NOVEL LUMINESCENT METALLOPOLYMERS OF Pt(II),Ag(I),Cu(I): THEIR

SYNTHESIS,CHARACTERIZATION AND POTENTIAL OPTOELECTRONIC

APPLICATIONS

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

IN THE GRADUATE SCHOOL OF THE

TEXAS WOMAN'S UNIVERSITY

COLLEGE OF ART AND SCIENCES

BY

PRIYANKA VASABHAKTULA, B.S.

DENTON,TEXAS

DECEMBER 2009

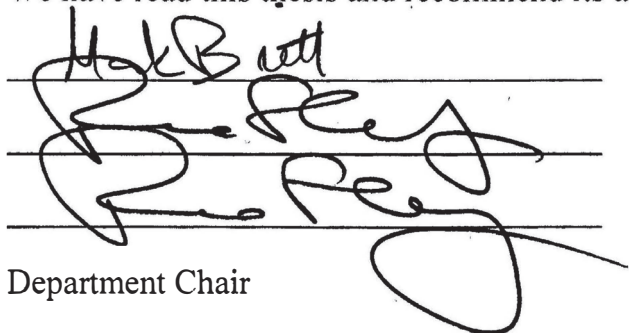TEXAS WOMAN'S UNIVERSITY
DENTON, TEXAS

November 6, 2009

To the Dean of the Graduate School:

I am submitting herewith a thesis written by Priyanka Vasabhaktula entitled "Novel Luminescent Metallopolymers of Pt(II),Ag(I),Cu(I):Their Synthesis, Characterization and Optoelectronic Applications."I have examined this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Chemistry.
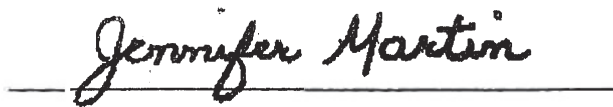
Dr. Manal Omary, Major Professor

We have read this thesis and recommend its acceptance:

Department Chair

Accepted:

Dean of the Graduate School

ACKNOWLEDGEMENTS

ABSTRACT

PRIYANKA VASABHAKTULA

NOVEL LUMINESCENT METALLOPOLYMERS OF Pt(II),Ag(I),Cu(I): THEIR SYNTHESIS, CHARACTERIZATION AND POTENTIAL OPTOELECTRONIC APPLICATIONS

DECEMBER 2009

This thesis with it 59 pp., 19 Figures and references is a study of group 10 and 11 based metallopolymers. This topic is a part of a research on metallopolymers for various optoelectronic applications. This thesis discusses the major chapters that involve synthetic strategies to obtain and enhance the phosphorescence of luminescent metallopolymer of Pt(II),Ag(I) and Cu(I).

The first chapter includes an introduction to photoluminescence, luminescent group 10 and 11 monovalent complexes, metallopolymers and their application as light emitting diodes. The second chapter includes the photophysical characterization of the Pt(II) metallopolymers, which have been found to exhibit Pt-centered phosphorescence. The third chapter includes the photophysical characterization of the silver (I) and copper(I) metallopolymers, which have been investigated as an inexpensive alternate to Pt(II) analogues and were also found to exhibit metal-centered phosphorescence.The spectroscopic and materials properties of all metallopolymers are compared and contrasted versus the metal ion, ligands in the metal precursor.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

This thesis is the study of the synthesis and spectroscopic properties of group 10(d8) and 11(d10) based phosphorescent metallopolymers. It is a study of their luminescence properties and their potential use in energy-saving optoelectronic devices. The following sections present a literature review of relevant topics. Section 1.1 describes in brief the photoluminescence process. Section 1.2 is an overview of metallopolymers and their applications in electronic devices. Section 1.3 gives an insight into the spectroscopy of group 11{Ag(I),Cu(I)} based coordination compounds. Section 1.4 gives an insight into the spectroscopy of group 10{Pt(II)} based coordination compounds.Section1.5 describes in brief the role of group 10 and 11 metallopolymers in the fabrication of a Polymer Light Emitting Diode(PLED). Section 1.6 concludes this chapter by giving an outline of how this thesis attempts to explain the strategic approach employed as well as possibly incorporate them into devices.

1.1   Introduction to Photoluminescence

Photoluminescence refers to fluorescence or phosphorescence emissions, and is the result of a photophysical process. The radiative and nonradiative transitions that lead to the observation of molecular photoluminescence are typically illustrated by an energy level

diagram called the Jablonski diagram.[1] A Jablonski diagram explains the mechanism of light emission in most organic and inorganic luminophores.

Singlet excited states   **Triplet excited states**

Internal Conversion   Vibrational relaxation

S_2 Intersystem Crossing

S_1 T_1

Absorption

E   Internal and external conversion

                    Flourescence   Phosphorescence

S_0

Ground state   Vibrational relaxation

λ_2 λ_1 λ'_r λ_r λ_3 λ_4
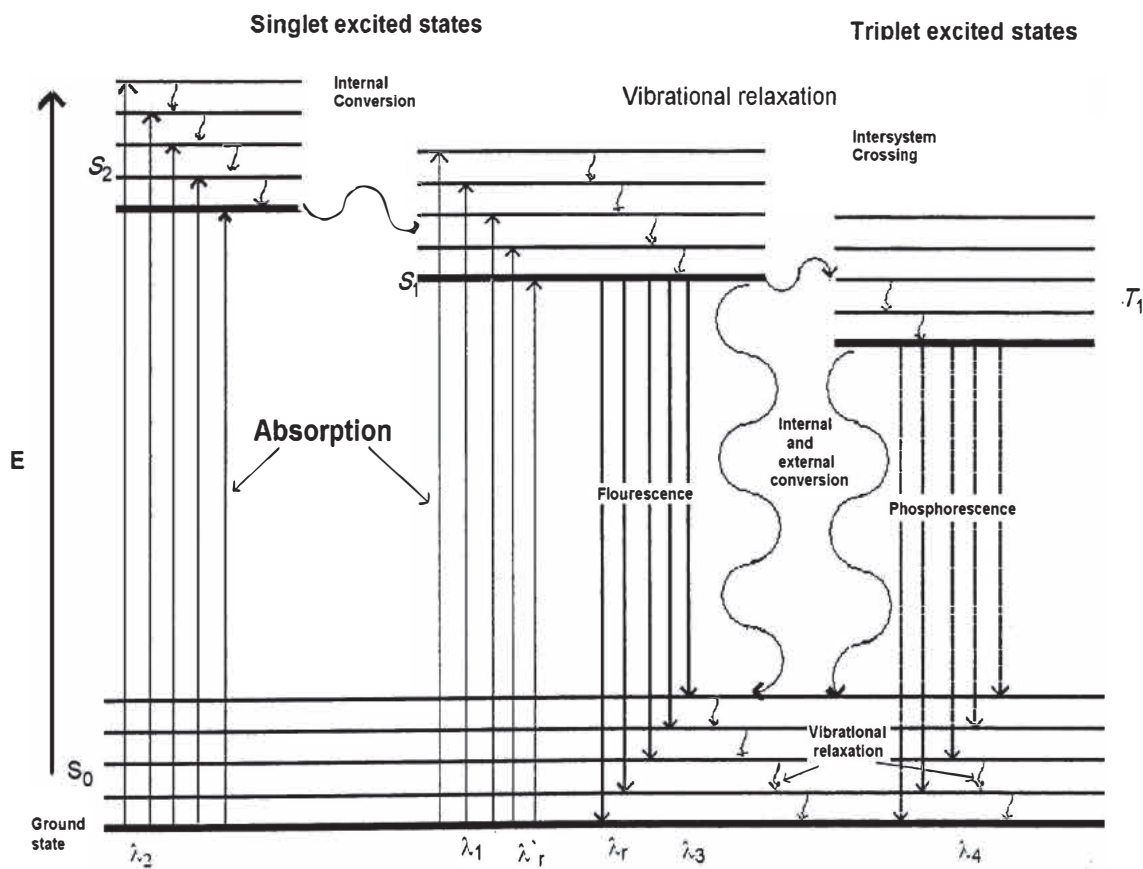
Figure 1.   Illustration of the possible radiative and non-radiative transitions of an organic molecule

For a photophysical transition to occur, a discrete quantum of light (photon), of the appropriate wavelength and energy should be absorbed, thus causing the molecule to gain an excess of energy, and resulting in the formation of an energetically unstable state (electronically excited state) relative to the ground state of the molecule. The excited molecule may consequently undergo a chemical reaction, or just dispel its energy by a

photophysical sequence of deactivation by non-radiative and radiative processes.[2,3] The radiative processes, depending upon spin selection rules for the electronic transitions can be classified as Fluorescence(spin-allowed) and Phosphorescence(spin-forbidden). Fluorescence results from a radiative transition between two electronic states of the same spin multiplicity,[2-5] while phosphorescence occurs due to the radiative transition between two states of different spin multiplicity.[2,6,7] The radiative transitions that result are allowed or forbidden, depending on whether they obey certain factors known as the selection rules. In general, the selection rules are governed by spin multiplicity, for example the forbidden transition is relatively slow and is featured by its longer lifetime, which can continue for several seconds for typical organic molecules in a process called phosphorescence whereas spin–allowed transitions occur rapidly and have a comparatively shorter lifetime.

1.2   Overview of Metallopolymers and Their Applications in Electronic Devices

The first attempt to use polymers in fabrication of light emitting devices was initiated by the discovery of the first luminescent polymer in 1989 at Cambridge University.[8] However, the efficiency of the initial devices was very low[9],in view of this fact, metallopolymers have attracted the interest of many researchers because they combine the physical and mechanical characteristics of polymers with the electrical and optical properties of transition metal complexes.[10] The presence of metals in the metal - based complexes have improved the performance of molecular materials in technologies that include polymer light emitting diodes (PLEDs), organic light-emitting diodes (OLEDs),[11]

thin-film field-effect transistors (OTFTs),[12a-b] and information storage devices[13a-b.]. Although main group elements (s, p block) as well as lanthanides and actinides (f-block) have been researched earlier[14] the incorporation of d-block metal complexes with d^{10} or d^8 configuration ,directly into conducting polymer materials to give luminescent metallopolymers has gained considerable attention for their interesting photophysical properties recently.[15] A better understanding of the metal *vs.* ligand role in the absorption, emission, conductivity for both the solids and solutions of these complexes is essential for the design of these molecular materials to fulfill the requirements needed to make electronic devices. This had been attempted in earlier studies through the use of specifically-designed ligands that possess both a binding site for a metal center and functional groups that undergo electropolymerization which aids the highly-controlled growth of conducting metallopolymer materials with a direct electronic communication between the metal centers and the polymer. With such inner-sphere arrangement, enhanced communication present in these hybrid materials must be exploited to take full advantage of the properties of both the polymers and the metal centers[16]. This thesis aims at addressing this issue.

1.3 Spectroscopic Studies of Group 11 /d^{10}

Metal-centered emissions in d^{10} complexes like Ag(I),Au(I) can typically occur when there are close metal–metal interaction due to argentophillic or aurophilic attraction. Argentophilic and aurophilic interactions have been known for nearly two decades and have been shown to lead to M•••M association mostly in the solid state of two coordinate

complexes.[17a-g] Structure-luminescence relationships in Ag(I) complexes are much less defined unlike analogous Au(I) complexes [18] so literature studies have focused on cases where there are significant argentophillic interactions in the solid state that give rise to the emissive behavior of Ag(I) complexes.[19a-b]

Several complexes of d^{10} metals have also been reported to exhibit remarkable luminescence properties that can be fine- and coarse-tuned with temperature, solvent or vapor exposure, concentration in solution or doping level in the solid state, excitation wavelength, controlled irradiation, etc. These remarkable spectral variations occur owing to changes in the M···M metallophilic interactions in response to the aforementioned stimuli.[20] A very recent example reported by Rawashdeh-Omary and coworkers[21] has illustrated that varying the coinage metal in cyclic trinuclear complexes of Cu(I), Ag(I), and Au(I) complexes leads to drastic variations in the solid-state packing, photophysical, and π acid-base properties. Among those, one of the complexes by itself exhibited fascinating photophysical behavior that included qualitative tuning of the luminescence color across the entire visible region by exposure to different solvents (luminescence solvatochromism), varying the temperature (luminescence thermochromism), medium rigidity (luminescence rigidochromism), concentration (concentration luminochromism), excitation wavelength (site-selective excitation), etc.[21]

1.4 Spectroscopic Studies of Group 10 /d^8

Luminescence of d8 complexes have received considerable attention due to the interesting observation of metal – metal interactions.[22-24] A number of d8 complexes with well defined metal-metal distances have been reported.[25] Appreciable absorption and emission spectra of these d8 complexes have been reported and attributed to the role of metal-metal interaction QJP. Che and co-workers[26-29] have synthesized a number of mononuclear and binuclear Pt(II) complexes which had exhibited intense emission in both the solid and solution state at room temperature in the visible region, they assigned this to $\sigma(p) \rightarrow \sigma^*(d)$ (metal–centered, MC) transition.[26,27,30] The same attributes were not seen in analogous Pd(II) and Ni(II) complexes. Square planar platinum(II) complexes have demonstrated promise in a range of applications due to their interesting ground and excited state properties. It is therefore vital to understand how to control the physical and chemical properties of such organometallic chromophores in order to be able to tune their photophysical properties according to application-specific requirements. Hence, this thesis research focuses on the photophysical, electrochemical, and spectroelectrochemical properties of a variety of organometallic platinum(II) complexes which possess accessible ligand-centered and charge transfer excited states.

