in the orbital energy. The addition of the sulfur bridge in the ligands
tzS and tzSO₂ increases the binding angle compared to bpy or phen (~ 90° vs 78° (bpy) and 80° (phen)) compared to ~ 100° for the sulfur bridged ligand (see section 4.3.2.1).²⁸⁶-²⁸⁷

Upon lowering the temperature, the emission intensity increases drastically for heteroleptic complexes containing sulfide or sulfone ligands (13) in the solid state. A small hypsochromic shift is observed upon cooling and the nature of the emitting state appears to be dependent on the oxidation state. Based on the 77 K emission spectra (Figure 4.9), [Ru(bpy)₂(tzS)]²⁺ has a structured emission that is representative of a ³MLCT emissive state, while [Ru(bpy)₂(tzSO₂)]²⁺ has a Gaussian-shaped emission which is characteristic of a ³MC emitting state.¹⁶⁹

The energy of emission of the ruthenium(II) containing ligands 13 is found to be at much higher energy than reported for [Ru(btz)₃]²⁺ (682 nm at 298 K and 647 nm at 77 K).²⁵⁰-²⁵¹ The nature of the emission of this compound is assigned to be a π*-dπ ³MLCT state. The only report of photophysics of this compound was in water solution, while only solid state emission at room temperature was obtained for the compounds in this Chapter.²⁵⁰ Furthermore, no photophysical characterization of [Ru(bpy)₂(btz)]²⁺ has been reported.

Figure 4.9 Emission of solid state films of complexes A. [Ru(bpy)₂(tzS)]²⁺ and B. [Ru(bpy)₂(tzSO₂)]²⁺ excited at 430 nm at indicated temperatures.
Table 4.5 Maximum emission wavelength for ruthenium(II) complexes 18-20 at room temperature as solid and in polymer matrix and 77 K for selected compounds.

<table>
<thead>
<tr>
<th></th>
<th>Neat&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PMMA&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
</tr>
<tr>
<td>293 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)&lt;sub&gt;2&lt;/sub&gt;(tzS)]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>626; 666; (725)</td>
<td>615</td>
</tr>
<tr>
<td>[Ru(bpy)&lt;sub&gt;2&lt;/sub&gt;(SO&lt;sub&gt;2&lt;/sub&gt;)]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>669; (725)</td>
<td>652</td>
</tr>
<tr>
<td>[Ru(phen)&lt;sub&gt;2&lt;/sub&gt;(tzS)]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>615; (659); (740)</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Ru(phen)&lt;sub&gt;2&lt;/sub&gt;(tzSO&lt;sub&gt;2&lt;/sub&gt;)]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>667; (730)</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Ru(tzS)&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>671 (735)</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Ru(tzSO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;(MeCN)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>668 (735)</td>
<td>&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> cast from CH<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup> not attempted; ( ) shoulders

4.3.3.3 Electrochemistry

The electrochemical potentials of metal complexes can give insight on the π-acceptor/π-donating nature of the ligands, the energies of the frontier orbitals (HOMO and LUMO) and the stability and reactivity of the excited/oxidized/reduced state. In most polypyridyl ruthenium(II) complexes, the redox processes involve the same orbitals as the optical transition (absorption or emission). The Ru<sup>3+</sup>/Ru<sup>2+</sup> couple of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> involves the π(t<sub>2g</sub>) orbital of the metal and can be modulated with the introduction of different ligands: the π-back-donation between the ligand and the metal increases as the interaction between the π* ligand orbital and the π(t<sub>2g</sub>) of the metal increases. Furthermore, in the case of mixed ligand systems, the HOMO energy can be modulated by the π-donor/π-acceptor ability of the ligand where the π-acceptor ligand stabilizes the orbital and causes the oxidation potential to shift to higher potentials. As previously discussed, light induced dissociation of the complexes in a coordinating solvent such as acetonitrile was observed by NMR spectroscopy. However, when the solution is kept in the dark and spectra measured promptly, the UV-vis absorbance spectra are unchanged in both non-coordinating dichloromethane and coordinating acetonitrile. This indicates that the complexes are stable under these conditions.
conditions. Therefore, electrochemical measurements of the complexes were performed in acetonitrile (the most suitable solvent for these measurements), assuming that the complexes remain intact in this solvent (Figure 4.10, Figure A2.9- Figure A2.12).

The Ru$^{3+}$/Ru$^{2+}$ half-wave oxidation for [Ru(bpy)$_3$]$^{2+}$ is at 1.54 V (forward scan) and the ruthenium becomes slightly more difficult to oxidize when one of the bpy ligands is replaced by btz (1.56 V for [Ru(bpy)$_2$(btz)]$^{2+}$), which is representative of a stabilization of the HOMO.$^{253,290}$ The complexes 18-20 were compared to literature values of analogous ruthenium complexes and they are represented schematically in Figure 4.11. The heteroleptic complexes (18 and 19) when compared to the homoleptic complexes ([Ru(bpy)$_3$]$^{2+}$ and [Ru(phen)$_3$]$^{2+}$) have their HOMO slightly destabilized when a sulfide is present (1.52 V and 1.59 V for 18-S and 19-S, respectively), while the tzSO$_2$ ligand stabilizes the HOMO (1.88 V and 1.63 V for 18-SO$_2$ and 19-SO$_2$, respectively).

![Cyclic voltammetry of [Ru(bpy)$_2$(tzS)]$^{2+}$ (18-S) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using a platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.5 V; B. zoom of cathodic process; C. zoom of anodic process.](image)

