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ALLOSTERIC TUNING OF RUTHENIUM 2,2'-BIPYRIDYL
LUMINESCENT SENSOR SYSTEMS

by

Daqing Gan

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
December 2000

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2000

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Daqing Gan

ALLOSTERIC TUNING OF RUTHENIUM 2,2'-BIPYRIDYL
LUMINESCENT SENSOR SYSTEMS

Daqing Gan, M.A.

Western Michigan University, 2000

A series of new ruthenium bipyridyl crown supramolecular sensor systems containing two binding sites were synthesized. The crystal structure and photophysical properties of the developed sensor systems were thoroughly studied using x-ray, nuclear magnetic resonance and photophysics methods. It turned out that the chelation of transition metal on the remote sites of the bipyridyl crown ligands greatly reduced the reactivity of the crown cavity. It is believed that the chelation of transition metal on the nitrogen atoms forces the bipyridyl function towards coplanarity and restricts the conformational freedom of the crown ring. The conformational rigidity in turn influences the binding capability of the crown. It is significant to note this allosteric effect on the development of conformational tunable sensor systems.

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INTRODUCTION

The objective of this project was to develop a fast, inexpensive method to determine the presence of some environmental important metals. Most of the methods currently used require very expensive instrument and are inappropriate for field analysis. We proposed to develop luminescent sensor to facilitate fast, and inexpensive field analysis of environmental samples. Luminescent sensor method is very sensitive and requires relatively simple instrumentation if a suitable luminescent sensor is used. We expected that the luminescent sensor systems possess following properties: high analyte selectivity and high analyte sensitivity, binary emission or drastic luminescent property changes in the presence of the target analyte. In order to accomplish this goal we employed superamolecular approach to develop luminescent sensor systems.

Supramolecular chemistry is a relatively new area of chemistry which has attracted lot of attention and has experienced rapid development since the pioneering work of C.J. Pedersen,^{1, 2} Donald.J. Cram,^{3, 4} and J-M Lehn^{5, 6} etc. Supramolecule can be viewed as an association of two or more chemical species. Supramolecular chemistry spans organic synthesis, physics, and biology and has found

more and more applications in supramolecular catalysis, DNA probes, luminescent sensing, and phase transfer catalysis.

Molecular recognition is one of the important branches of supramolecular chemistry. Supramolecular approach is that an appropriate receptor, possessing structural and chemical features suitable for substrate recognition can be designed. In general a supramolecular sensor system consists of three components - receptor, spacer, and reporter.

The receptor is a sub-unit of supramolecule possessing structural, electronic, and chemical features complementary to those of substrate to be bound with a balance between rigidity and flexibility suitable for the desired function to be performed. Receptor moiety is responsible for guest complexation and decomplexation. A receptor is usually a concave structure. Most receptors are macrocycles such as crown ether, cryptates, thia-ether, or aza crowns. Macrocycles are normally chosen over open chain counter parts due to the "macrocyclic effect". A reporter is another part of the sensor system that displays a well-defined and perceptible luminescent property. Such a property should change drastically when receptor-substrate interaction is taking place and report this change to the external operator. Therefore the luminescent properties of reporter should be controlled

or switched by the receptor-substrate interaction. A spacer is a bridge through which receptor and reporter are linked together to form a complete supramolecular sensor system. The function of the spacer is significant although many people ignore this significance. The spacer will determine the configuration of the whole sensor system, which in turn influences the mechanism of the sensor.

The design of the supramolecular luminescent sensor system is a highly interdisciplinary field and it may include synthetic organic chemistry, inorganic chemistry, physical chemistry, biochemistry, and biology. In order to develop a suitable sensor one should consider the possible mechanism of sensor-substrate interaction and pay close attention to the nature of the receptor and reporter. The steric effects that are largely determined by the spacer also need to be considered. The length and the nature of the spacer may affect the force ranges of the sensor and change the mechanism. The most important thing is that we should be able to anticipate the interaction between the receptor and the substrate and the communication between the receptor and the reporter. Different design logics have been developed based on the mechanism, the substrates to which the sensor system will be applied, nature of the receptor and the nature of the reporter.^{7, 8, 9} Luminescent sensors have been widely used

for the recognition of cations, anions, neutral molecules and as biological probes.