Square-planar platinum(II) complexes have long been known to exhibit metal-metal interactions in the solid state.[31] An interesting example of d^8 compounds showing remarkable luminescence properties is Pt(diimine)bis(arylacetylide) which forms square planar complexes. It has two vacant coordination sites one below and one above the

molecular plane, allowing for metal-metal interactions. These interactions are responsible for interesting spectroscopic and conducting properties known for a long time for Pt(II) complexes such as the tetracyanoplatinates(II).[32] A fine example is represented by Pt(diimine)bis(arylacetylide) complexes, which show emissive behavior in solution at room temperature with quantum efficiency measured to be 36% in dichloromethane with 3.1 μs lifetime that confirms phosphorescence nature.[33] The luminescent state in these metals(d^8) exhibiting the M···M metallophilic interactions has been assigned to a metal-centered (^3MC) excimeric triplet state with contracted M-M distance in extended stacks of Pt(II) d^8 square planar complexes.[34]

1.5   A Brief Overview about PLED's

Polymer light-emitting diodes (PLEDs), in particular, have been studied extensively since the first fabrication of a functioning diode utilizing a conjugated polymer as the electroluminescent material in 1990.[34] Compared to inorganic electroluminescent materials such as Ga,In,Ti, polymer materials have several attractive features including mechanical strength, flexibility, ease of processing, and the potential to be of low cost.[35] Commercially available polymers like polyvinylpyridine, polyvinyl carbazole are a good choice because of their good conductive properties.[36]

A typical molecular PLED usually consists of a thin layer of an undoped fluorescent conjugated polymer sandwiched usually by spin coating or inkjet printing, between two electrodes on top of a glass substrate.[37]Typically, fluorescent polymers can achieve an

upper limit of 25% efficiency of their electroluminescence in PLEDs. Appreciable improvement in efficiency can be obtained by doping phosphorescent transition metal complexes as emissive species in the polymer.[38]These transition metal complexes are often referred to as triplet emitters. When triplet emitters are used in an electroluminescent device, the maximal internal efficiency can be as high as 100% since the triplet emitters can harvest both singlet and triplet excitons from the polymer or small molecule host.[38]

Figure 2 is an illustration of the basic structure of a PLED device which consists of several layers, each performing a specific function such as charge injection, charge transport and emissive light layer.
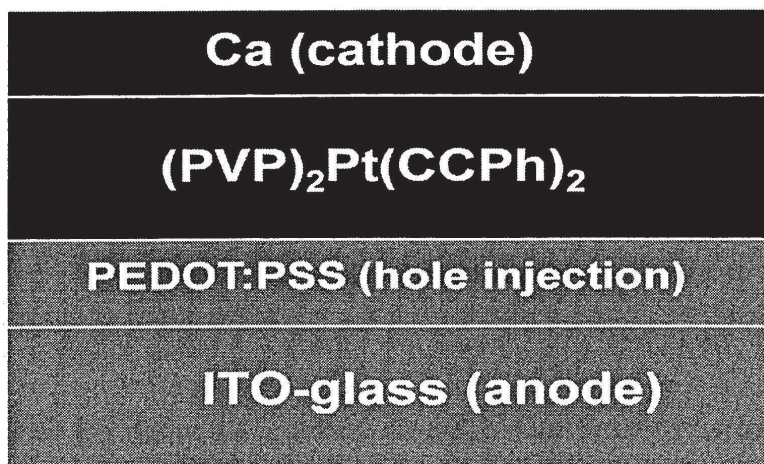
Figure 2.　　　Basic Structure of PLEDs devices.

Usually solution-casted PLEDs remain well-short of the theoretical upper limit even when the polymers are doped with phosphorescent transition metal complexes. One contributing factor is that the triplet state of the polymer host often lies at a lower energy than the triplet state of the phosphorescent complex doped into the polymer, resulting in reverse energy transfer from the complex to the polymer. This is a quenching pathway that greatly decreases the efficiency because the triplet state of the polymer is non-luminescent or "dark" state that depopulates the emissive state of the phosphorescent complex. Existing PLED's often make use of electronically luminescent polymers which have inherent fluorescence. Typical organic materials have non-luminescent triplet state, however, upon bonding to transition metals in the proposed Pt(II),Cu(I) and Ag(I) based metallopolymers, the strong spin-orbit coupling of the **heavy metal** atom leads to a rapid intersystem crossing from the lowest excited singlet state to the lowest triplet state. The latter can exhibit short phosphorescence lifetime suitable for rapid on/off switching as needed in PLEDs.[35]

1.6 Rationale of this Thesis

The pursuit of this research has been to synthesize and characterize strongly luminescent metallopolymers containing Platinum(II), Copper(I) and Silver(I) metal centers for potential use in PLED's and other optoelectronics. Our strategy is to coordinate the σ donor polymer to σ acceptor metal complex which can lead to novel class of phosphorescent metallopolymers. For this purpose we have used the commercially

available polymer Poly- 4 Vinyl Pyridine (PVP) to coordinate it with the metal centre to obtain the hybrid metallopolymer complexes. By varying the anionic ligands and metals we will investigate if there is variation in the absorption and phosphorescence energy/color, lifetime, solubility, and long-term stability of the resulting metallopolymers. The resulting phosphorescent metallopolymers shall have the interesting spectral properties of the small metal complexes mentioned earlier in section 1.3 and 1.4 along with the desirable photophysical and material properties of the polymer. This study employs electronic absorption, NMR, TGA and IR investigations to characterize these materials.

CHAPTER 2

THE SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC MEASUREMENTS OF Pt(II) METALLOPOLYMERS

Introduction

This chapter discusses the synthesis, characterization and photoluminescence of Pt(II)metallopolymers. In our proposed strategy we try to directly coordinate the Pt(THT)$_2$(Y)$_2$ precursors (THT= tetrahydrothiophene)(Y= C$_6$H$_5$CCH,C$_6$F$_5$CCH) to a σ donating polymer Poly (4-vinyl pyridine) (PVP). The THT is replaced by the N-donor polymer (PVP) when it coordinates to the Pt(II) precursors to obtain a new class of Pt(II) metallopolymers with interesting photophysical properties. We simultaneously investigated the Pt-Pt interaction and its effect on the photoluminescence of the metallopolymer complexes. The following sections in this chapter discuss the synthesis and the photophysical characterization of this nouveau class of Pt(II) metallopolymers in details. Section 2.1 features the synthesis procedure of various Pt(II) metallopolymers. Section 2.2 gives a brief description of the chemicals and materials used in the synthesis as well as the instrumentation used to characterize and collect the photophysical spectra of the Pt(II) metallopolymers. Section 2.3 discusses the spectroscopic measurements obtained for the Pt(II) metallopolymers in terms of emission, excitation, lifetime. Finally

section 2.4 concludes this chapter with a brief overview of the accomplished research and prospective work for the aforementioned Pt(II) metallopolymer complexes.

2.1 Chemicals, Materials and Photophysical Measurements

Chemicals and Materials

Phenylacetylene (PhCCH),n-Butyl Lithium (1.6M in Hexane), TetrachloroPlatinate(K_2PtCl_4), Tetrahydrothiophene (THT) and poly-(4-vinylpyridine) (PVP) (AMW =60,000) were purchased from Sigma Aldrich and used as is. Pentafluoro Phenylacetylene (F_5PhCCH) was purchased from Paragos-Germany. HPLC grade Tetrahydrofuran, Acetonitrile, (THF), Dichloromethane (DCM), Methanol, Toluene and Benzene were purchased from Aldrich, and used after drying with conventional methods. THF, DCM were used after distillation using conventional drying agents, degassed and kept under nitrogen.[$PtCl_2THT_2$],[$PHCC)_2Pt(THT)_2$] were prepared according to literature methods. All reactions were carried out under atmospheric conditions unless indicated otherwise. Standard Schlenk line techniques under nitrogen atmosphere were employed.

Photophysical Measurements

The luminescence measurements were carried out for the products obtained. Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-3/2006SE scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The excitation and emission spectra were corrected above 350nm and 250nm. Temperature-dependent studies were acquired with an Oxford optical cryostat using liquid nitrogen as

a coolant. Lifetime data were acquired using a high speed pulsed xenon lamp source interfaced to the PTI instrument along with an autocalibrated "QuadraScopic" monochromator for excitation wavelength selection.

Absorption spectra were acquired with a Perkin-Elmer Lambda 900 double beam UV/VIS/NIR detector. The ^{1}HNMR was carried out on a Varian Mercury 500MHz NMR spectrometer. The chemical shifts are expressed in parts per million from Tetramethylsilane as an internal standard. Melting points were determined on Mel-Tem capillary melting point apparatus and infrared spectra were determined with a Nicolet 380 FT infrared spectrometer. Thermal gravimetric analysis (TGA) were determined by TA Q50 TGA equipped with a high sensitivity balance and Integrated Mass Flow Controllers.

2.2 Syntheses

2.2.1 Synthesis of $PtCl_2THT_2$

Reaction

$$K_2PtCl_4 + 2THT \longrightarrow PtCl_2THT_2 + 2KCl$$

According to literature methods[39] $PtCl_2THT_2$ was synthesized using 0.5mmol of the platinum salt (K_2PtCl_4) and the ligand tetrahydrothiophene (2mmol) which were stirred together in water (20ml) overnight at room temperature. The yellow precipitate was filtered off and washed copiously with water followed by a small quantity of cold

13

ethanol. The residue was then dissolved in a minimal amount of CH_2Cl_2 and the solution was dried over anhydrous $MgSO_4$. The $MgSO_4$ was then filtered off and the solvent removed at reduced pressure. Melting point 143-145°C and percentage yield (58%) were obtained and found to be similar to literature [1]. $PtCl_2THT_2$ will be used as the starting material.

2.2.2 Synthesis of the Metallopolymer $(H_5C_6CC)_2$-Pt-PVP
Reaction

PhCCH + nBuLi $\xrightarrow{\text{-40° C}}$ PhCCLi + n Butane

2PhCCLi + PtCl2THT2 $\xrightarrow{\hspace{2cm}}$ PhCC$_2$PtTHT$_2$ + 2LiCl

PhCC$_2$PtTHT$_2$ + PVP $\xrightarrow{\hspace{2cm}}$ PhCC$_2$PtPVP + 2THT
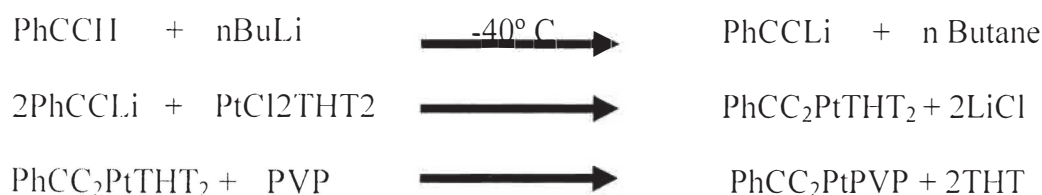
By slight modification of the literature methods[40] $PhCC_2PtTHT_2$ was synthesized. This was achieved in two steps, firstly, by replacing the chlorine ligand with phenylacetylide and finally replacing the THT with the polymer poly(4-vinyl Pyridine) in the second step of the synthesis. Standard Schlenk line techniques under nitrogen atmosphere were employed wherever necessary.

In a 50 ml schlenk flask 5 ml THF was taken and kept at -40° C using dry ice/acetonitrile. To this phenylacetylene (0.1ml/5.10x1010^{-4} mmol Mol wt 102.14 g/mol density 0.93g/ml) was added and N-BuLi (0.320 ml/5.10 X 10^{-4} mmol, 1.6 M in hexanes) was added drop wise. This mixture was allowed to stir for 2.5 hours and then $PtCl_2THT_2$,which was dissolved in DCM, was added to this flask under positive pressure

and allowed to stir further for another 2 hours while allowing it to slowly attain room temperature. We see the formation of a yellow colored solution, which was filtered and the residue collected and dissolved in MeOH. To this a stoichiometric ratio of PVP (MW = 60,000 as obtained from Aldrich) in dichloromethane was added and the reaction was kept at room temperature overnight. Two different molar ratios of 1:6 and 1:12 (Pt:Polymer respectively) were attempted. A creamy yellow colored precipitate which gave a bright blue luminescence at room temperature was obtained with a melting point of 220° C. The Pt content was analyzed by Thermal Gravimetric Analyses (TGA) and the Pt % was found to be 33.61% which was found to correspond to 41.46% of the polymer occupied of PVP that was occupied. FT-IR(KBr pellet): υ = 1615 cm^{-1} (C-C), υ= 2088.97cm-1 C$\equiv$C Stretch, υ = 2937cm^{-1} (C-H) for PHCC , υ=1450cm^{-1} (C=N),υ= 1599.20cm^{-1}(C=C stretch) (for PVP) are observed .