**Figure 4.10** Cyclic voltammetry of [Ru(bpy)$_2$(tzS)]$^{2+}$ (18-S) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using a platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.5 V; B. zoom of cathodic process; C. zoom of anodic process.
Multiple reduction waves are observed for the heteroleptic complexes and are assigned to ligand based reductions. The first reduction potentials are observed at -0.74 V, -0.57 V, -0.71 V and -0.85 V for complexes 18-S, 18-SO₂, 19-S and 19-SO₂ respectively (Table 4.6) and are at more positive potentials than in the respective homoleptic complexes ([Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺). Using the oxidation potential and the first reduction potential, the electrochemical HOMO-LUMO gaps can be calculated and they are found to be 2.26, 2.45, 2.30 and 2.48 eV for 18-S, 18-SO₂, 19-S and 19-SO₂, respectively. The electrochemical HOMO-LUMO gap is dependent on the oxidation state of the bridging sulfur, while only a small difference is observed going from bpy (18) to phen (19) containing complexes. The complexes bearing sulfide ligands (13-S) exhibit a smaller band gap than the complexes with the sulfone containing ligand (13-SO₂) (Table 4.6). When compared to the electrochemical HOMO-LUMO gaps, the optical HOMO-LUMO gap appears to be less sensitive to the presence of the sulfide or the sulfone, as they only differ from 18 to 19 but not from -S to -SO₂. It is possible that this is caused by the orbitals involved in the reduction not being the same orbitals involved in the optical transition, which changes the value of the HOMO-LUMO gap. Furthermore, the homoleptic complexes have a drastic difference between the HOMO-LUMO gap calculated by electrochemical or optical measurements, once again suggesting that the redox events might not involve the same orbital than the optical transition.
Figure 4.11 Redox potentials of the complexes 18-20 and comparisons to literature complexes. a. [167], b. [289], c. [253]. Black: cathodic process; purple: anodic process.

The sulfide-containing homoleptic complex (20-S) shows a stabilized HOMO compared to [Ru(bpy)$_3$]$^{2+}$ and [Ru(btz)$_3$]$^{2+}$ while the homoleptic complex [Ru(tzSO$_2$)$_2$(MeCN)$_2$]$^{2+}$ (20-SO$_2$) has an irreversible first oxidation and is found to be at much lower potential (0.96 V). The irreversible oxidation wave is typical of complexes with acetonitrile ligands; the oxidation of [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ is reported to be at 1.69 V and to be irreversible.$^{291}$ The first reduction is found at a much higher potential for [Ru(tzS)$_3$]$^{2+}$ than for the free ligand (-1.92 V for 13-S), however the [Ru(tzSO$_2$)$_3$]$^{2+}$ reduction is found 0.15 V higher than the free ligand (-0.95 V for 13-SO$_2$). This suggest a larger amount of electron density is donated to the ruthenium(II) center from the tzSO$_2$ (13-SO$_2$) ligand, which is also reflected in the low oxidation potential of [Ru(tzSO$_2$)$_2$(MeCN)$_2$]$^{2+}$. 
Table 4.6 Redox potentials of ruthenium(II) complexes (18-20) and selected literature complexes vs NHE along with the electrochemical and optical band gaps.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{ox}}$(Ru$^{3+}$/Ru$^{2+}$) (V)</th>
<th>$E_{\text{red}}$(V)</th>
<th>$E_g$(eV)</th>
<th>$E_{\text{echem}}$</th>
<th>$E_{\text{optical}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>1.54</td>
<td>-1.08; -1.27; -1.51; -2.15</td>
<td>2.62</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(tzS)]$^{2+}$</td>
<td>1.52</td>
<td>-0.74; -1.31; -1.58</td>
<td>2.26</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(tzSO$_2$)]$^{2+}$</td>
<td>1.88</td>
<td>-0.57; -0.78</td>
<td>2.45</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(btz)]$^{2+}$</td>
<td>1.56</td>
<td>-0.84; -1.20; -1.42</td>
<td>2.40</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Ru(phen)$_3$]$^{2+}$</td>
<td>1.61</td>
<td>-1.19; -1.29; -1.59; -1.99</td>
<td>2.80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Ru(phen)$_2$(tzS)]$^{2+}$</td>
<td>1.59</td>
<td>-0.71; -1.04</td>
<td>2.30</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>[Ru(phen)$_2$(tzSO$_2$)]$^{2+}$</td>
<td>1.63</td>
<td>-0.85</td>
<td>2.48</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>[Ru(tzS)$_3$]$^{2+}$</td>
<td>1.62</td>
<td>-0.75; -1.23</td>
<td>2.19</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>[Ru(tzSO$_2$)$_3$]$^{2+}$</td>
<td>0.95</td>
<td>-0.80; -1.09</td>
<td>1.75</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>[Ru(btz)$_3$]$^{2+}$</td>
<td>1.11</td>
<td>-0.79; -1.00; -1.26</td>
<td>1.9</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

4.3.4 Copper(I) Complexes

4.3.4.1 UV-vis Spectroscopy

The absorbance spectra of the copper(I) complexes 21 and 22 are summarized in Table 4.7 and Figure 4.12. A marked shift is observed upon complexation of the free ligand (dashed traces) to the copper(I) center (solid traces) for complexes 21-S and 22. A $^1$MLCT transition is observed for [Cu(POP)(tzSO$_2$)]$^+$ and [Cu(POP)(hbtz)]$^+$ and centered at 425 nm while no low energy transition typical for a $^1$MLCT absorption band was measured for [Cu(POP)(tzS)]$^+$. In all cases, the complexes have a ligand based transition that resembles the free ligand transition profile and energy. A contribution from the phenyl rings of the POP ligand is expected in the 200-320 nm region and is observed as a shoulder at ~240 nm.$^{256}$ The extended conjugation of the hbtz ligand is observed as a lower energy transition centered at 332 nm.
Figure 4.12 Absorbance of the copper(I) complexes (21-22) and the free ligands (13 and hbtz) in CH₂Cl₂ at 293 K.

Table 4.7 Absorbance maxima of the copper(I) complexes (21-22) in solution, solid thin films and in polymer matrices.

<table>
<thead>
<tr>
<th></th>
<th>Solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Neat&lt;sup&gt;b&lt;/sup&gt;</th>
<th>PMMA&lt;sup&gt;c&lt;/sup&gt;</th>
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</thead>
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<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td></td>
</tr>
<tr>
<td>Hbtz</td>
<td>332</td>
<td>294</td>
<td>290</td>
</tr>
<tr>
<td>[Cu(POP)(tzS)]&lt;sup&gt;+&lt;/sup&gt; (21-S)</td>
<td>277</td>
<td>292</td>
<td>290, 292</td>
</tr>
<tr>
<td>[Cu(POP)(tzSO₂)]&lt;sup&gt;+&lt;/sup&gt; (21-SO₂)</td>
<td>280, 421</td>
<td>292, 410</td>
<td>290, 406</td>
</tr>
<tr>
<td>[Cu(POP)(hbtz)]&lt;sup&gt;+&lt;/sup&gt; (22)</td>
<td>(271), 346, 407</td>
<td>(290, 352, (408))</td>
<td>290, 350, 400</td>
</tr>
</tbody>
</table>

<sup>a</sup> in CH₂Cl₂; <sup>b</sup> casted from CH₂Cl₂; <sup>c</sup> casted from CH₂Cl₂; ( ) shoulders.