Most of the work in luminescent sensor area has involved sensors in which the fluorescent molecular fragments (fluorophores) are aromatic organic groups that will interact with analyte species to undergo signal transduction.^{10, 11} One of the major problems with these organic-type sensor systems is that the absorbance and emission are typically in UV region and their susceptibility to interferences from the redox quenchers. A better approach is that uses sensors with transition metal luminescent fragments. The advantages of inorganic luminophores over their organic analogs lie in rich diversity of electronic excited states available to transition metals. Additionally, transition metal complexes typically absorb and emit light in the visible region of the spectrum. Transition metal based sensors offer the ability to develop complex molecules with tunable functional realms that can be made to interact in predictable and desirable ways.^{12, 13, 14, 15}

Our new sensor system was constructed based on the photophysical properties of 2,2'- trisbipyridyl dication $\text{Ru}(\text{bpy})_3^{2+}$. $\text{Ru}(\text{bpy})_3^{2+}$ was employed as the reporter and the crown ether acts as receptor. $\text{Ru}(\text{bpy})_3^{2+}$ is the precursor of many luminescent sensor systems. $\text{Ru}(\text{bpy})_3^{2+}$ -type sensor may be the most important inorganic sensor class due to

their numerous applications, their chemical stability, their redox potentials, excited state reactivity, and long luminescent lifetimes.^{16, 17, 18} Many chemists such as P.D.Beer have done outstanding work in this area especially in the development of the $\text{Ru}(\text{bpy})_3^{2+}$ -type sensors for anion recognition.^{19, 20, 21}

In order to understand how we can tune the luminescent behavior of $\text{Ru}(\text{bpy})_3^{2+}$ when constructing new $\text{Ru}(\text{bpy})_3^{2+}$ -type sensor it is necessary to have a solid knowledge about the photophysical and photochemical properties of $\text{Ru}(\text{bpy})_3^{2+}$.

The ground state structure of $\text{Ru}(\text{bpy})_3^{2+}$ in its hexafluorophosphate salt has been determined by x-ray crystallography. The complex is a d^6 complex possessing a D_3 symmetry. The ground and low-lying excited state involve t_{2g} and e_g orbitals originating from the 4d orbitals of Ru(II) and π -bonding and π^* -antibonding orbitals of the aromatic system of the ligand. In ground state the π_2 , π_1 and t_{2g} orbital levels are all doubly filled. Upon the absorption of photon, several electronic transitions may take place and result in different excited states such as MC (metal center), LC (ligand center), LMCT (ligand to metal charge transfer), and MLCT (metal to ligand charge transfer). The π to π^* transitions are observed in UV region at 185nm, 208nm, and 285nm. The $d \rightarrow d$ transitions are found at 238nm, 250nm, 323nm, and

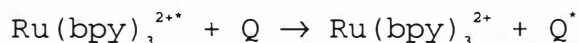
345nm. At 450nm there is an intense absorption band due to the MLCT. The aqueous solution of $\text{Ru}(\text{bpy})_3^{2+}$ show bright orange-yellow emission around 600nm at room temperature and a much more intense emission band centered at 579nm at 77K. The intense emission occurred at longer wavelength than did ligand centered $\pi \rightarrow \pi^*$ phosphorescence and this shift indicates that there is a significant contribution to the excited state from an interaction between the metal d orbital and the ligand π system. Such an interaction gives rise to a large spin-orbit coupling, which will cause significant mixing between the singlet and triplet states. As a result of mixing between different degeneracy states, the emission can be described as occurring from a manifold of spin-orbit states rather than a singlet-triplet state. The excited state of $\text{Ru}(\text{bpy})_3^{2+}$ has a C_2 symmetry. In the excited state the transferred electron is localized at only one bpy ligand and the excited state structure can be described as $[\text{Ru}^{3+}(\text{LL})_2(\text{LL}^-)]^{2+}$.