X= PhCC-; C6F5CC-; thiolates
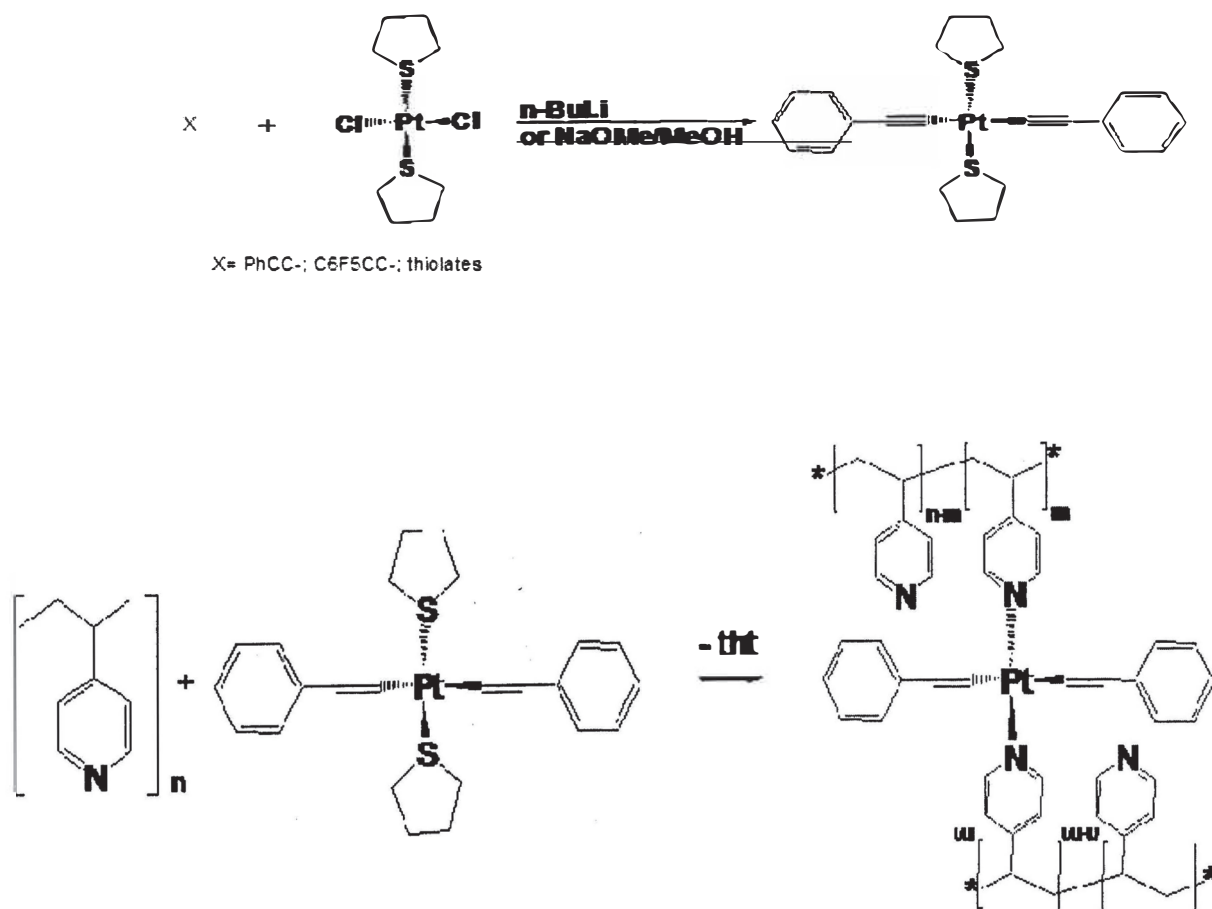
Figure 3. Illustration of the synthesis of PtPHCC$_2$PVP

2.2.3   Synthesis of the Metallopolymer $(F_5C_6CC)_2$-Pt-PVP

Reaction

C_6F_5CCH + nBuLi $\longrightarrow$ C_6F_5CCLi + n Butane

C_6F_5CCLi + $PtCl_2THT_2$ $\longrightarrow$ $(C_6F_5CC)_2$-Pt-THT_2 + 2 LiCl

$(C_6F_5CC)_2$-Pt-THT_2 + PVP $\longrightarrow$ $(C_6F_5CC)_2$-Pt-PVP + 2THT

By slightly varying literature methods[41], $(C_6F_5CC)_2$-Pt-THT_2 was synthesized as follows. Standard Schlenk line techniques under nitrogen atmosphere were employed wherever necessary.

A 50 ml schlenk flask, 5 ml THF was taken and kept at -40° C using dry ice/acetonitrile. To this pentafluoro phenylacetylene(0.100 ml (5.10×10^{-4} mmol Mwt. 102.14 g/mol d 0.93g/ml) was added and N-BuLi (0.320 ml/5.10×10^{-4} mmol, 1.6 M in hexanes) was added drop wise.This mixture was allowed to stir for 2.5 hours and then $PtCl_2THT_2$, which was dissolved in DCM was added to this flask under positive pressure and allowed to stir further for another 2 hours while allowing it to slowly attain room temperature. A yellow colored solution is obtained and this solution was filtered off. The residue was collected and dissolved in MeOH. To this, a molar ratio of 1:12 (Pt:PVP) respectively (MW = 60,000 as obtained from Aldrich) in dichloromethane was added and the reaction was kept at room temperature overnight. A golden yellow colored precipitate, which gave bright yellow luminescence at room temperature, was obtained with a melting point of 185°C. FT-IR (KBr pellet):υ =1435cm^{-1} (C=N),υ= 1599 cm^{-1}(C=C stretch) (for PVP) are observed.

Figure 4.   Illustration of the synthesis of the metallopolymer $(F_5C_6CC)_2$-Pt-PVP

2.3 Results and Discussion

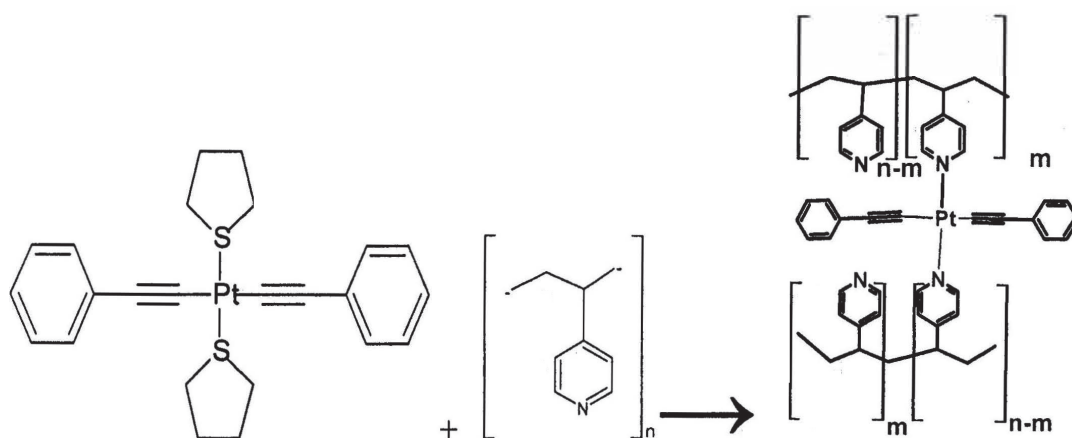Conjugated molecules with d^8 metals incorporated into the backbone have been a topic of intense study for quite some years. This could probably be attributed to the fact that such incorporation of these metals relaxes the spin selection rules for phosphorescence through spin-orbit coupling[42] due to the heavy metal effect. In this chapter we will discuss two phosphorescent metallopolymer compounds $(C_6F_5CC)_2$-Pt-PVP,$(C_6H_5CC)_2$-Pt-PVP synthesized using $PtCl_2THT_2$.The commercially-available N-donor polymer poly(4-vinylpyridine) is used to replace the labile THT molecule. This metallopolymer PVP-Pt-$(PhCC)_2$ emitted a bright blue luminescence at both cryogenic and room temperature It was synthesized using various molar ratios of $PHCC_2Pt(THT)_2$ to PVP respectively to determine the effect of the metal: polymer ratio on the luminescence of the compound. Temperature dependent photoluminescence and photoluminescence excitation spectra and lifetimes of the metallopolymers synthesized using 1:6 & 1:12 are shown in Figure 5 and 6 respectively. These data reveal the sensitivity of the luminescence intensity of the metallopolymer to the temperature. The spectra show broad emission peaks with an emission maxima λ_{em}=450nm and an excitation maxima of λ_{exc}=350nm at both cryogenic and room temperature .The broad profile of the emission as well as the microsecond lifetimes of 11.6 μs and 7.5 μs at 77K and room temperature respectively indicate triplet state phosphorescence. The metal to polymer ratio was changed from 1: 6 in figure 5 to

1:12 (metal: polymer respectively) in figure 6 respectively to observe the effect of Pt content on the photoluminescence and solubility properties as well as to reduce the cost of synthesizing these compounds. Interestingly it could be observed that although the luminescence did not change drastically, the solubility property of these complexes were found to have been affected. The solubility seemed to have increased with an increase in the molar ratio of the polymer compared to the metal. This was proved by its partial solubility in solvents like dichloromethane, methanol, benzene etc.
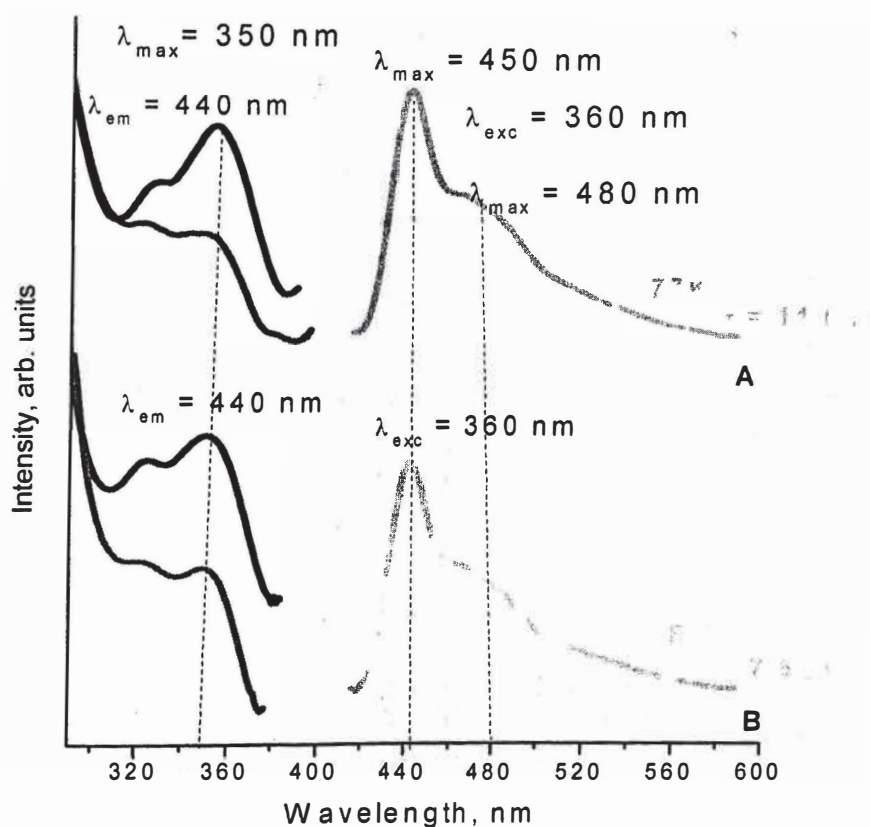
Figure 5.   Temperature dependent (1:6) Photoluminescence excitation (left) emission (right) spectra at (A) 77K and (B) 290K of solid $(C_6H_5CC)_2PtPVP$
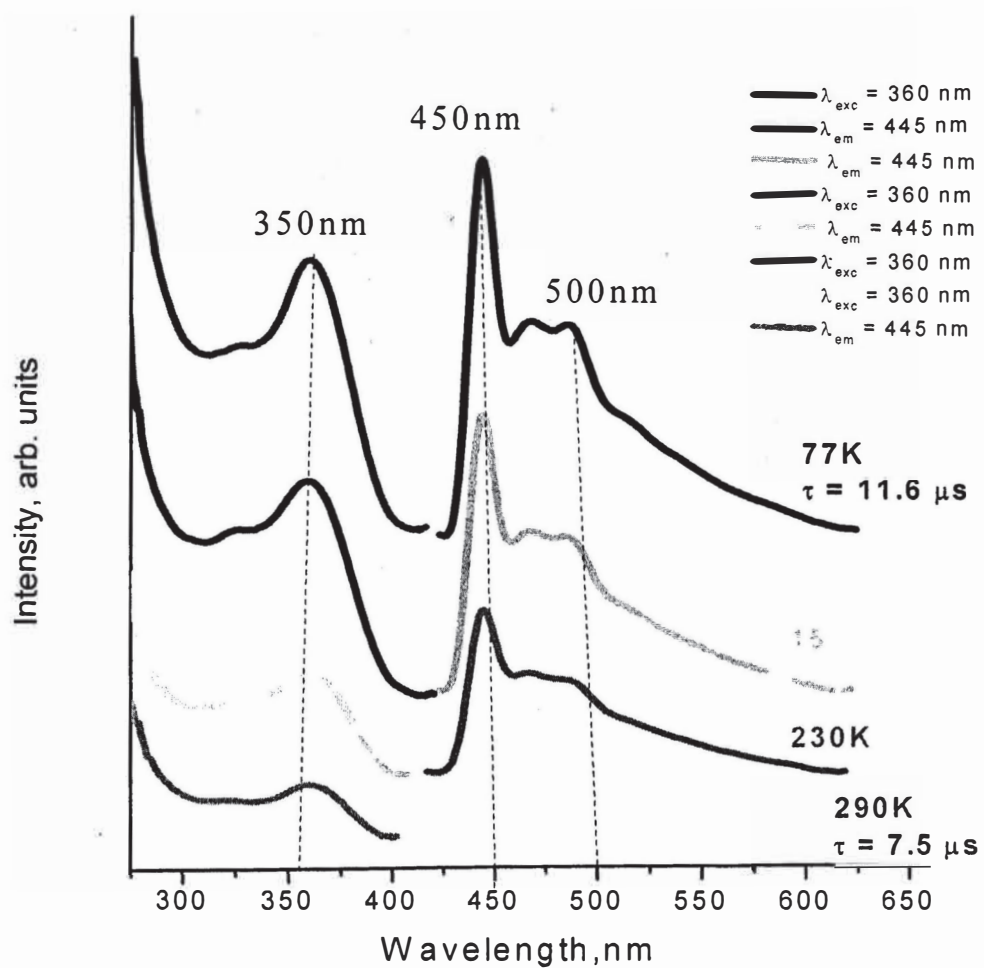
Figure 6. Temperature dependent (1:12) Photoluminescence excitation (left) and emission (right) spectra at (A) 77K (B) 150 K (C) 230K and (D) 290K of solid $(C_6H_5CC)_2$ Pt PVP