4.3.4.2 Photoluminescence

Copper(I) complexes are known to undergo non-radiative decay as the excited state undergoes a geometry change from tetrahedral to square planar (with copper(II) character) in solution<sup>172</sup>. This can be overcome by increasing the steric bulk around the ligand and restricting the motion in the solid state or in a polymer matrix to prevent formation of the square planar geometry.<sup>162, 176, 257</sup> Emission from [Cu(POP)(hbtz)]<sup>+</sup> (22)
was expected due to the alkyl chains present at the 4- positions of the thiazole rings. However, the only emission observed at room temperature in solution was ligand based (overlap with the free ligand emission at 388 nm). The lack of emission from 22 can be explained by the ligand coordinating in a N^S fashion in solution, leading to decay through geometry change or by solvent quenching (see section 4.3.2.2 and 4.3.4.3). In the solid state, complexes [Cu(POP)(tzS)]⁺ (21-S) and [Cu(POP)(hbtz)]⁺ (22) are emissive when irradiated at 409 nm, while [Cu(POP)(tzSO₂)]⁺ (21-SO₂) only shows weak emission. However, when the complexes are confined in a polymer matrix (PMMA) they are all emissive. [Cu(POP)(hbtz)]⁺ (22) has a similar emission energy in the solid state and in a polymer matrix whereas 21-SO₂ shows a higher energy and more defined emission when in PMMA. In contrast, 21-S shows a decrease in the emission energy when going from neat solid to a polymer matrix and has an emission energy higher in the polymer matrix. The increase in emission in the solid state can be attributed to restriction of molecular motion and the absence of solvent to quench the emission. The emission profile of 21-S in PMMA shows slight structure, which may be assigned to the emission from a ³MLCT state.

Figure 4.13 Absorbance and emission of copper(I) complexes in the solid state A. neat and B. in PMMA matrix at 293 K, λ_exc = 405 nm for all except [Cu(POP)(tzS)]⁺ in PMMA λ_exc = 430 nm.
Table 4.8 Maximum emission wavelength for copper(I) complexes 21-22 in solution, solid film and in polymer matrix.

<table>
<thead>
<tr>
<th></th>
<th>Solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Neat&lt;sup&gt;b&lt;/sup&gt;</th>
<th>PMMA&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>[Cu(POP)(tzS)]&lt;sup&gt;+&lt;/sup&gt; (21-S)</td>
<td>-</td>
<td>594</td>
<td>675</td>
</tr>
<tr>
<td>[Cu(POP)(tzSO&lt;sub&gt;2&lt;/sub&gt;)]&lt;sup&gt;+&lt;/sup&gt; (21-SO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>-</td>
<td>650</td>
<td>603</td>
</tr>
<tr>
<td>[Cu(POP)(hbtz)]&lt;sup&gt;+&lt;/sup&gt; (22)</td>
<td>388</td>
<td>619</td>
<td>610</td>
</tr>
</tbody>
</table>

<sup>a</sup> in CH<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup> casted from CH<sub>2</sub>Cl<sub>2</sub>; ( ) shoulders.

4.3.4.3 Electrochemistry

The copper(I) complexes exhibit irreversible oxidation and reduction waves in acetonitrile at 293 K (Figure 4.14, Figure A2.13 and Figure A2.14). The highest potential oxidation is attributed to the Cu<sup>2+</sup>/Cu<sup>+</sup> redox couple, 1.67, 1.56 and 1.89 V for complexes 21-S, 21-SO<sub>2</sub> and 22 respectively. These values are similar to those for previously reported copper(I) POP mixed ligand complexes (1.5 - 1.8 V).<sup>256</sup> The oxidation potential decreases as the oxidation state of the sulfur-bridge increases (0.9 V from 21-S to 21-SO<sub>2</sub>) and the removal of the sulfur bridge (complex 22) leads to a lowering in oxidation potential of 0.22 V compared to [Cu(POP)(tzS)]<sup>+</sup> (21-S). This can be related to the energy of the HOMO which is most stabilized in the absence of the sulfur-bridge (22) while the electron density increases on the copper center as the ligand is changed from tzS to tzSO<sub>2</sub> resulting in a more destabilized HOMO in [Cu(POP)(tzSO<sub>2</sub>)]<sup>+</sup> (21-SO<sub>2</sub>). The Cu<sup>2+</sup>/Cu<sup>+</sup> redox potential is highly dependent on the steric bulk of the ligands, where a bulky ligand resists rearrangement to the square planar geometry favored for copper(II) and results in a higher oxidation potential.<sup>176</sup>
Figure 4.14 Cyclic voltammetry of [Cu(POP)(tzS)][BF₄] (21-S) in 0.1 M NH₄PF₆ acetonitrile solution using a platinum working electrode vs NHE at 293 K.

The first reduction potentials are observed at -0.8 and -1.32 V for complexes 21-S and 21-SO₂ respectively and are attributed to the reduction of the N^N ligand. In the case of [Cu(POP)(hbtz)]^+, no one clear reduction event is observed, but rather multiple small reduction waves are observed at 0.72 V to 0.13 V, -0.62 V and -1.05 V. These events are attributed to the potential presence of a dinuclear species (as discussed in section 4.3.2.2) where the reductions of the two copper(I) center and the N^N ligand (or N^S in the binuclear specie) are observed. The electrochemical and optical HOMO-LUMO gaps are in agreement for complexes 21-SO₂ and 22 while 21-S has a much higher optical HOMO-LUMO gap. This can be attributed to different orbitals being involved in optical and electrochemical events for 21-S.
**Figure 4.15** Redox potentials of the complexes 21-22

**Table 4.9** Electrochemical potentials (vs NHE) of copper(I) complexes measured in 0.1M NH₄PF₆ acetonitrile solution at 293 K