The orbital nature of the lowest excited state is a key step toward the design of useful sensor. We knew that higher excited states of transition metal complexes undergo radiationless deactivation to the lowest excited state. Thus only the lowest excited state and the upper states that can be populated on the basis of the Boltzman equilibrium law may play a role in luminescence emission.

For most $\text{Ru}(\text{bpy})_3^{2+}$ type sensors the lowest excited state is $^3\text{MLCT}$. As we pointed out before $\text{Ru}(\text{bpy})_3^{2+}$ is d^6 complex with D_3 symmetry. For all d^6 octahedral complexes MC and LMCT excited states are strongly displaced with respect to the ground state geometry along the metal-ligand vibrational coordinates. When the lowest excited state is MC or LMCT it undergoes fast radiationless deactivation to ground state or ligand dissociation. As a consequence, the excited state lifetime is very short with no luminescence emission or no bimolecular reactions observed at room temperature. ^3LC and $^3\text{MLCT}$ excited states are usually not strongly displaced compared to the ground state geometry. Thus when the lowest excited state is LC or MLCT it does not undergo fast radiationless decay to the ground state and luminescence can usually be observed. The radiative deactivation rate constant is large for $^3\text{MLCT}$ than for ^3LC because of the larger spin-orbit coupling effect. For this reason the ^3LC excited states are longer lived at low temperature in a rigid matrix and $^3\text{MLCT}$ excited states are more likely to exhibit luminescence at room temperature. It is very important to note that the energy position and orbital level orders of MC, MLCT, and LC excited states depend on the structure of the complex, the ligand field strength, the redox potential of the metal and ligands, the intrinsic properties of the ligands, respectively.

There are three main deactivation processes which may occur to deactivate the excited states of $\text{Ru}(\text{bpy})_3^{2+}$ -type luminescent sensors. Upon absorption of a photon one electron will be promoted from the metal center to one of the bpy ligands. The transferred electron may undergo radioactive decay to the ground state and emit light with stoke's shift. We are more interest in two nonradiative deactivation processes corresponding to energy transfer and electron transfer. Photoprocesses and photoreactions of $\text{Ru}(\text{bpy})_3^{2+}$ type complexes involving energy or electron transfer quenching have been widely observed. The principal reason for the quenching is that the edge of the bpy ligands is part of the aromatic ring system and this edge affords an efficient pathway for energy or electrons to flow from the excited $\text{Ru}(\text{bpy})_3^{2+}$ ion to the added quencher.

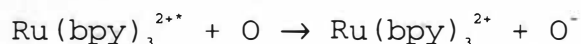
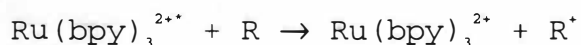
Energy transfer can occur from T_1 state of $\text{Ru}(\text{bpy})_3^{2+}$ when the added quencher has a lower triplet energy than the triplet energy of $\text{Ru}(\text{bpy})_3^{2+}$ excited state, which is estimated to be 204KJ.mol^{-1} .



The most convincing criterion for assigning a reaction as an energy transfer quenching process is the observation of emission from triplet states of the quencher Q. Energy transfer efficiency depends on the spectra overlap of the reactants. One of the applications of energy transfer in

the complexes of $\text{Ru}(\text{bpy})_3^{2+}$ is to harvest light using the complex as an antennae and to then transfer the energy to the site where it is used to effect a chemical reaction. Macrocyclic complexes have been covalently bound to the bpy ligand of modified $\text{Ru}(\text{bpy})_3^{2+}$ -type complex. Quenching of the emission of $^3\text{MLCT}$ excited state of ruthenium complex due to the interaction of this emissive state with the attached macrocyclic complex is observed.^{22, 23}

In electron transfer reactions, as an electron is transferred from the filled t_{2g} orbital of the metal into the empty π^* orbital of the bpy ligand, it creates an electron hole at the metal center. At the same time an electron is placed on one of the bpy ligands. The dipolar excited state can therefore act as either an oxidizing or a reducing agent. The electron hole at the metal center is available to accept an electron from a reductant and the unpaired electron localized on the bpy ligand is available to be transferred to an oxidant.