Luminescence of PtPHCCPVP
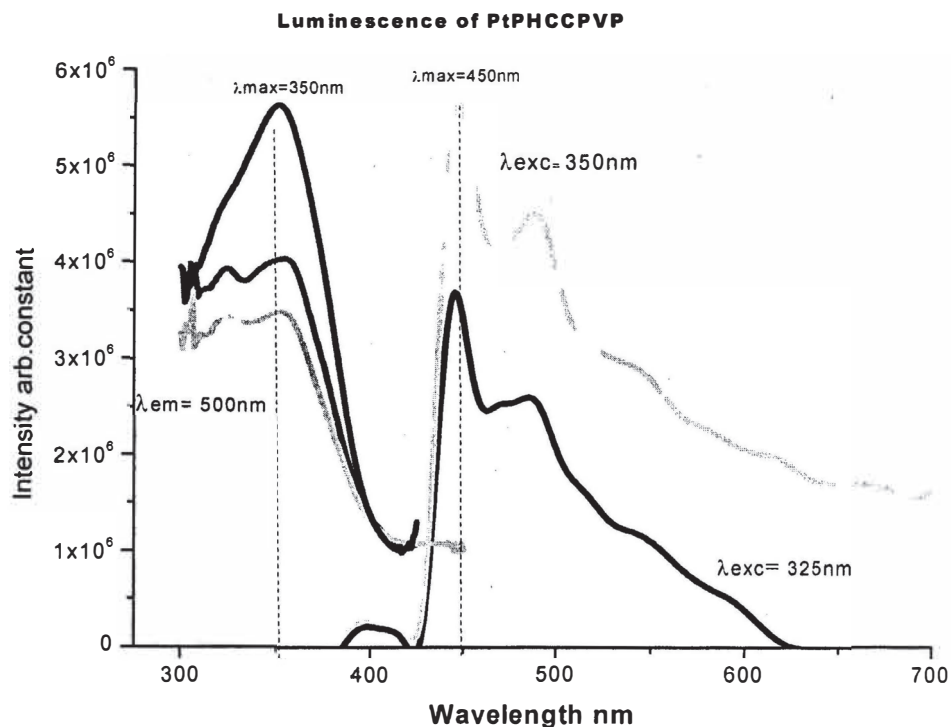
Figure 7. Photoluminescence excitation (left) and emission (right) spectra at 290K of a thin film of $(C_6H_5CC)_2$-Pt-PVP(1:12) in Methanol.

Figure 7 is the luminescence spectra obtained by making a thin film of the $(C_6H_5CC)_2$-PVP in methanol using 1:12 metal to polymer ratio at room temperature. PLED's require the compound to be solution processible. This compound was soluble in methanol and it was possible to make a thin film using it. Thus, we also tried to use it to make a PLED device at UT-Dallas. The luminescence data obtained for the thin film of the metallopolymer $C_6H_5CC_2$-Pt-PVP is similar to the data obtained in the solid state as shown in Figure 5 and 6. Figure 8 is the data we obtained after making an initial device at UT-Dallas. Although the data was promising, the current produced was slightly low for

22

light emission. To fix this, the charge balance needs to be improved. This can be achieved by adding electron-transport layer from cathode side, which would allow recombination of electron and hole to form the exciton in the metallopolymer layer.

ITO/PEDOT:PSS/PVP Pt/Ca/Ag
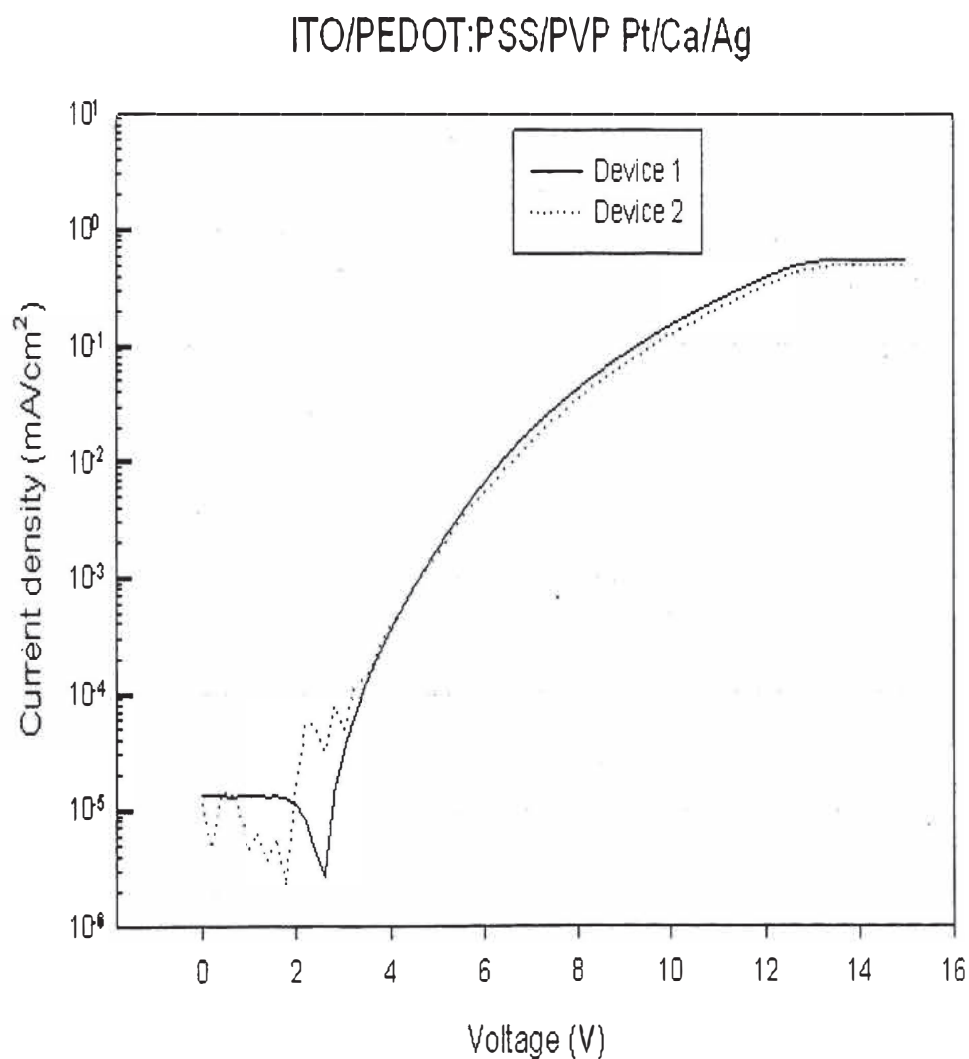
Figure 8. Initial device of a thin film of $C_6H_5CC_2$-Pt-PVP(1:12) in Methanol.
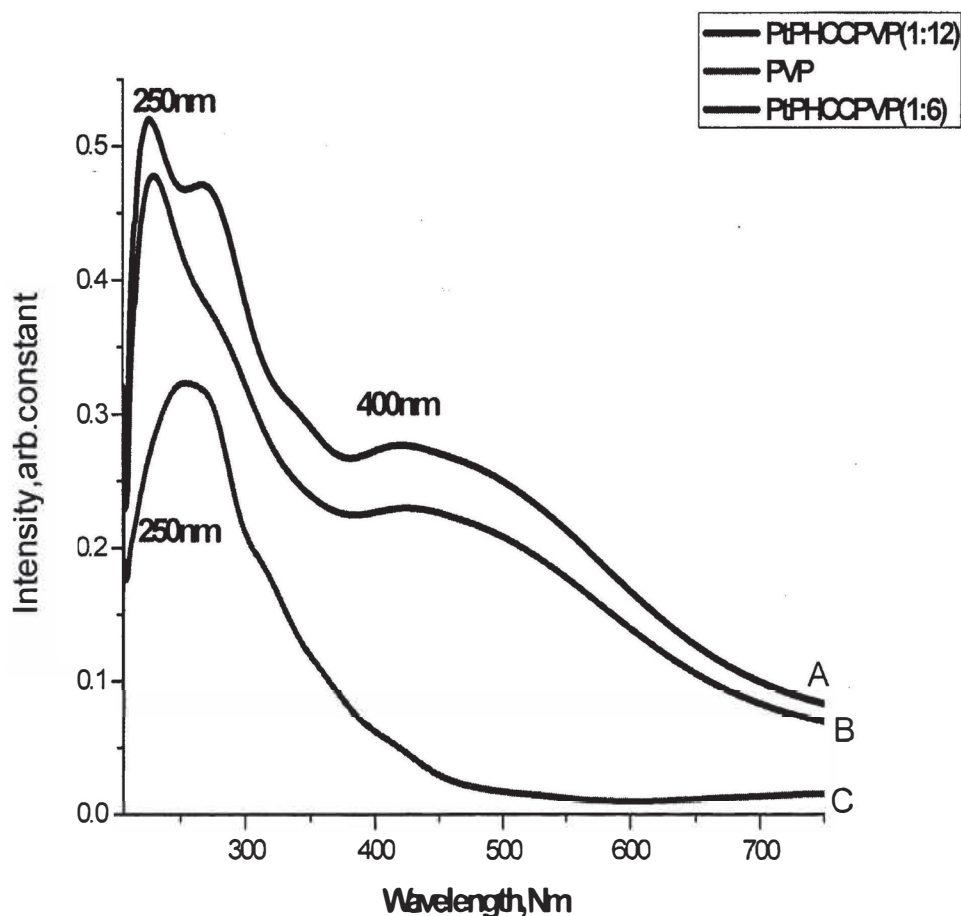
Figure 9. Solid state diffuse reflectance spectra of the complex $(C_6H_5CC)_2PtPVP$ {black[1:12],blue[1:6]} and polymer PVP (red)

Figure 9 represents the solid state diffuse reflectance spectra of the metallopolymer $(C_6H_5CC)_2$-Pt-PVP for both the 1:12 and 1:6 ratios. The two compounds exhibit a strong absorption peak around 250 nm which, based on literature, can be assigned to the intraligand л→ л* transition from PVP and were found to occur in highly conjugated systems. A broad shoulder at 400nm is also observed for this compound. Based upon

24

literature reviews, this can be assigned to a LMLCT transition[43] from the $(C_6H_5CC)_2Pt$ to the polymer PVP.

Furthering our research on Pt(II) based metallopolymers, we changed the anionic ligand from electron rich ligand C_6H_5CC to the electron poor ligand C_6F_5CC to study the effect on properties such as solubility, luminescence etc. This change in the anionic ligand resulted in the red shift in the absorption and emission bands of the metallopolymer $(C_6F_5CC)_2PtPVP$. This compound is strongly luminescent at room temperature in the solid state and gives a bright golden yellow luminescence at both cryogenic and room temperature. Figure 10 represents the temperature dependent photoluminescence(PL) and photoluminescence excitation spectra of $(C_6F_5CC)_2PtPVP$. The complex $(C_6F_5CC)_2PtPVP$ shows two emission peaks at λmax = 550nm and 620nm.The emission spectra were obtained by exciting at two different wavelengths at λexc =410nm and 450nm. As seen in figure 10, when exciting at 410nm a highly structured emission peak is seen which which becomes less structured at higher temperatures. Exciting the metallopolymer at 450nm gives a structured emission peak at 77K which becomes unstructured at higher temperatures. The lifetime for this compound ranges from as high as 124μs at 77K to 100μs at RT, making this compound useful for optoelectronics like PLED's. The compound shows substantial sensitivity to temperature as can be observed by enhancement of the intensity of the emission and excitation spectra. The fluorinated metallopolymer complex is seen as an efficient means of electron-hole injection/transportation thus finding use in PLED's which make use of this nature of the