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{ox}}) (V)</th>
<th>(E_{\text{red}}) (V)</th>
<th>(E_g) (eV)</th>
<th>(E_{\text{chem}})</th>
<th>(E_{\text{optical}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu(POP)(tzS)}]^+)</td>
<td>1.67; 0.94</td>
<td>-0.86</td>
<td>2.53</td>
<td></td>
<td>3.12</td>
</tr>
<tr>
<td>([\text{Cu(POP)(tzSO}_2]^+)</td>
<td>1.56</td>
<td>-1.32</td>
<td>2.84</td>
<td></td>
<td>2.56</td>
</tr>
<tr>
<td>([\text{Cu(POP)(hbtz)}]^+)</td>
<td>1.89; 0.71; 0.16</td>
<td>-0.62; -1.05</td>
<td>2.51</td>
<td></td>
<td>2.43</td>
</tr>
</tbody>
</table>

**4.4 Conclusions**

The synthesis of sulfur-bridged thiazole bidentate ligands was carried out and the complexation of these ligands to ruthenium(II) and copper(I) centers was successful. The complexes were found to be stable in MeCN (in the dark) or CH₂Cl₂ which allowed for facile NMR characterization and growth of single crystals. The NMR analysis gave insight on the stability of the complexes in presence of coordinating ligands, and homoleptic complexes were found to be more stable while heteroleptic underwent photoejection. The crystal structures further the understanding of the bonding and the impact of the oxidation state of the bridging sulfur where the bite angle was found to increase upon oxidation in the case of the ruthenium(II) and copper(I) complexes. All the complexes were found to be non-emissive in fluid solution however upon cooling (in the case of the ruthenium complexes 18 and 19) or in the solid state, emission was observed. The electrochemical behavior of the complexes was investigated and a small stabilization of the HOMO of the ruthenium(II) complexes was observed with the increase of the oxidation state of the bridging sulfur. In
the case of the copper(I) complexes, destabilization of the HOMO was observed upon oxidation of the sulfur bridge.

Even though the sulfur-bridged ligands did not result in highly emissive complexes, the homoleptic [Ru(tzS)$_3$]$^{2+}$ complex were found to be stable and possess a higher energy MLCT than analogous [Ru($N^N$)$_3$]$^{2+}$ complexes. This high energy stable complex can be potentially used as photocatalysis or electrocatalysis, and may catalyze reactions that are not possible under other conditions, due to the high reducing potential of the complex.
Chapter 5: Conclusions

In Chapter 2, the incorporation of sulfur bridge in macromolecules (oligomers and polymers) were investigated. The oligomers were obtained by the successive condensation of 2-bromothiophene with 2-thiophene thiol and the resulting compounds were compared to fully conjugated α-oligothiophenes. The energy of the LUMO was found to be dependent on the oxidation state of the sulfur bridge and the length of the oligomer while the HOMO was only dependent on the oxidation state, in contrast to α-oligothiophenes where the LUMO and HOMO energies decrease with the length of the compound. This was attributed to the electronic nature of the sulfide (electron rich) which makes the oxidation easier than with an electron poor sulfone. Furthermore, the band gap of the sulfur-bridged compounds decreased as the number of thiophene (and sulfur bridges) increases which is consistent with the fully conjugated α-oligothiophenes. A more intense emission was observed in the sulfone containing oligomers, while the sulfides exhibit conjugated-like behavior. The incorporation of sulfur bridges in polymeric material was achieved using DHAP coupling 2,5-dibromo-3,4-dialkylthiophene with 2,2'-thienylsulfide or sulfone which led to polymers containing terthiophene conjugated segments separated by sulfur atoms. The polymeric materials were compared to sulfur-bridged terthiophenes and PT. Sulfur containing polymers exhibit conjugated like behavior while the sulfones showed increased emission intensity similarly to model terthiophene.

Further work might include conductivity measurements upon chemical, electrochemical and photochemical doping of the polymer material. Furthermore, the incorporation of larger chromophores in sulfur-bridged trimers could led to interesting chemistry, along with the possibility of creating push-pull systems. In the latter, the center would be an electron rich chromophore while the two end units would be intrinsically electron deficient (or vice versa). This would enhance the charge transfer state stability and possibly enhance the lifetime of the chromophore, with possible application as organic photocatalysis or in light harvesting. Finally, the expected low conductivity of the sulfur-containing polymers could be
statistically integrated in copolymerized with larger conductivity, such as PT, either through chemical or electrochemical methods.

In Chapter 3, the method developed in Chapter 2 was applied to the synthesis of copolymers containing electron rich or electron deficient comonomers. The energy of the HOMO and LUMO was found to be dependent on the nature of the comonomers while no clear trend was observed, the HOMO level is lowered in sulfone-containing polymers. This lower HOMO energy was attributed to the ease of oxidation of the electron rich sulfide over the electron poor sulfone. The emission intensity of the polymers was significantly larger for the sulfone-containing polymers in solution and in the solid state. Furthermore, the incorporation of bithiazole moieties was possible and led to coordination of metal ions. The presence of metals led to a shift in the $^1$H NMR, absorption and emission spectra. Coordination of palladium(II) with polymers containing sulfide and bithiazole was the most stable and led to the largest shift in NMR and emission quenching.

Future work with the copolymers containing sulfur bridges could include the incorporation of the highly emissive polymers in OLED devices. Synthesis and isolation of metal containing polymers with different metals (Ru, Pd, Pt, Os…) and the measurement of their photophysical and electrochemical properties in solid state is of interest for applications such as solid state catalysis and photocatalysis. Furthermore, the coordinating moieties in the polymer backbone along with the metal could be tuned to obtain emissive polymers.

In Chapter 4, sulfur-bridged thiazoles were used as ligands on ruthenium(II) and copper(I). Heteroleptic complexes were obtained with 2,2'-bipyridine and 1,10-phenanthroline for ruthenium(II), and DPEPhos for copper(I). A single example of a homoleptic complex was obtained with ruthenium using 2,2'-bithiazole sulfide (21-S), where attempts to complex the 2,2'-bithiazole sulfone (21-SO$_2$) led to the bis(acetonitrile) complex. The ruthenium (II) heteroleptic complexes undergo photoejection when irradiated with UV light in coordinating solvent, where the sulfur containing ligand is replaced by two solvent molecules. All sulfur-bridged complexes were emissive in the solid state, while no emission was observed in solution at room
temperature. Upon cooling, the intensity of emission in solution and in the solid state increased in all cases, with the exception of the homoleptic ruthenium(II) which did not show emission at 77 K in solution. The electrochemical measurements revealed a small stabilization of the HOMO with an increase in oxidation state of the bridging sulfur for the ruthenium(II) heteroleptic complexes while it led to a small destabilization of the HOMO in the case of the copper(I) complexes.