Because of its overall higher energy content than the ground state, the excited state is both a stronger oxidant and reductant than is the ground state from which it originated. Redox potential is an important property of luminescent sensor systems and many redox switchable sensors have been constructed.²⁴

Crown ether first drew attention after C. J Pederson synthesized dibenzo-18-crown-6 (DB18C6) and discovered its special properties in 1967.²⁵ DB18C6 and many other crown ethers have appreciable binding strength and selectivity toward alkali and alkaline earth metal ions. The study of crown ethers and their derivatives has led to important advances in area of molecular recognition. Three important characteristics of crown ethers are the number and type of donor atoms (not limited to oxygen crown ethers), the dimensions of the macrocyclic cavity, and the pre-organization of the host molecule for most effective guest coordination.

Crown ethers are widely used as receptors in molecular recognition devices.^{26, 27, 28} The complexation ability and stability between crown ethers and cations depend on the sizes and the nature of the crown ring and the coordinated cations. Usually the complex's stability is strongest when the size of the macrocyclic ring cavity and the cation are about the same. For examples, the diameters of 18C6, 15C5, and 12C4 cavities are 260-320pm, 170-220pm, and 120-150pm, respectively. The ion diameters of K^+ , Tl^+ , Rb^+ , and Na^+ are 266pm, 288pm, 296pm, and 190pm respectively. Thus K^+ , Tl^+ , and Rb^+ are the correct sizes to fit into 18C6 and are effective templates for the preparation of 18C6, but Na^+ is the suitable ion for 15C5. For the synthesis and coordination of 12C4, Li^+ will be

the best because the size of the 12C4 cavity coincides well with the diameter of Li^+ . It is very important to note that although crown ethers usually complexes with "hard ions" such as alkali and alkali earth metal ions, some crown ethers form stable complexes with Hg^+ , Hg^{2+} , Cd^{2+} , Pb^{2+} ions and all these ions are of environmental important. Another significant feature is that crown ethers usually do not form complexes with transition metals.

An important aspect of the chemistry of $\text{Ru}(\text{bpy})_3^{2+}$ is that the complex is stable and that the ligand system is amenable to chemical modifications. Usually there are two ways to modify the excited state as well as the photoproperties of $\text{Ru}(\text{bpy})_3^{2+}$ -type complexes. The first modification that can be made involves changing the metal from ruthenium to a different kinetically inert metal ion. Such a modification would be to use Fe or Os, where the difference in ligand field splitting energy (Δ_0) and the spin-orbit coupling from those of the second row of the transition metal ions will lead to differences in $^3\text{MLCT}$ energies and excited state lifetimes. A consequence of these changes in energy levels is that variations can be made in triplet energies and excited state redox potential of the complexes.

The second and most important modification is the substitution of bpy ligands. Changes in the substituents

on the ligand are particularly important because excitation into the $^3\text{MLCT}$ state places the excited electron on the ligand. Substituent changes not only lead to differences in the excited state energies, lifetime, and redox potentials, but also to steric differences that can have major effects on the chemical reactivity of the excited states. The luminescent properties of a complex as well as its ability to play the role of excited state reactant, or excited state product are all related to the energy order of its low energy excited states and particularly to the orbital nature of its lowest excited state. As pointed out previously the energy position of MC, MLCT, and LC excited states depend on the ligand field strength, the redox properties of the metal and ligands, and the intrinsic properties of the ligands. Thus, in a series of complexes of the same metal ion such as Ru(II) , the energy ordering of various excited states and particularly the orbital nature of the lowest excited state, can be controlled by a judicious choice of the ligands. In this way it is possible to design complexes having, at least to a certain degree, the desired properties. For example substitution of one bpy in Ru(bpy)_3^{2+} with two CN^- ions will greatly lower the redox potential²⁹. Conformational changes resulting from the substitution of bpy ligand also play an important role in the modification of the excited state as well as the

photophysical properties of the $\text{Ru}(\text{bpy})_3^{2+}$ -type sensor system. Conformational changes can alter excited state energy levels, change redox potentials, and facilitate electron and/or energy transfer deactivation pathways.