25

metallopolymer. The microsecond lifetimes and emission indicate the triplet state phosphorescence of this metallopolymer.
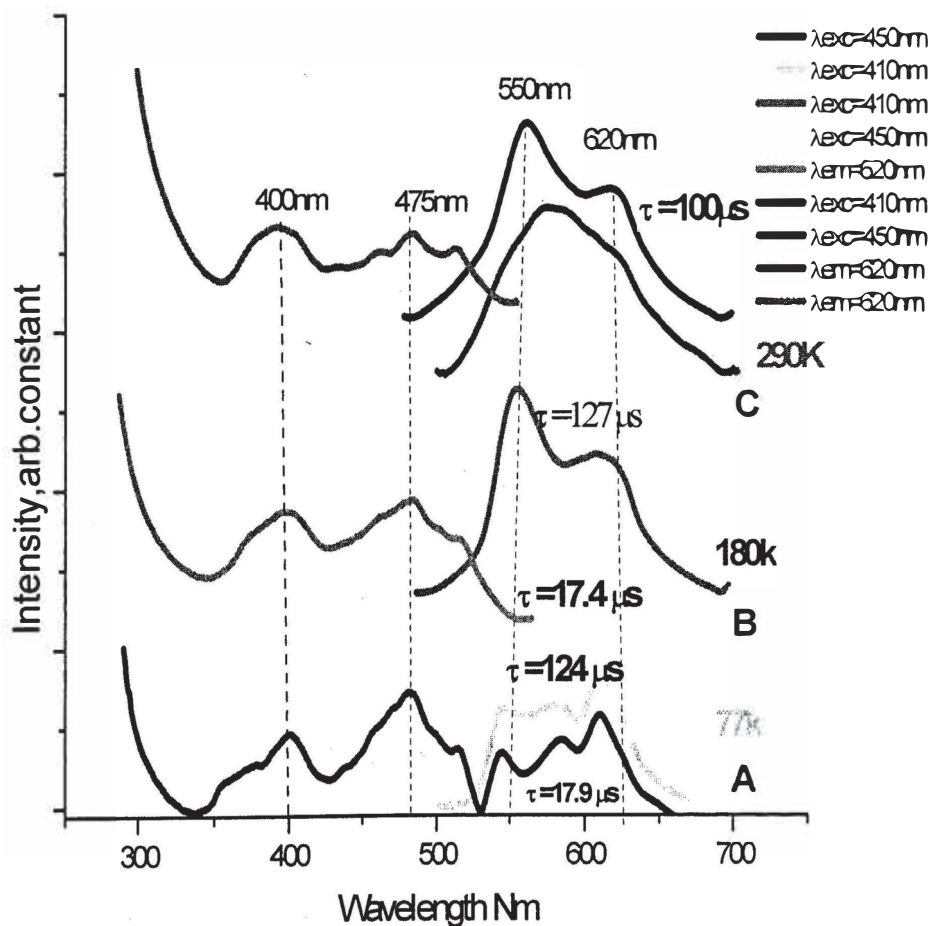
Figure 10. Temperature dependent Photoluminescence excitation (left) and emission (right) spectra at (A) 77K (B) 180K and (C) 290K of solid $C_6F_5CC_2PtPVP$.
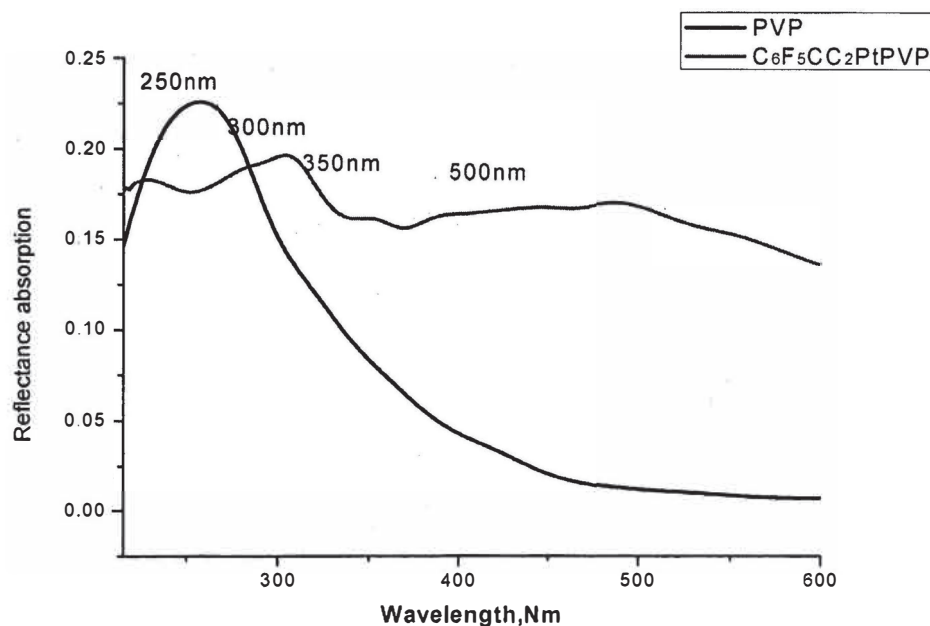
Figure 11. Solid state diffuse reflectance spectra of the complex $(C_6F_5CC)_2PtPVP$ (red) and polymer PVP (black)

Figure 11 shows the solid state diffuse reflectance spectra of $(C_6F_5CC)_2PtPVP$

metallopolymer. This compound exhibits a strong absorption peak around 250-290 nm

which based on literature can be assigned to the intraligand л→ л* transition from PVP.

The compound also exhibits very broad peaks between 350nm and 500nm. Based on

literature we can assign this to a LMLCT transition[43] from the $C_6F_5CC_2Pt$ to the polymer

PVP.

2.4 Conclusions

This chapter focuses on the synthesis and spectral properties of platinum-containing metallopolymers that are inherently phosphorescent with tunable emission colors. The main focus of this research was to synthesize and charaterize these metallopolymer complexes as well as to study their photoluminescence versus various factors like ligand (anionic chromophores), polymer:metal ratio and temperature. Significant changes in the PLE spectra was observed by changing the anionic ligand, altering the polymer: metal ratio and temperature. Coordination of Pt(II) precursor materials to an N-donor polymer such as poly(4-vinylpyridine) PVP, led to these brightly phosphorescent metallopolymers with interesting photophysical properties, including emissions spanning the blue and yellow regions in the visible region at room temperature in solid state. Figures 6 and 10 are representative of the effect of the ligand and temperature on the photoluminescence of the metallopolymers $C_6H_5CC_2PtPVP$ and $C_6F_5CC_2PtPVP$ respectively.

Since the mid 1990s, soluble, well-characterized high molecular weight metal-containing polymers[35]had gained the interest of scientists and has led to a rapidly expanding interest in their properties and uses in various solution processible optoelectronics like PLED's etc. These metallopolymers combine the processing advantages of polymers with the functionality provided by the presence of metal centers. Hence, this research also focuses on synthesizing such solution processible metallopolymer complexes. We are trying to

activate the polymer triplet state by coordinating it to the metal. Therefore, instead of the common method of "physical doping" of a small phosphorescent molecule into a polymer host, we tried to utilize polymers that can coordinate to a metal center so as to make the T1 state of the polymer become "light-emitting" instead of being "dark".This leads to having an advantage over available PLED's which exhibit electroluminescence that inherently fluoresce and are considered less efficient than phosphorescence .[35]

These Pt(II) containing polymers have the potential for being used in solution processible, ultra-thin PLED lighting devices and flexible displays that will operate at lower voltages than common OLED devices. Most unfunctionalized conjugated polymers suffer from poor solubility which limits the ability to characterize the materials in solution and to process them for applications. To resolve this issue, significant efforts have been made to focus on the synthesis of conjugated polymers with pendant organic functional groups. This approach has been quite successful in enhancing the solubility in organic solvents, and introducing new functionalities. However, we still feel that more efforts need to be made on improvising the solubility.

Further studies utilizing different polymers and metals complexes to improve the emission and processing properties in relation to device fabrication will be implemented.

CHAPTER 3

THE SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC MEASUREMENTS OF MONOVALENT Cu(I) AND Ag(I) METALLOPOLYMERS

Introduction

The cyclic trinuclear complexes of group 11 are representative of materials that are capable of exhibiting fascinating photophysical properties like luminescence thermochromism, rigidochromism, vapochromism and solvatochromism across the visible region. Apart from these features varying the metal in these trinuclear complexes also led to drastic variations in the solid-state packing, photophysical and π acid-base properties These features were illustrated in detail by Rawashdeh-Omary et al in their work on the brightly phosphorescent trinuclear coinage metal complexes[44,21]. These trinuclear complexes were reported to exhibit remarkable spectral variations in response to the aforementioned stimuli. This was attributed to the cuprophilic and argentophilic (M⋯M)metallophilic interactions. These metal-pyrazolate complexes exhibit a bright luminescence in the solid state by themselves. In our research we tried to further explore some of the interesting features of these trinuclear complexes by trying to coordinate them with a N-donor polymer such as poly(4-vinylpyridine), known as PVP. Consequently we obtained brightly phosphorescent metallopolymers with emissions spanning the green and yellow regions in the visible spectrum. An interesting feature

30

which could be observed is the change in the luminescence of these trinuclear complexes after coordination to the PVP. This chapter will also focus on this specific feature.

The synthesis of silver (I) and copper (I) metallopolymers was attempted as an inexpensive alternative to the analogous Pt(II) metallopolymers discussed in the previous chapter. In addition we tried to observe the effect of changing the metal and ligand on the luminescence and other properties like solubility etc. In this chapter we will discuss the synthesis, characterization and photoluminescence of the copper (I) and silver(I) metallopolymers. The following sections discuss the relevant topics. Section 3.1 details the synthesis, chemicals and materials used for the metallopolymers. Section 3.2 discusses the spectroscopic measurements obtained for both the copper (I) and silver (I) metallopolymers. Section 3.3 summarizes the conclusions of this project and its prospective work for the aforementioned complexes.

3.1 Materials and Instrumentation

Silver (I) Oxide (Ag_2O), copper (I) oxide (Cu_2O) and poly-(4-vinylpyridene) (PVP) (AMW =60,000) were purchased from sigma Aldrich and used as is. HPLC grade Tetrahydrofuran, Acetonitrile, (THF), Dichloromethane (DCM), Methanol, Toluene and Benzene were purchased from Aldrich, and used after drying with conventional methods. THF, DCM were used after distillation using conventional drying agents, degassed and kept under nitrogen. All reactions were carried out under atmospheric conditions unless indicated otherwise. Standard Schlenk line techniques under nitrogen atmosphere were employed.

The luminescence measurements were carried out for the products obtained . Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-3/2006SE scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The excitation and emission spectra were corrected above 350nm and 250nm . Temperature-dependent studies were acquired with an Oxford optical cryostat using liquid nitrogen as a coolant. Lifetime data were acquired using a high speed pulsed xenon lamp source interfaced to the PTI instrument along with an autocalibrated "QuadraScopic" monochromator for excitation wavelength selection.

Absorption spectra were acquired with a Perkin-Elmer Lambda 900 double beam and UV/VIS/NIR detector. The ^{1}HNMR was carried out on a Varian Mercury 500MHz NMR spectrometer. The chemical shifts are expressed in parts per million from Tetramethylsilane as an internal standard. Melting points were determined on Mel-Tem capillary melting point apparatus and Infrared spectra were determined with a Nicolet 380 FT infrared spectrometer. Thermal gravimetric analysis (TGA) were determined by TA Q50 TGA equipped with a high sensitivity balance and Integrated Mass Flow Controllers.

3.2 Syntheses

3.2.1 Syntheses of the Metallopolymer $[[3,5-(CF_3)_2Pz]Cu-PVP]_2$

Reaction:

$$Cu_2O \ + \ [3,5-(CF_3)_2Pz]H \quad \xrightarrow{\text{reflux @65°C}} \quad \{(3,5-(CF_3)_2Pz)Cu\}_3$$

$$[(3,5-(CF_3)_2Pz)Cu]_3 + \ PVP \quad \xrightarrow{\text{reflux @70°C}} \quad \{[3,5-(CF_3)_2Pz]_2Cu_2-PVP\}$$

The synthesis of $[[3,5-(CF_3)_2Pz]Cu]_3$ was carried out as described in literature[45]. $[3,5-(CF_3)_2Pz]H$ (0.50gm,2.45mmol) and Cu_2O(0.19gm,1.43mmol) were allowed to react in 20ml of benzene at a temperature of 50-60°C while maintaining reflux for 48 hrs. The resulting solution was cooled and then filtered through a bed of celite . The solvent was removed under reduced pressure to obtain $[[3,5-(CF_3)_2Pz]Cu]_3$ as a white solid. Melting point of 188-190°C, NMR and IR were obtained and were found to be similar as reported in literature[45]. All reactions were carried out using standard Schlenk line techniques under inert atmosphere.