Further work could include the synthesis of ruthenium(II) bithiazole analogues to directly measure the impact of the sulfur-bridged ligands on the complex chemistry. Moreover, the synthesis of mixed ligand ruthenium(II) complexes with 2,2'-bithiazole and the sulfur-bridged ligands are novel structures that have not been investigated and based on the explored chemistry in Chapter 4 would show interesting electrochemistry behavior. Furthermore, the investigation of the sulfoxide bridged ligand could led to interesting N^O coordination motifs and potential N^O→N^S photoswitching. All of the ruthenium(II) complexes, both those synthesized and those proposed, would be interesting candidates to test for electrocatalytic CO2 reduction. Additionally, the synthesis of homoleptic copper(I) complexes might have noteworthy electrochemistry, especially with an increase of the bulk in the 4,4' positions of the 2,2'-bithiazole sulfide and sulfone which could led to decreased geometry relaxation and improve the emission intensity of the copper(I) complexes. Finally, the addition of a charged group in the 4,4' position of the sulfur-bridged bithiazole could result in a neutral complex with ruthenium(II) which is desirable for the applications in optoelectronic devices.162,292
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Appendices

Appendix 1 - NMR Spectroscopy

Figure A1.1 1D and 2D proton NMR spectra of P3 in CD$_2$Cl$_2$ at 298 K.
Figure A1.2 1D and 2D proton NMR spectra of P4 in CD$_2$Cl$_2$ at 298 K.
Figure A1.3 1D and 2D proton NMR spectra of P5 in CD$_2$Cl$_2$ at 298 K.
Figure A1.4 1D and 2D proton NMR spectra of P6 in CD$_2$Cl$_2$ at 298 K.
Figure A1.5 1D and 2D proton NMR spectra of P7 in CD$_2$Cl$_2$ at 298 K.
Figure A1.6 1D and 2D proton NMR spectra of P8 in CD₂Cl₂ at 298 K.
Figure A1.7 1D and 2D proton NMR spectra of P9 in CD$_2$Cl$_2$ at 298 K.
Figure A1.8 1D and 2D proton NMR spectra of P10 in CD$_2$Cl$_2$ at 298 K.
Figure A1.9 $^1$H NMR spectra of P1 in the presence of Ag(OTf), Pd(AC)$_2$ and [Cu(MeCN)$_4$][BF$_4$] at 298 K in CD$_2$Cl$_2$. 
Figure A1.10 $^1$H NMR spectra of P2 in the presence of Ag(OTf), Pd(Ac)$_2$ and [Cu(MeCN)$_4$][BF$_4$] at 298 K in CD$_2$Cl$_2$. 
Figure A1.11 $^1$H NMR spectra of P5 in the presence of Ag(OTf), Pd(Ac)$_2$ and [Cu(MeCN)$_4$][BF$_4$] at 298 K in CD$_2$Cl$_2$. 
Figure A1.12 $^1$H NMR spectra of P6 in the presence of Ag(OTf), Pd(Ac)$_2$ and [Cu(MeCN)$_4$][BF$_4$] at 298 K in CD$_2$Cl$_2$. 
Figure A1.13 $^1$H NMR of [Ru(bpy)$_2$(tzSO$_2$)$_2$]$_{2+}$(18-SO$_2$) in A. DCM B. DCM + 10 eq. of MeCN in the dark at t = 20 min, C. DCM + 10 eq. of MeCN in the sunlight at t = 2 min, D. DCM +10 eq. of MeCN in the sunlight at t = 48 h, E. DCM + 10 eq. of MeCN under UV light t = 15 min and F. DCM + 10 eq. of MeCN under visible light t = 15 min at 298 K.
Figure A1.14 NOESY NMR in CD$_3$CN at 298 K of A. [Ru(bpy)$_2$(tzS)]$^{2+}$ (18-S) and B. [Ru(bpy)$_2$(tzSO$_2$)]$^{2+}$ (18-SO$_2$).
Figure A1.15 400 MHz A. $^1$H NMR and B. COSY of the complexes [Ru(bpy)$_2$(tzS)]$^{2+}$ (18-S) in CD$_2$Cl$_2$ at 298 K.
Figure A1.16 400 MHz A. $^1$H NMR and B. COSY of the complexes [Ru(bpy)$_2$(tzSO$_2$)]$^{2+}$ (18-SO$_2$) in CD$_2$Cl$_2$ at 298 K.
Figure A1.17 400 MHz A. $^1$H NMR and B. COSY of the complexes [Ru(phen)$_2$(tzS)]$^{2+}$ (19-S) in CD$_2$Cl$_2$ at 298 K.
**Figure A1.18** 400 MHz A. $^1$H NMR and B. COSY of the complexes $[\text{Ru(phen)}_2(\text{tzSO}_2)]^{2+}$ (19-SO$_2$) in CD$_2$Cl$_2$ at 298 K.
Figure A1.19 $^1\text{H}$, $^{13}\text{C}$,$^1\text{H}$ and $^{31}\text{P}$,$^1\text{H}$ of [Cu(POP)(tzS)]$^+$ (21-S) performed on a 400 MHz NMR in CD$_3$CN at 298 K.
Figure A1.20 $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) of [Cu(POP)(tzSO$_2$)]$^+$ (21-SO$_2$) performed on a 400 MHz NMR in CD$_2$Cl$_2$ at 298 K.
Figure A1.21 $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} of [Cu(POP)(hbtz)]$^+$ (22) performed on a 400 MHz NMR in CD$_3$CN at 298 K.
Appendix 2 - Electrochemical Measurements