The new sensor system is an assembly of $\text{Ru}(\text{bpy})_3^{2+}$ and crown ether with different ring size as shown in Figure 1.

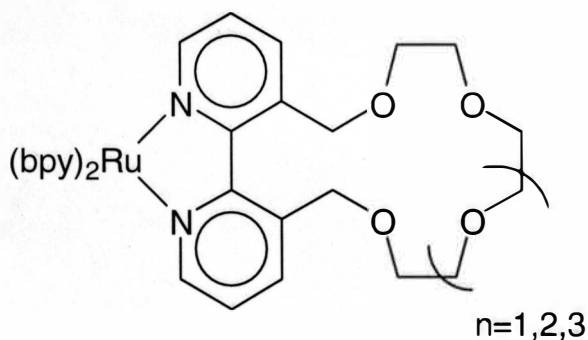


Figure 1. The New Ruthenium Bipyridyl Luminescent Sensor Systems.

There are two ways to view this new sensor system. The attachment of $(\text{bpy})_2\text{Ru}$ moiety to bpy-crown fragment forces the initially twisted bipyridine-crown toward coplanarity and restrict the conformational freedom of the crown rings. Since the complexation selectivity and stability of crown ethers are sensitive to the changes in conformation and effective "size" of the crown ring, chelation of transition metal at bipyridyl site will alter the reactivity of the crown ether³⁰. This is so-called allosteric effect proposed by J.Rebek. Allosteric

tuning has become one of the very interesting fields of supramolecular chemistry.³¹ Ru(bpy)₃ moiety within this molecule acts as a reporter via a metal to ligand charge transfer phosphorescence while the crown ether ring functions as the receptor.

A successful luminescent sensor should exhibit drastic changes in luminescent intensity or absorption and emission wavelength when the selected analyte interacts with the receptor. Complexation of metal ions into the crown ether cavity will change the conformation of the sensor and may change the photophysical properties of the new sensor. As the conformation changes to planar, it is expected to lower the π^* orbital energy and thus lower the energy difference between ³MLCT excited state and the ground state. If energy gap law is valid in this case the decrease of energy gap will cause nonradiative deactivation rate to increase and result in either red shift of emission band or quenching of the luminescence. Other important considerations are the electron-drawing nature of the coordinated cation and the planar conformation of the bipyridine-crown fragment. Both factors will increase the opportunity of PET and/or the opportunity of electronic energy transfer (EET) of the promoted electron on the bipyridine ligand that is attached to the crown ether. The PET and/or EET processes will deactivate the excited state and result in quenching

the luminescence of the sensor system. In this way we can signal the presence of target analyte via luminescence changes. As a very encouraging example Dr. Perkovic has collected some preliminary data using the similar but different sensor system $\text{Ru}(\text{bpy})_2(\text{bpy}-3,3'\text{-dicarboxylic acid})^{2+}$. This sensor has an intense absorption band at about 450nm and a typical $^3\text{MLCT}$ emission centered at 656nm in aqueous solution at room temperature. In the presence of as little as $100\mu\text{M}$ Pb^{2+} at pH 7, the emission exhibited red-shift with increase in intensity.

EXPERIMENTAL SECTION

Reagents

All the reagents were purchased from Aldrich unless otherwise stated.

Instrumentation

Mass spectra were obtained from QUATTRO II, Micromass Mass spectrometer. Proton and carbon NMR data were collected on Oxford 400M NMR. X-ray structures were examined by Enraf 0586-0205 X-ray machine. The UV-vis spectra were collected on BECKMEN DU 7400.

Synthesis

2,2'-Binicotinic Acid³²

2,2'-binicotinic acid was synthesized by oxidation of 1,10-phenanthroline. 1,10-phenanthroline crystal 16g, sodium hydroxide 6.4g, and potassium permanganate 38g were dissolved in 700ml of water and the mixture was boiled while magnetically stirred. After refluxing for two and half hours, the precipitate of magnesium dioxide MnO_2 was removed by filtration and the pale pink filtrate evaporated to approximately 300ml on a rotary evaporator. The pH of the concentrate was adjust to about 2 with

concentrate hydrochloric acid and the color of the filtrate became yellow. The resulting solution was evaporated to about 200ml and a white powder precipitated during evaporation. The white precipitate was collected by filtration, and washed with 100ml of cold water and 50ml of cold ethanol. The precipitate was air-dried overnight and 15.32 g of the crude binicotinic acid was recovered. The crude binicotinic acid was redissolved in 100ml of absolute ethanol and let the ethanol evaporate to about 25ml. Then the ethanol was decanted and the remaining product air-dried overnight. White and shining crystals was obtained. The yield was 60%.