In the next step , $[[3,5-(CF_3)_2Pz]Cu]_3$ (0.500 g, 0.6 mmol) was dissolved in toluene (15 mL) and to this PVP (0.661 g, 7.0mmol)was added and allowed to react by refluxing at a temperature of 60°C for 72 hours to obtain a yellow precipitate. The reaction mixture was filtered and the product was washed with toluene to remove traces of any starting material. The solution obtained was evaporated to dryness under vacuum. The product was collected as a yellow solid (yield 82 %) with bright yellow luminescence. Thermal Gravimetric Analyses gave Copper (% wt): 35.74% that corresponds to 60.66% of

occupied positions in the polymer. FT-IR(KBr pellet): υ=2922 cm^{-1} (Aromatic C-H Stretch)υ =~1400 cm^{-1} (C=N),υ=855cm^{-1} (C-H out of plane) υ=1598 cm^{-1} (C=C)for PVP,υ=1435 cm^{-1} (C=N) for pyrazolate ligand.^{1}H NMR(500Mhz CDCL3) :δ 7.03(CH),8.39,1.46 and 6.39 (Pyridine ring)
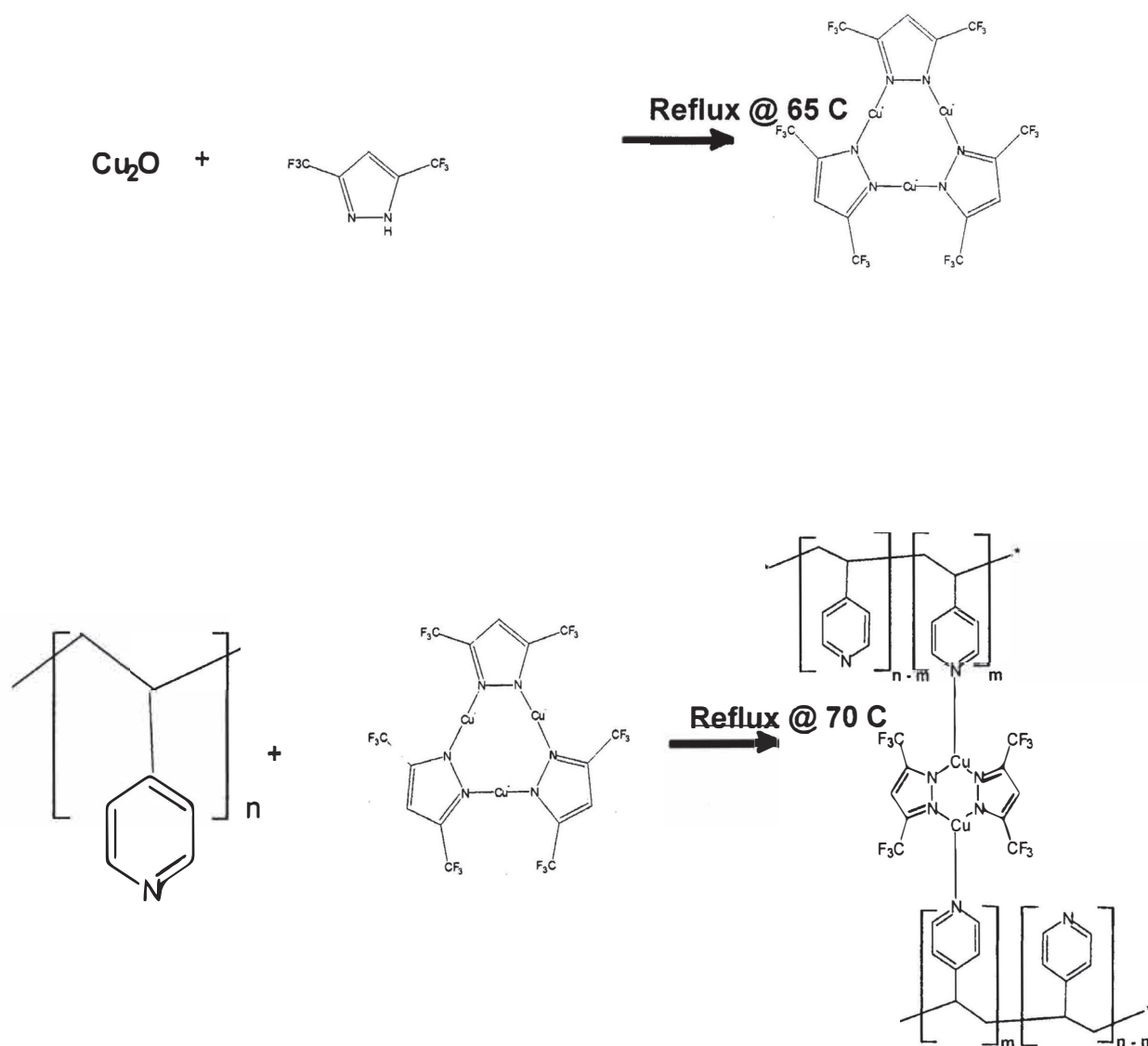

Figure 12. Illustration of the synthesis of {[3,5-(CF$_3$)$_2$Pz]$_2$Cu$_2$-PVP}

3.2.2 Syntheses of the Metallopolymer [[3,5-(C₃F₇)₂Tz]Ag-PVP]₂

Reaction:

$$Ag_2O \quad + \quad [3,5\text{-}(C_3F_7)_2Tz]H \longrightarrow [[3,5\text{-}(C_3F_7)_2Tz]Ag]_3$$

$$[[3,5\text{-}(C_3F_7)_2Tz]Ag]_3 \; + \; PVP \longrightarrow [[3,5\text{-}(C_3F_7)_2Tz]Ag\text{-}PVP]_2$$

[[3,5-(C₃F₇)₂Pz]Ag]₃ was prepared according to literature[46] by reacting Ag₂O(0.14gm,0.6mmol) with [3,5-(C₃F₇)₂Tz]H(0.50gm,1.2mmol) in about 40ml of toluene. The resulting mixture was heated at 70-80°C under nitrogen overnight. After cooling to 40°C, the solution was filtered through a bed of celite and the filtrate was collected . The solvent was removed under reduced pressure to give a white powder with a melting point of 156-157°C. All reactions were carried out using standard Schlenk line techniques under inert atmosphere.

In the next step, {[3,5-(C₃F₇)₂Tz]Ag}(0.500 g, 0.32 mmol) was dissolved in hot toluene (10 ml). To this solution, PVP (0.5 g, 5.0 mmol) was added. The reaction mixture was stirred for 72 hours under reflux at a temperature of 65°C. This solution was then filtered and the residue was washed with toluene to remove traces of starting material. The filtrate obtained was evaporated to dryness under vacuum. The product was collected as a white solid which gave a yellow luminescence at room temperature (yield 82 %). Thermal Gravimetric Analysis (% wt) gave 35.55 % Ag that corresponds to 84% of

occupied positions in the polymer. FT-IR (KBrpellet) $\upsilon= 3411cm^{-1}$(N-H), $\upsilon= 1588cm^{-1}$(C=N), $\upsilon=2915cm^{-1}$ (C-H).
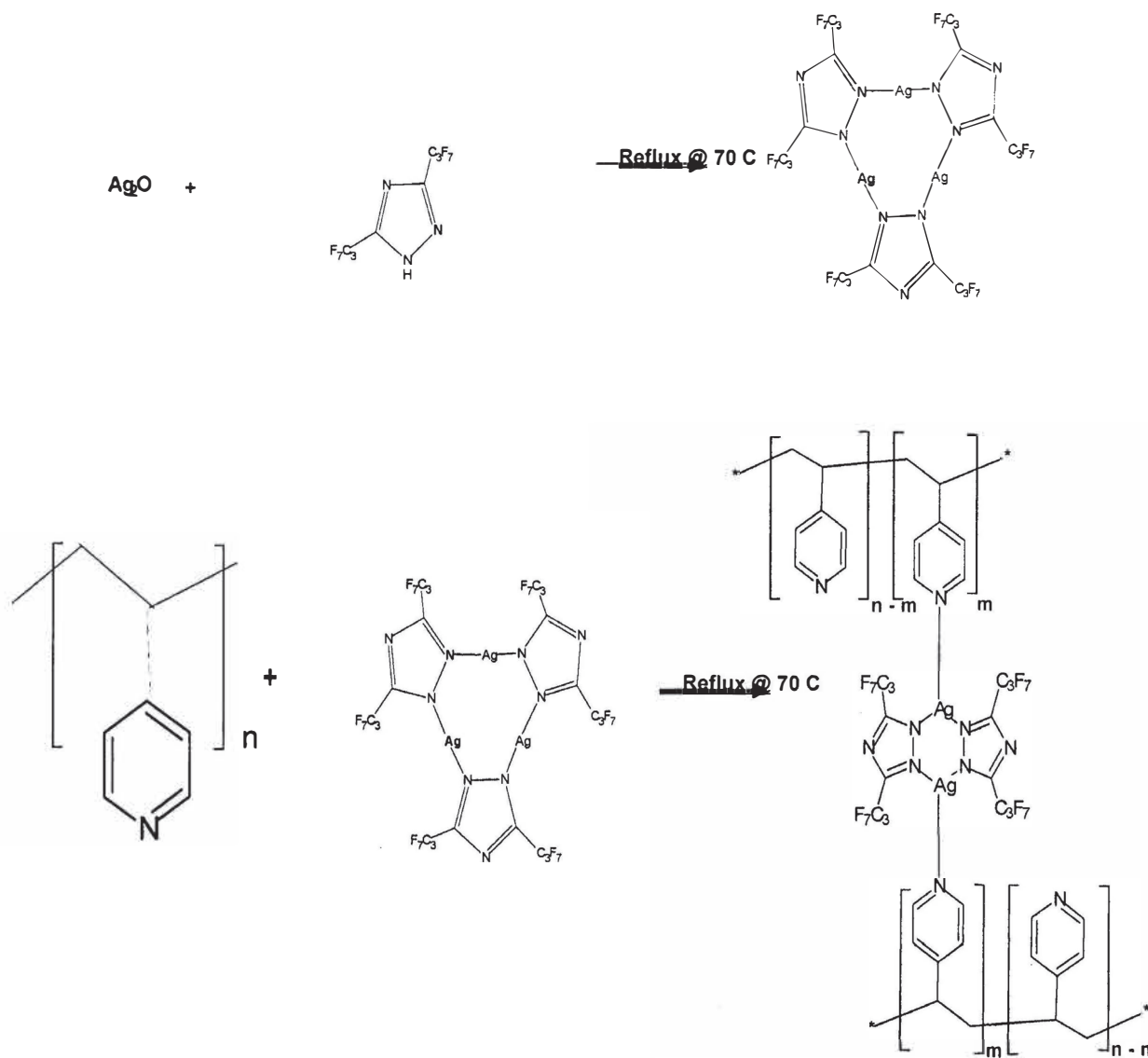
Figure 13.   Illustration of synthetic route of [[3,5-(C₃F₇)₂Tz₂]Ag₂-PVP] metallopolymer

3.3 Results and Discussion

The reaction of the trinuclear complexes of $\{[3,5\text{-}(C_3F_7)_2Tz]Ag\}_3$ and $[3,5(CF_3)_2Pz\ Cu]_3$ with the polymer poly-4 vinyl pyridine (PVP) probably led to three coordinate Ag(I) and Cu(I) metallopolymer complexes respectively. Our prediction is based upon the literature reviews for similar three coordinate complexes of [3,5(CF3)2PzAg1(2,4,6-collidine)]2 crystals[47]. The $[[3,5\text{-}(C_3F_7)_2Tz]Ag]_3$ trimer formed a three coordinate complex when it reacted with collidine. Synthesis of the [3,5(CF3)2PzAg1(2,4,6-collidine)]2 complex was reported by Rawashdeh-Omary et all .[47] Figure 12 and 13 are illustrations of the suggested structures for the copper (I) and silver(I) metallopolymer respectively. The new metallopolymer complex $[3,5(CF_3)_2PzCu\text{-}PVP]_2$ exhibits a bright greenish-yellow photoluminescence (PL) in the solid state. Photoluminescence and photoluminescence excitation spectra and lifetimes of the 1:20 and 1:15 molar ratios of metal to polymer respectively at cryogenic and room temperature are shown in the Figures 14 and 15 respectively. These data reveal the change in the intensity of the luminescence energies with change in temperature as seen for the $\{[3,5\text{-}(CF_3)_2Pz]_2Cu_2\text{-}PVP\}$.This metallopolymer shows a broad unstructured emission with a peak maxima of 575nm at both cryogenic and room temperatures in Figures 3 and 4. Both the molar ratios of 1:15 and 1:20 showed emission maxima at 575 nm upon varying the temperature. The lifetimes of the phosphorescence emissions of these metallopolymer complexes in both the ratios (1:15 and1:20) was found to be 19.68 µs and 17.07 µs respectively at cryogenic temperature and 8.42 µs and 5.41 µs respectively at room temperature. This microsecond

37

scale broad unstructured emission is indicative of the metal centered phosphorescence of the $[3,5(CF_3)_2PzCu-PVP]_2$ complex. An interesting feature of this research was observing the hypsochromic or blue shift in the luminescence of the metallopolymer. The $[3,5(CF_3)_2Pz]Cu_3$ by itself exhibits a very bright orange luminescence in the solid state at room temperature with unstructured emission (λmax=650nm) and excitation (λmax=260nm). Upon coordination to the polymer we can observe the blue shift in the emission maxima. This supports our presumption that changing the ligands does affect the luminescence of the metallopolymer complexes.

Apart from the aforesaid interesting features of the complex, its ease of solubility in most organic solvents like dichloromethane, benzene etc makes it suitable for solution processible Polymer Light Emitting Diodes(PLED's).