Figure A2.1 Cyclic voltammetry onset measurement of oxidation for calculation of the HOMO of A. 5-S, B. 5-SO₂, C. 6-S, D. 6-SO₂, E. 7-S and F. 7-SO₂.
Figure A2.2 Cyclic voltammetry onset measurements of reduction for calculation of the LUMO of A. 5-S, B. 5-SO₂, C. 6-S, D. 6-SO₂, E. 7-S and F. 7-SO₂.
Figure A2.3 Cyclic voltammetry onset measurements of A. P1-C reduction, B. P1-C oxidation, C. P2-C reduction and D. P2-C oxidation for calculation of the HOMO and LUMO.
Figure A2.4 Cyclic voltammetry (vs NHE) of polymer P1 and P2 adsorbed on a glassy carbon electrode in 0.1 M NH₄PF₆ MeCN solution under inert atmosphere.
Figure A2.5 Cyclic voltammetry (vs NHE) of polymer P3 and P4 adsorbed on a glassy carbon electrode in 0.1 M NH₄PF₆ MeCN solution under inert atmosphere.
Figure A2.6 Cyclic voltammetry (vs NHE) of polymer P5 and P6 adsorbed on a glassy carbon electrode in 0.1 M NH₄PF₆ MeCN solution under inert atmosphere.
**Figure A2.7** Cyclic voltammetry (vs NHE) of polymer P7 and P8 adsorbed on a glassy carbon electrode in 0.1 M NH₄PF₆ MeCN solution under inert atmosphere.
**Figure A2.8** Cyclic voltammetry (vs NHE) of polymer **P9** and **P10** adsorbed on a glassy carbon electrode in 0.1 M NH₄PF₆ MeCN solution under nitrogen.
Figure A2.9 Cyclic voltammetry of [Ru(bpy)$_2$(tzSO$_2$)][PF$_6$]$\text{$_2$}$ (18-SO$_2$) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.0 to 2.5 V; B. zoom of cathodic process; C. zoom of anodic process.
Figure A2.10 Cyclic voltammetry of [Ru(phen)$_2$(tzS)][PF$_6$]$_2$ (19-S) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.0 V; B. zoom of cathodic process; C. zoom of anodic process.
Figure A2.11 Cyclic voltammetry of \([\text{Ru(phen)}_2(\text{tzSO}_2)][\text{PF}_6]_2\) (19-SO$_2$) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2 V; B. zoom of cathodic process; C. zoom of anodic process.
Figure A2.12 Cyclic voltammetry of [Ru(tzS)$_3$][PF$_6$]$_2$ (20-S) in 0.1 M NH$_4$PF$_6$ acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.0 V; B. zoom of cathodic process; C. zoom of anodic process.
Figure A2.13 Cyclic voltammetry of \([\text{Cu(POP)(tzSO}_2)]\text{[BF}_4]\) (21-SO\(_2\)) in 0.1 M NH\(_4\)PF\(_6\) acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.0 V; B. zoom of cathodic process; C. zoom of anodic process.
Figure A2.14 Cyclic voltammetry of [Cu(POP)(hbtz)][BF₄] (22) in 0.1 M NH₄PF₆ acetonitrile solution using platinum working electrode vs NHE at 293 K. A. Full scan from -1.5 to 2.0 V; B. zoom of anodic process.
Appendix 3  Physical Characterization

Figure A3.1 Representative GPC trace of P1 eluted in THF; - light scattering, - differential refractometer, - viscosity.
Figure A3.2 Differential scanning calorimetry of the copolymers (P1-P10) third cycle of heating at 10 °C/min from -10 °C to 180 °C.
Figure A3.3 Thermal gravimetric measurements of polymers P1-P7 under nitrogen.
Figure A3.4 Thermal gravimetric measurements of P7-P10 under nitrogen.
Appendix 4 - Photophysical Characterization

Figure A4.1 UV-vis absorbance of the polymers (P1-P10) in CH₂Cl₂, PhCl and THF at 293 K.
Figure A4.2 UV-vis absorbance of polymer (P1-P10) films casted from THF, PhCl and CHCl$_3$ at 293 K.
Figure A4.3 Emission spectra of the polymers (P1-P10) in PhCl, THF and CH$_2$Cl$_2$ corrected for their optical density at 293 K and referenced to the most emissive polymer P8.
Figure A4.4 Emission spectra of the polymers (P1-P10) film casted from CHCl₃, PhCl and THF at 293 K.

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<th>Solid state CHCl₃</th>
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<td>580</td>
<td>581</td>
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<tr>
<td>P2</td>
<td>515</td>
<td>509; 541</td>
<td>520</td>
</tr>
<tr>
<td>P3</td>
<td>615</td>
<td>614</td>
<td>616</td>
</tr>
<tr>
<td>P4</td>
<td>550</td>
<td>551</td>
<td>554</td>
</tr>
<tr>
<td>P5</td>
<td>566</td>
<td>601</td>
<td>596</td>
</tr>
<tr>
<td>P6</td>
<td>668</td>
<td>667</td>
<td>666</td>
</tr>
<tr>
<td>P7</td>
<td>622</td>
<td>612; 646</td>
<td>612</td>
</tr>
<tr>
<td>P8</td>
<td>478</td>
<td>479; 500</td>
<td>504</td>
</tr>
<tr>
<td>P9</td>
<td>569</td>
<td>567</td>
<td>573</td>
</tr>
<tr>
<td>P10</td>
<td>591</td>
<td>598</td>
<td>597</td>
</tr>
</tbody>
</table>

a. Solvent from which the films were casted
Figure A4.5 UV-vis spectra of the polymer in the presence of excess metal. P1 with
A. Pd(COOCF$_3$)$_2$, B. Cu(COOCH$_3$)$_2$, C. Ag(OTf) and P2 with D. Pd(COOCF$_3$)$_2$, E. Cu(COOCH$_3$)$_2$
F. Ag(OTf).
Figure A4.6 UV-vis spectra of the polymer in the presence of excess metal. P5 with
A. Pd(COOCF₃)₂, B. Cu(COOCH₃), C. Ag(OTf) and P2 with D. Pd(COOCF₃)₂, E. Cu(COOCH₃), F. Ag(OTf).
Figure A4.7 Impact of the concentration of Cu(COOCH₃) on the emission of P₁, P₂, P₅ and P₆ in THF at 293 K.
Figure A4.8 Impact of the concentration of Ag(OTf) on the emission of P1, P2, P5 and P6 in THF at 293 K.
Figure A4.9 Impact of the concentration of Ag(COOCF₃) on the emission of P1, P2, P5 and P6 in THF at 293 K.
Figure A4.10 Impact of the concentration of Pd(COOCH$_3$)$_2$ on the emission of P1, P2, P5 and P6 in THF at 293 K.
Figure A4.11 Impact of the concentration of Pd(COOCF₃)₂ on the emission of P1, P2, P5 and P6 in THF at 293 K.
Figure A4.12 Impact of the concentration of Pd[cod]Cl$_2$ on the emission of P1, P2, P5 and P6 in THF at 293 K.