It should be noted that some articles have reported that decolorising charcoal was added and the solution was boiled to decolorize the yellow colour of the filtrate after the adjustment of pH value to 2. My experience and observation is that once the decolorising charcoal was added and the solution was boiled the color of solution became permanent deep red and no precipitate except evaporating to dryness.

3,3'-Dicarbomethoxy-2,2'-Bipyridine ³³

3,3'-dicarbomethoxy-2,2'-bipyridine was synthesized from the reaction of binicotinic acid and methanol. There are two methods available and both of them were used in the synthesis. The first method is very classical. 4g of

binicotinic acid crystal were transferred to a 100ml round bottom flask containing 30ml absolute methanol. To the above solution, about 4ml of sulfuric acid was added drop wisely with great care. The mixture was then heated under reflux for 5h. The methanol was removed by evaporation; water (5ml) was added and the solution was neutralized with sodium carbonate. The white powder precipitate was collected and washed with water and cold ethanol. The compound was dried in vacum for another 24h. The yield of this product was 85%.

The second method was based on the synthesis introduced by J.Rebek³³. Added 3.22g of binicotinic acid crystals and 2.93ml of N-methylmorpholine to a pre-dried 250ml flask containing 100ml of absolute methanol. After 5 minutes the solution became clear and 2.04ml of methylchloroformate were added drop wise over a 10min period while the temperature was kept 0°C. Smoke was generated and the ordor of methylmorpholine was very disagreeable. Extra care should be taken when handling and transferring methylchloroformate. After the solution was stirred at room temperature for 30min the solvent was evaporated. The solid residue was dissolved in 100ml of chloroform and then 25ml of saturated bicarbonate solution was added to the solution. Gas was generated upon the addition of NaHCO_3 . The organic layer was separated and washed with three portions of bicarbonate

solution until no bubbles found. The solvent was then evaporated to give 3.58g of solid. The solid was recrystallized from pure methanol. The actual yield was about 70%.

3,3'-Dimethylol-2,2'-Bipyridine ³³

The preparation of 3, 3'-Dimethylol-2, 2'-bipyridine was a critical step in the synthesis of the subsequent compounds. The reducing agent selected for reduction of diester to corresponding diol is Red-Al (sodium bis[2-methoxyethoxy]aluminum hydride). Other reducing agents such as LiAlH_4 did not work. Because Red-Al is extremely moisture sensitive and will vigorously reacts with the moisture in air generating large amount of heat, several precautions should be taken to prevent explosions. Prior to the experiment all glassware used in the reaction must be pre-dried. The THF solvent should be dried by refluxing with potassium metal till the bezonphenone indicator changes color to blue. All of the manipulations and reactions should be conducted under a N_2 atmosphere to avoid explosions.

1.5g of the diester was added to a pre-dried flask and then 150ml of dried THF was transferred with syringe under N_2 atmosphere. 30ml of Red-Al was then added drop wise to the mixture over 30min through a pre-dried addition funnel under a N_2 atmosphere. An ice-bath was

used to keep the temperature around 0°C . After 1h at 0°C the excess Red-Al was decomposed by addition of saturated NH_4Cl solution. A white-yellow precipitate formed on addition of NH_4Cl (note: Saturated NH_4Cl solution should also be added drop wisely while magnetically stirred because lot of heat and gas will be generated upon the addition of NH_4Cl solution). The precipitate was filtered off and then added 100ml of chloroform to the filtrate. A semi-solid precipitate was formed upon addition of the chloroform. The solution was then filtered. The residue was washed with another 300ml of chloroform. Evaporation of the combined organic CH_2Cl layers gave a tan solid. The tan solid was re-crystallized from benzene and then the methanol solution. The solid was washed with THF and white shining diol crystal was obtained. The yield was 70%.