Figure 14. Solid state photoluminescence excitation (left) and emission (right) spectra at(A,B) 77K using an excitation of 330nm and 360nm respectively (C) 298K using an excitation of 350nm for {[3,5-(CF3)2Pz]2Cu2-PVP}in ratio of 1:20
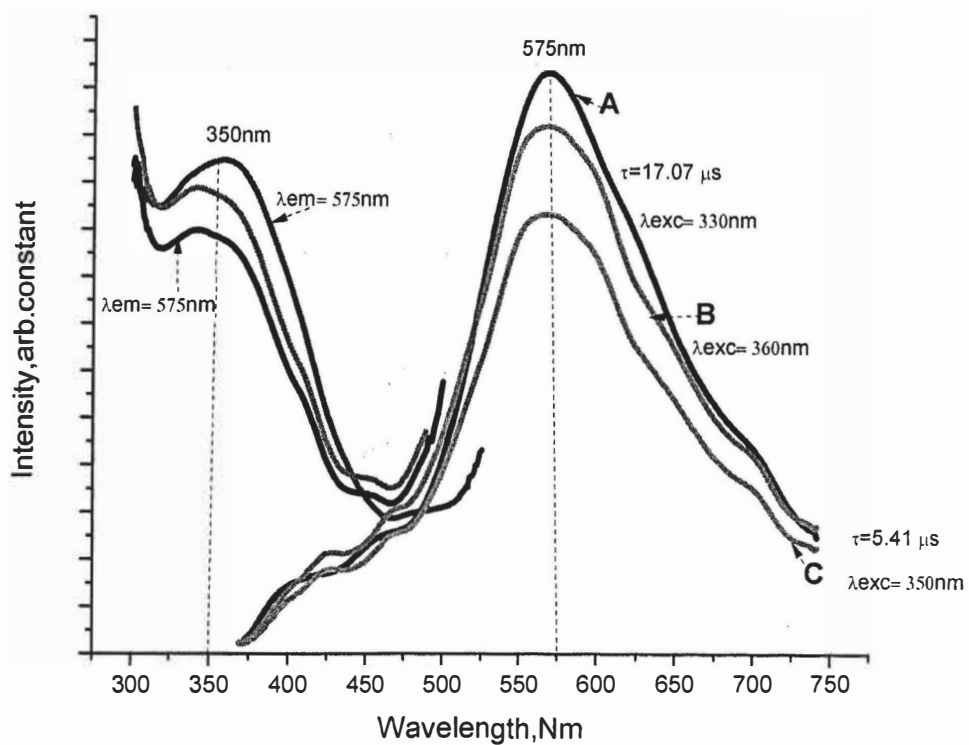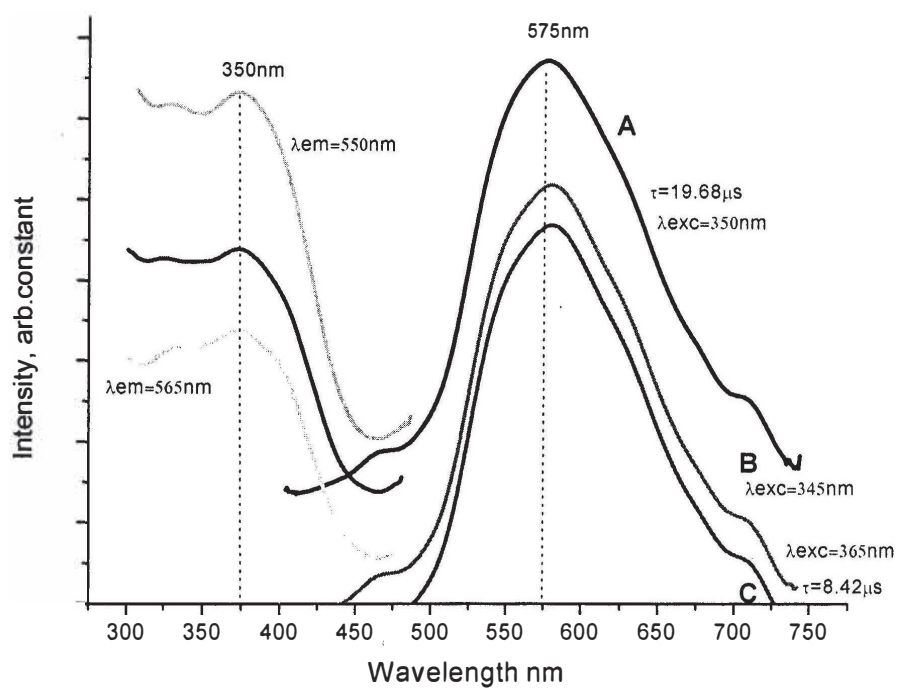
Figure 15. Solid state photoluminescence excitation (left) and emission right) spectra at (A,B) 77K using an excitation of 350nm and 345nm respectively and(C) 298K using an excitation of 65nm for {[3,5-$(CF_3)_2$Pz]$_2$Cu$_2$-PVP}in ratio of 1:15
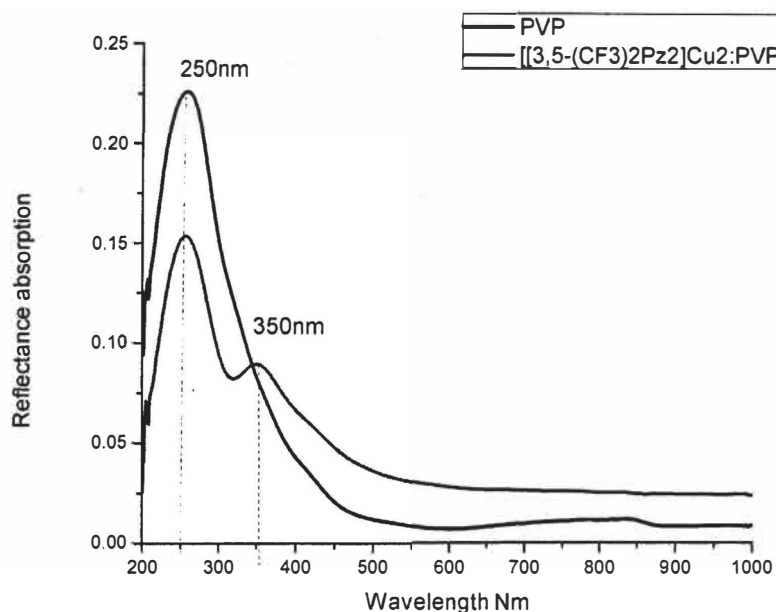
Figure 16. Solid state diffuse reflectance spectra of the metallopolymer {[3,5-(CF$_3$)$_2$Pz]$_2$Cu$_2$-PVP} indicated in red and in black for the polymer PVP.

Figure 16 shows the solid state diffuse reflectance spectra for the metallopolymer {[3,5-(CF$_3$)$_2$Pz]$_2$Cu$_2$-PVP}. It shows two unstructured absorption peaks at 250nm and 350 nm. The absorption band at 250 nm could be mostly due to the π-π* transition of the coordinated PVP polymer. The peak (350nm) probably could be due to a ligand–to- metal based charge transfer (LMCT). Following literature reviews of the compound [3,5(CF3)2PzAg1(2,4,6-collidine)] [47], we assign the band at 350nm to charge transfer to LMLCT that is from [3,5(CF$_3$)$_2$Pz-Cu] to PVP. Although two different metal: polymer ratios (1:15, 1:20) were attempted, no substantial change in the luminescence could be observed.

41

Silver Triazoles

Further research on trinuclear complexes led to the synthesis of another three coordinate metallopolymer complex $[[3,5-(C_3F_7)_2Tz]Ag-PVP]_2$. The trimer compound $[3,5-(C_3F_7)_2Tz)Ag]_3$ exhibits a bright blue luminescence in the solid state by itself. Upon coordination to the polymer PVP we observe a bathochromic or "redshift" in the luminescence of the new product. The metallopolymer exhibits a bright yellow colored luminescence in the solid state at both cryogenic and room temperature. Figures 18 and 19 show cryogenic and room temperature photoluminescence and photoluminescence excitation data for this metallopolymer complex using a molar ratio of 1: 15 and 1:30 of the metal to polymer respectively. This metallopolymer shows broad unstructured emission and excitation peaks with a excitation peak maxima of 350 nm and emission peak maxima of 585 nm. Microsecond lifetimes of 34.69μs and 27.83μs at cryogenic and room temperatures respectively have been observed. Figures 18 and 19 show the effect of temperature on the intensity of the emission and excitation peaks. At cryogenic temperature we can observe an enhancement in the intensity of the spectra. These spectra apparently do not demonstrate any sensitivity of the luminescence energies to excitation wavelength Increasing the polymer: metal molar ratio has not shown any considerable effect on the emission and excitation maxima of the $[[3,5-(C_3F_7)_2Tz]Ag-PVP]_2$ metallopolymer. The microsecond lifetimes of these compounds as well as their broad unstructured emission indicates triplet state metal centered emission.

Figure 17. Solid state photoluminescence excitation (left) and emission (right) spectra at (A,B) 77K using an excitation of 360nm and 345nm respectively and (C)298K using an excitation of 330nm for $[(3,5\text{-}(C_3F_7)_2Tz)Ag\text{-}PVP]_2$ in ratio of 1:15
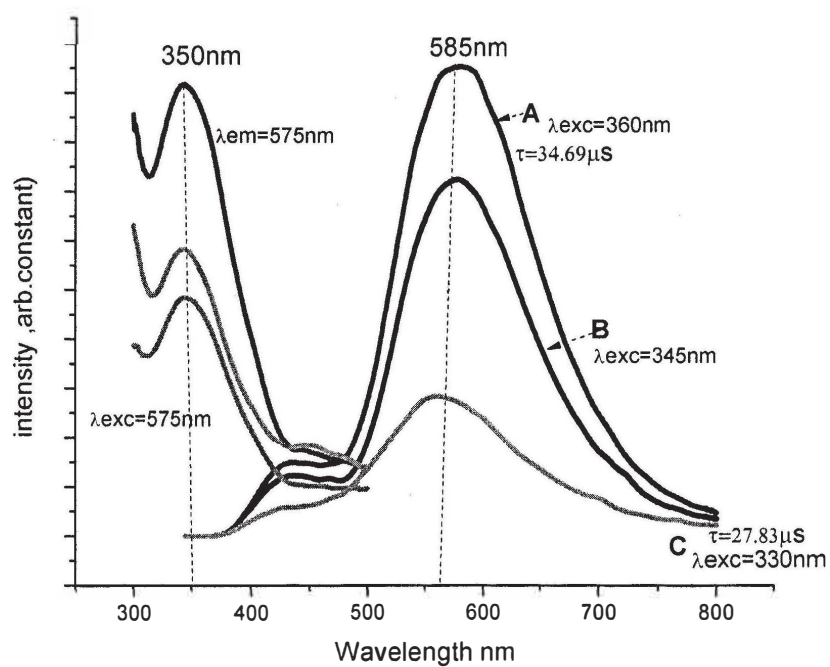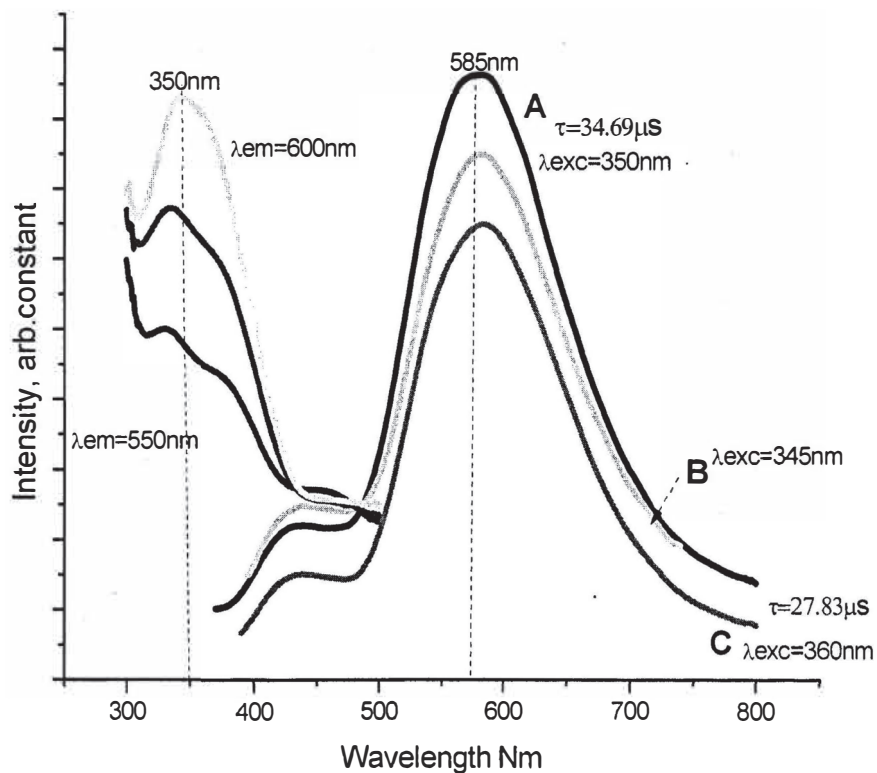
Figure 18. Solid state photoluminescence excitation (left) and emission (right) spectra at(A,B) 77K using an excitation of 350nm and 345nm respectively (C) 298K using an excitation of 360nm for {[3,5-(C$_3$F$_7$)$_2$Tz]Ag-PVP}$_2$ in ratio of 1:30.