Figure A4.13 Impact of metal cations on the emission of P1 in THF at 293 K.
Figure A4.14 Impact of metal cations on the emission of $\textbf{P2}$ in THF at 293 K.
Figure A4.15 Impact of metal cations on the emission of P5 in THF at 293 K.

Figure A4.16 Impact of metal cations on the emission of P6 in THF at 293 K.
Figure A4.17 Absorbance of $[\text{Ru(bpy)}_2(tz\text{SO}_2)]^{2+}$ (18-SO$_2$) in acetonitrile in the dark and after sunlight irradiation for 72 hours at 293 K.

Figure A4.18 Absorbance and emission of ruthenium(II) complexes A.18, B. 19 and C. 20 as films casted from CH$_2$Cl$_2$ at 293 K.
Figure A4.19 Absorbance and emission of ruthenium(II) complexes A. 18 and B. 19 in PMMA films at 293 K.
Appendix 5 - Single Crystal X-Ray Diffraction

13-S

13-SO₂

Figure A5.1 Solid state structures of proligand 13-S and 13-SO₂. Thermal ellipsoids are drawn at 50% probability. Counter ions and occluded solvent molecules are omitted for clarity.
Table A5.1 Selected crystal structure data for proligands 13-S and 13-SO$_2$.

<table>
<thead>
<tr>
<th></th>
<th>tzS (13-S)</th>
<th>tzSO$_2$ (13-SO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>formula</strong></td>
<td>C$_6$H$_4$N$_2$S$_3$</td>
<td>C$_6$H$_4$N$_2$O$_2$S$_3$</td>
</tr>
<tr>
<td><strong>dimension / mm</strong></td>
<td>0.499 × 0.401 × 0.201</td>
<td>0.466 × 0.301 × 0.010</td>
</tr>
<tr>
<td><strong>temperature / K</strong></td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>cryst syst</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>Cc</td>
<td>P2$_1$/n</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>5.1947(7)</td>
<td>5.6977(6)</td>
</tr>
<tr>
<td><strong>b / Å</strong></td>
<td>13.717(2)</td>
<td>21.8113(2)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>10.9339(16)</td>
<td>7.5732(11)</td>
</tr>
<tr>
<td><strong>α / °</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β / °</strong></td>
<td>93.100(5)</td>
<td>111.635(5)</td>
</tr>
<tr>
<td><strong>γ / °</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>V / Å$^3$</strong></td>
<td>778.0(2)</td>
<td>874.92(18)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>μ / mm$^{-1}$</strong></td>
<td>0.878</td>
<td>0.810</td>
</tr>
<tr>
<td><strong>R[F$_2$&gt;2σ(F$_2$)]$^a$</strong></td>
<td>0.0342</td>
<td>0.0485</td>
</tr>
<tr>
<td><strong>R_F$^a$</strong></td>
<td>0.0861</td>
<td>0.1170</td>
</tr>
<tr>
<td><strong>goodness of fit</strong></td>
<td>0.889</td>
<td>0.951</td>
</tr>
<tr>
<td><strong>C3-S2-C4 angle / °</strong></td>
<td>101.68(15)</td>
<td>104.46(12)</td>
</tr>
</tbody>
</table>

*Function minimized by R = Σ |F$_{0}$| - |F$_c$| /Σ |F$_{0}$|, R$_w$ = [Σ(w(F$_{0}$-F$_c$)$^2$)]/Σ(Σw(F$_{0}$)$^2$)]$^{1/2}$.*
Table A5.2 Selected crystal structure data for [Ru(bpy)$_2$(tzS)][PF$_6$]$_2$ (18-S) and [Ru(phen)$_2$(tzSO$_2$)][PF$_6$]$_2$ (19-SO$_2$).

<table>
<thead>
<tr>
<th></th>
<th>[Ru(bpy)$_2$(tzS)][PF$_6$]$_2$</th>
<th>[Ru(phen)$_2$(tzSO$_2$)][PF$_6$]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{26}$H$</em>{20}$N$_6$RuS$_3$P$<em>2$F$</em>{12}$</td>
<td>C$<em>{30}$H$</em>{20}$N$_6$O$_2$RuS$_3$P$<em>2$F$</em>{12}$</td>
</tr>
<tr>
<td>dimension / mm</td>
<td>0.123 $\times$ 0.101 $\times$ 0.090</td>
<td>0.123 $\times$ 0.101 $\times$ 0.050</td>
</tr>
<tr>
<td>temperature / K</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>cryst syst</td>
<td>triclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>P$\bar{1}$</td>
<td>Pbca</td>
</tr>
<tr>
<td>a / Å</td>
<td>9.9194(10)</td>
<td>12.8317(8)</td>
</tr>
<tr>
<td>b / Å</td>
<td>12.2967(12)</td>
<td>15.276(1)</td>
</tr>
<tr>
<td>c / Å</td>
<td>15.4919(16)</td>
<td>36.552(2)</td>
</tr>
<tr>
<td>$\alpha$ / $^\circ$</td>
<td>83.535(2)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ / $^\circ$</td>
<td>78.175(2)</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$ / $^\circ$</td>
<td>71.471(1)</td>
<td>90</td>
</tr>
<tr>
<td>V / Å$^3$</td>
<td>1751.4(3)</td>
<td>7164.8(8)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>$\mu$ / mm$^{-1}$</td>
<td>0.729</td>
<td>1.199</td>
</tr>
<tr>
<td>$R[F^2&gt;2\sigma(F^2)]^a$</td>
<td>0.0486</td>
<td>0.0825</td>
</tr>
<tr>
<td>$R_w(F^2)^a$</td>
<td>0.1325</td>
<td>0.2115</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>0.929</td>
<td>1.071</td>
</tr>
</tbody>
</table>

$^a$ Function minimized by $R = \Sigma |F_0|-|F_c|/\Sigma |F_0|$, $R_w = [\Sigma (w(F_0^2-F_c^2)^2)/\Sigma (w(F_0^2))^2]^{1/2}$. 