Figure 19 illustrates the diffuse reflectance spectra of the metallopolymer [[3,5-$(C_3F_7)_2$Tz]Ag-PVP]$_2$ measured in the solid state. The spectra exhibits two absorption bands at 250 nm and 350nm. Following literature reviews[47] the peak at 350 nm can be assigned as a ligand to metal [[3,5-$(C_3F_7)_2$Tz]Ag]$_3$ to ligand (PVP) charge transfer (LMLCT)

Figure 19.   Solid state diffuse reflectance spectra of the metallopolymer
{[3,5$(C_3F_7)_2$Tz]Ag-PVP}$_2$ using two different ratios indicated in blue for
the ratio[1:30] and red for the ratio [1:15] as well in black for the polymer
PVP

3.4| Conclusions

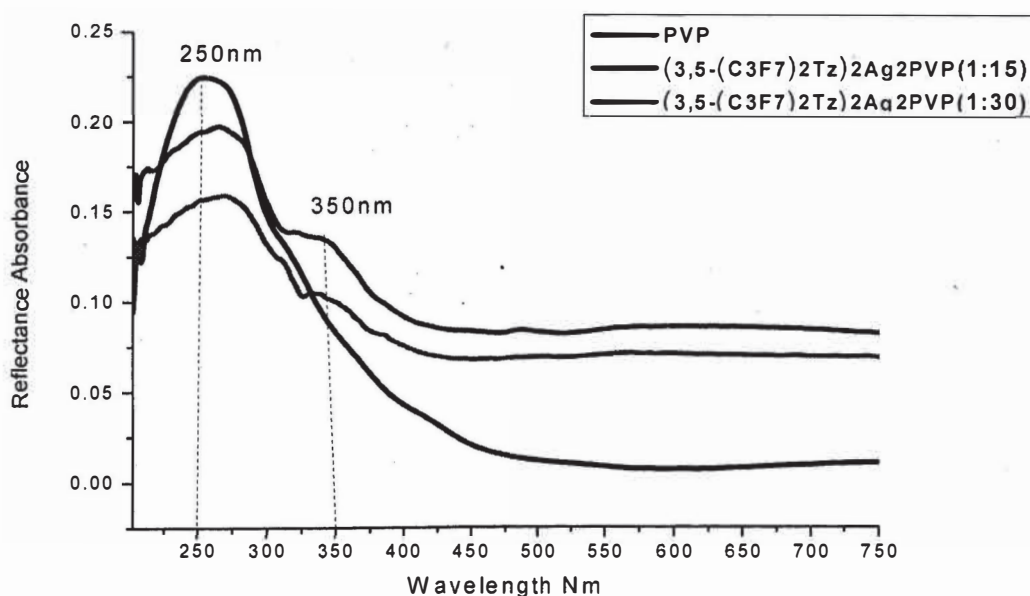The results presented in this thesis discuss the syntheses of d^{10} Ag (I) and copper Cu(I) based metallopolymer complexes, their characterization and photophysical behavior. The focus was to study the photoluminescence of these metallopolymers vs different ligands, metal: polymer molar ratio, temperature and comprehend how these factors influence the PL and other properties . These complexes exhibit metal based phosphorescent emissions and are brightly luminescent in the solid state at both room temperature and cryogenic temperature. This could be evidenced from the unstructured emissions and microsecond lifetimes. McClure et al[48] in their research had demonstrated the effect of external heavy atoms on processes involving the triplet state of aromatic molecules. Our data presented earlier shows that the presence of a heavy metal does enhance the phosphorescence due to spin-orbit coupling.

The metallopolymer [3,5 $(CF_3)_2$Pz-Cu^{I}PVP]$_2$ exhibits an emission maxima of 575 nm as well as excitation maxima at 350nm and lies in the green-yellow region of the UV-VIS spectrum. Average lifetimes of 18.4μs and 6.9μs at cryogenic and room temperatures respectively and unstructured emissions are indicative of the metal centered phosphorescence from a triplet excited state. The metallopolymer complex [[3,5-$(C_3F_7)_2$Tz]Ag-PVP]$_2$ also shows a very bright yellow phosphorescent emission with an emission maxima of 585nm and an excitation maxima of 350nm with average microsecond lifetimes of 34.69μs and 27.83μs at cryogenic and room temperatures respectively.

Use of a non-phosphorescent polymer with the transition metal complexes gave brightly phosphorescent metallopolymers in the solid state at ambient temperature. These complexes could be fine tuned across the visible spectrum especially between green and yellow regions. The partial insolubility of these complexes [[3,5-$(C_3F_7)_2$Tz]Ag-PVP]$_2$as well as the instability of the complex in solution [3,5 $(CF_3)_2$Pz-Cu^{1}PVP]$_2$ proved to be a challenge. Further efforts would be pursued to assess the performance of this class of metallopolymers as an inexpensive alternative to the Pt(II) metallopolymers in optoelectronics like PLED's.

REFERENCES

1.   Turro, N. J. *Modern Molecular Photochemistry*. Menlo Park: Benjamin/Cummings, **1978**

2.   Curie, D. *Luminescence in crystals*; Methuen; Wiley: London, New York, **1963**

3.   Bowen, E. J. *Luminescence in chemistry*; Van Nostrand: London, Princeton, N.J, **1968**

4.   Lumb, M. D. *Luminescence spectroscopy*; Academic Press: London, New York, **1978**

5.   Farnau, E. F. *Luminescence* [Ithaca, N.Y.], **1913**

6.   Faraday society, L. *Luminescence; a general discussion*; Published for the Faraday society by Gurney and Jackson: London [etc.], **1939**

7.   De Ment, J. *Fluorochemistry; a comprehensive study embracing the theory and applications of luminescence and radiation in □hysic-chemical science*; Chemical publishing company, Inc.: Brooklyn, N.Y., **1945**

8.   Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *v347*, p539

9.   Wai-Yeung Wong, G.-J. Z. Z. H. K.-Y. C. A. M.-C. N. A. B. D.; Cacute; Chan, W.-K. *Macromolecular Chemistry and Physics* **2008**, *209*, 1319

10. Wolf, M. *Journal of Inorganic and Organometallic Polymers and Materials* **2006**, *16*, 189

11. Review: Yersin, H. Top. *Curr. Chem.* **2004**, *241*, 1

12. a) Dimitrakopoulos C. D.; Mascaro D. J. *IBM J. Res. & Dev.* **2001**, 45

     b) Casseri, W. *Plat. Met. Rev.* **2004**, *48*, 91

13. a) Kim, K. Y.; Hassenzahl, J. D.; Selby, T. D.; Szulczewski, G. J.; Blackstock, S. C.*Chem. Mater,* **2002,** *14,* 1691

    b) Szulczewski, G. J.; Selby, T. D.; Kim, K.-Y.; Hassenzahl, J.; Blackstock, S. C. *J Vac. Sci. Technol., A* **2000,** *18*, 1875

14. Vorotyntsev, M. A.; Vasilyeva, S. V. *Advances in Colloid and Interface Science,* **2008**, 139, 97

15. Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. *Photophysical and Photochemical Properties of Gold(I) Complexes.* In *Optoelectronic Properties of Inorganic Compounds,* Roundhill, D. M.; Fackler, J. P., Jr. (Eds.); Plenum: New York, **1999**

16. Chen, Xiao-Yan; Yang, Xiaoping; Holliday, Bradley J.) *J. Am. Chem. Soc.*, **2008,** *130*

17. For example see

    a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 24, 391

    b) Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch. B* **1996**, *51*, 790

    c) Mathieson, T. J.; Langdon, A. G.; Milestone, N. B.; Nicholson, B. K. *J. Chem Soc.,Dalton Trans.* **1999**, 201

    d) Bonati, F.; Minghetti, G. *Gazz. Chim. Ital.* **1973**, *103*, 373

    e) Lentz, D.; Willemsen, S. *J. Organomet. Chem.* **2000**, *612*, 96

    f) Eggleston, D. S.; Chodosh, D. F.;Webb, R. L.; Davis, L. L. *Acta Crystallogr.* **1986**, *C42*, 36

    g) Ecken, H.; Olmstead, M. M.; Noll, B. C.; Attar, S.; Schlyer, B.; Balch, A. L.

J.Chem. Soc., Dalton Trans. **1998**, 3715

18. Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. *Photophysical and Photochemical Properties of Gold(I) Complexes.* In *Optoelectronic Properties of Inorganic Compounds,* Roundhill, D. M.; Fackler, J. P., Jr. (Eds.); Plenum: New York, **1999,**Chapter 6

19. For example, see:

a) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 11237

b) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 10371

20. Roundhill, D. M.; Fackler, J. P.Jr., *Optoelectronic Properties of Inorganic Compounds*, (Eds.); Plenum: New York, 1999

21. Omary,M.A.;RawashdehOmary,M.A.;Gonser,A.M.W.;Elbjeirami,O.;Grimes, T.; Cundari T.R.; Diyabalanage, H.K.; Gamage, C.S.P.;Dias,H.V.R. *Inorg.Chem.***2005**, 44, 8200

22. Zipp, A. P. *Coord. Chem. ReV.* **1988**, *84*, 47

23. Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**,*22*, 55

24. (a) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *J. Am. Chem. Soc.***2002**, *124*, 6506

(b) Yam, V. W.-W.; Tang, R. P.-L.; Wong, K.M.-C.; Lu, X.-X.; Cheung, K.-K.; Zhu, N. *Chem. Eur. J.* **2002**, *8*, 4066

(c) Lai, S.-W.; Lam, H.-W.; Lu, W.; Cheung, K.-K.; Che, C.-M.*Organometallics* **2002**, *21*, 226

.(d) McMillin, D. R.; Moore, J. J.*Coord. Chem. ReV.* **2002**, *229*, 113

(e) Neve, F.; Crispini, A.; Pietro,C. D.; Campagna, S. *Organometallics* **2002**, *21*, 3511

25. (a) Jain, V. K.; Jain, I. *Coord. Chem. ReV.* **2005**, *249*, 3075

(b) Hummel, H.-U. *Transition Met. Chem.* **1987**, *12*, 172

(c) Janka,M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2000**, *19*, 5071

(d) Kunkely, H.; Vogler, A. *J. Am. Chem. Soc.* **1990**, *112*, 5625

(e) Cera, M.; Cerrada, C.; Laguna, M.; Mata, J. A.; Teruel, H. *Organometallics* **2002**, *21*, 121

(f) Richmond, M. K.; Scott, S. L.; Yap, G. P. A.; Alper, H. *Organometallics* **2002**, *21*, 3395

(g) Pamplin, C. B.; Rettig, S.J.; Patrick, B. O.; James, B. R. *Inorg. Chem.* **2003**, *42*, 4117

26. Xia, B.-H.; Che, C.-M.; Phillips, D. L.; Leung, K.-H.; Cheung, K.-K. *Inorg. Chem.* **2002**, *41*, 3866

27. Che, C.-M.; Yam, V. W.-W.; Wong, W.-T.; Lai, T.-F. *Inorg. Chem.* **1989**, *28*, 2908

28. Xia, B.-H.; Che, C.-M.; Zhou, Z.-Y. *Chem. Eur. J.* **2003**, *9*, 3055

29. Yip, H.-K.; Lai, T.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 1639

30. Pan, Q.-J.; Zhang, H.-X. *Chem. Phys. Letters.* **2004**, *294*, 155

31. Miller, J. S. *Extended Linear Chain Compounds;* Plenum New York (1983).

32. Gliemann. G. *Struct. Bonding* **1985**, *62*, 87

33. WadasT.J.,Chakraborty.S.,Lachicotte.R.J.;Wang.Q.M.;Eisenberg.R*inorg.Chem*,**2005**, 44, 2628

34. Lee, Y.; McGarrah, J. E.; Lachicotte R. J.; Eisenberg, R. *J. AM. CHEM. SOC.* **2002**, 124, 10662

35. Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Frechet J. M. J. *J. AM. CHEM. SOC.* **2004**, 126, 15388

36. Barlow, I. A.; Kreouzis, T.; Lidzey, D. G *Organic Electronics* **2007**, 8,621

37. Cho, J-Y; Domercq, B; Barlow, S; *Organometallics*, **2007**, 26, 4816

38. Dijken,A.V.; Bastiaansen,J.J.A.M.; Kiggen,N.M.M.; Langeveld.B.M.W.; Rothe,C.; Bach,I.; Stossel,P.; Brunner,K. *J. AM. CHEM. SOC.* **2004**, 126, 7718

39. Abel, Edward; Booth, Martin; Orrell, Keith *JCS, Dalton Transactions Inorganic Chemistry* **1979**, (12), 1994

40. Salah, Omar A.; *Journal of Organometaflic Chemistry*, 387 **,1990,** 123

41. Fern´andez, E. J.; Laguna, A.; Lo´pez-de-Luzuriaga, J. M.; Monge, M.;Montiel, M.; Olmos, M. E.; Pe´rez, J.; Rodrı´guez-Castillo, M. *Gold Bull.* **2007**, *40*, 172

42. Luke A. Emmert, Wonsook Choi, Jason A. Marshall, Jing Yang, Lauren A. Meyer, and James A. Brozik *J. Phys. Chem. A*, **2003**, *107* (51), 11340

43. Biwu Ma, Jian Li, Peter I. Djurovich, Muhammed Yousufuddin, Robert Bau, and Mark E. Thompson.; *J. Am. Chem. Soc.*, **2005**, *127* (1), 28

44. H. V. Rasika Dias.; Himashinie V. K. Diyabalanage.; Maha G. Eldabaja.;Oussama Elbjeirami.;Manal A. Rawashdeh-Omary.;Mohammad A. Omary.*J. Am. Chem. Soc.* 9 Vol. 127, No. 20, **2005**, 7501

45. H.V. Rasika Dias., Sharon A. Polacha, Ziyun Wang *Journal of Fluorine Chemistry* 103 **2000** 163

46. H. V. Rasika Dias.; Shreeyukta Singh.;Charles F. Campana*. Inorg.Chem.* **2008,** 47, 3943

47. Mohammad A. Omary.; Manal A. Rawashdeh-Omary.; Himashinie V. K. Diyabalanage; H. V. Rasika Dias *Inorg.Chem.* **2003,** 42, 8612

48. D. 8. McClure, *J. Chem. Phys.,* 17, *905* , **1949**