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Table A5.3 Selected crystal structure data for [Ru(tzS$_3$)][PF$_6$]$_2$ (18-S) and [Ru(tzSO$_2$)$_3$][PF$_6$]$_2$ (18-SO$_2$).

<table>
<thead>
<tr>
<th></th>
<th>[Ru(tzS)$_3$][PF$_6$]$_2$</th>
<th>[Ru(tzSO$_2$)$_3$][PF$_6$]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{18}$H$</em>{12}$N$_6$RuS$_9$PF$_6$</td>
<td>C$<em>{16}$H$</em>{14}$F$_{12}$N$_6$O$_4$P$_2$RuS$_6$</td>
</tr>
<tr>
<td>dimension / mm</td>
<td>0.120 × 0.117 × 0.101</td>
<td>0.333 × 0.304 × 0.090</td>
</tr>
<tr>
<td>temperature / K</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>P2$_1$/c</td>
<td>Pbca</td>
</tr>
<tr>
<td>a / Å</td>
<td>20.740(2)</td>
<td>15.7488(10)</td>
</tr>
<tr>
<td>b / Å</td>
<td>11.2518(11)</td>
<td>10.2530(6)</td>
</tr>
<tr>
<td>c / Å</td>
<td>19.1696(19)</td>
<td>18.1104(11)</td>
</tr>
<tr>
<td>a / °</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β / °</td>
<td>110.755(5)</td>
<td>90</td>
</tr>
<tr>
<td>γ / °</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V / Å$^3$</td>
<td>4183.2(7)</td>
<td>2924.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>μ / mm$^{-1}$</td>
<td>1.257</td>
<td>1.191</td>
</tr>
<tr>
<td>R[F$^2$&gt;2σ(F$^2$)]$^a$</td>
<td>0.1235</td>
<td>0.0225</td>
</tr>
<tr>
<td>R$_w$(F$^2$)$^a$</td>
<td>0.4000</td>
<td>0.0612</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>1.618</td>
<td>1.047</td>
</tr>
</tbody>
</table>

$^a$ Function minimized by $R = \Sigma |F_0| - |F_c| / |\Sigma |F_0|$, $R_w = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$. 

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Table A5.4 Selected crystal structure data for [Cu(POP)(TzS)][BF₄]₃ (21-S) and [Cu(POP)(TzSO₂)][BF₄] (21-SO₂).

<table>
<thead>
<tr>
<th></th>
<th>[Cu(POP)(TzS)][BF₄]</th>
<th>[Cu(POP)(TzSO₂)][BF₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₄₂H₃₂CuN₂OP₂S₃BF₄</td>
<td>C₄₂H₃₂CuN₂O₃S₃BF₄</td>
</tr>
<tr>
<td>dimension / mm</td>
<td>0.384 × 0.111 × 0.020</td>
<td>0.409 × 0.208 × 0.105</td>
</tr>
<tr>
<td>temperature / K</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a / Å</td>
<td>13.0385(9)</td>
<td>13.2844(6)</td>
</tr>
<tr>
<td>b / Å</td>
<td>44.590(3)</td>
<td>12.9331(6)</td>
</tr>
<tr>
<td>c / Å</td>
<td>14.4382(8)</td>
<td>25.3545(11)</td>
</tr>
<tr>
<td>α / °</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β / °</td>
<td>94.266(2)</td>
<td>93.737(2)</td>
</tr>
<tr>
<td>γ / °</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V / Å³</td>
<td>8370.9(9)</td>
<td>4346.9(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>μ / mm⁻¹</td>
<td>0.789</td>
<td>0.754</td>
</tr>
<tr>
<td>R[F²&gt;2σ(F²)]</td>
<td>0.0934</td>
<td>0.0788</td>
</tr>
<tr>
<td>Rₛ(F²)</td>
<td>0.2847</td>
<td>0.2360</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>1.049</td>
<td>1.132</td>
</tr>
</tbody>
</table>

*a.* Function minimized by R = Σ |F₀| - |Fₑ| / |Σ| |F₀|, Rₛ = [Σ(w(F₀²-Fₑ²)²) / Σ(w(F₀)²)]^{1/2}.
Table A5.5 Selected crystal structure data for [Cu(POP)(hbtz)][BF$_4$]$_2$ (22).

<table>
<thead>
<tr>
<th></th>
<th>[Cu(POP)(hbtz)][BF$_4$]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>formula</strong></td>
<td>C$<em>{54}$H$</em>{56}$CuN$_2$OP$_2$S$_2$BF$_4$</td>
</tr>
<tr>
<td><strong>dimension / mm</strong></td>
<td></td>
</tr>
<tr>
<td><strong>temperature / K</strong></td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>cryst syst</strong></td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P$ar{1}$</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>12.6003(14)</td>
</tr>
<tr>
<td><strong>b / Å</strong></td>
<td>13.8878(15)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>15.3231(16)</td>
</tr>
<tr>
<td><strong>α / °</strong></td>
<td>72.305(4)</td>
</tr>
<tr>
<td><strong>β / °</strong></td>
<td>71.948(4)</td>
</tr>
<tr>
<td><strong>γ / °</strong></td>
<td>66.698(4)</td>
</tr>
<tr>
<td><strong>V / Å$^3$</strong></td>
<td>2290.4(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>μ / mm$^{-1}$</strong></td>
<td>0.680</td>
</tr>
<tr>
<td><strong>R[F$^2$&gt;2σ(F$^2$)]$^a$</strong></td>
<td>0.0577</td>
</tr>
<tr>
<td><strong>R_w(F$^2$)$^a$</strong></td>
<td>0.1802</td>
</tr>
<tr>
<td><strong>goodness of fit</strong></td>
<td>1.070</td>
</tr>
</tbody>
</table>

*a. Function minimized by $R = \Sigma \left| |F_0| - |F_c| \right| / \Sigma |F_0|$, $R_w = [\Sigma (w(F_o^2-F_c^2)^2)/\Sigma (w(F_o^2)^2)]^{1/2}$.*
Appendix 6 - Catalytic Cycle

Figure A6.1 Catalytic cycle of the direct heteroarylation polymerization either using an additive (left) or no additive (right). Adapted from reference [99].