Bipyridine-4-Oxygen Crown Ether ³³

Before the experiment all the glassware was dried overnight and only anhydrous THF was used. Added 3g of NaH oil dispersion to a pre-dried 800ml flask. About 50ml of hexane was then transferred to the flask to wash off the oil. The mixture was magnetically stirred for 10min. The solution was allowed to settle down. The upper hexane layer was removed and another 50ml hexane was transferred into the flask. The washing procedure was repeated for at

least three times. At the end hexane was blown off using N_2 and 400ml of anhydrous THF were transferred to the flask containing NaH with great care. 2.57g of the diol was dissolved in 20ml of anhydrous THF and then transferred to the flask. The mixture was refluxed for one day. Triethylene glycol ditosylate in 50ml of THF was added and the solution was refluxed for another day. The cooled solution was then quenched by the addition of 10ml of H_2O followed by evaporation of THF solvent (Caution: addition of water to the cooled reaction flask may cause a fire by reacting with the NaH remains in the flask). The black solid residue was dissolved in 300ml of chloroform, then extracted into 1M of HCl ($3 \times 100ml$). The combined aqueous phases were neutralized with 2.5M of KOH, then extracted back to organic phase with $3 \times 100ml$ of chloroform. Evaporation of the chloroform gave the crude product of bipyridine-4-oxygen-crown.

The bipyridine-4-oxygen-crown ether was purified by column chromatography using alumina as the stationary phase and acetone- CH_2Cl_2 as eluent(3:7). The first fraction eluted off the column was a mixture of the solvent, some ditosylate impurities and complexes. The second portion was the product and the third portion was the unreacted diol if any. The bipyridine-4-oxygen crown was isolated as a liquid and became solid at room temperature after one day. The yield was 30%.

Bipyridine-5-Oxygen Crown Ether³³

Bipyridine-5-oxygen-crown ether was prepared and purified using the same procedures as for bipyridine-4-oxygen crown ether except that tetraethylene glycol ditosylate was used in stead of triethylene ditosylat. This crown was a waxy semi-solid at room temperature. The yield was 20%.

Bipyridine-6-Oxygen Crown Ether³³

Bipyridine-6-oxygen-crown ether was synthesized using the same procedure as that for the previous two crown ethers. Pentaethylene glycol ditosylate was used to react with the diol to form bipyridine-6-oxygen-crown ether. The bipyridine-6-oxygen-crown was a liquid and the overall yield was about 10% after purification.

Ruthenium Bipyridyl-4-Oxygen Crown Sensor

Ruthenium bipyridyl-4-oxygen crown complex can be synthesized employing the following procedure. 0.27g of bipyridine-4-oxygen-crown ether were added to a 50ml flask containing 20ml of absolute EtOH. Then 0.43g of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was added. The mixture was refluxed for 24hr and filtered while hot. Plenty of NH_4PF_6 was added to the filtrate and the mixture was cooled and stored in refrigerator overnight. The orange yellow precipitate was

collected by filtration and washed with 30ml of ether. The solid was dried in vacuum and the crude yield was 70%.

Purification of ruthenium bipyridyl complexes was tedious. Several methods such as ion exchange were tried but the best result was obtained using chromatography on an alumina column. The problem with ion exchange was that the desired product almost did not move along the column. The best eluent was acetone- CH_2Cl_2 (4:7). Methanol could not be used as the eluent as no luminescent compounds were eluted by methanol. The appropriate fraction was evaporated nearly to dryness and then water and NH_4PF_6 were added followed by the addition of NaClO_4 salt. The mixture was put in refrigerator and the ruthenium crystals were allowed to grow for one week.

Ruthenium Bipyridyl-5-Oxygen Crown Sensor

Same synthetic reaction and purification procedures as used in the Ruthenium-4-oxygen sensor were employed in the synthesis and purification of ruthenium bipyridyl-5-oxygen crown sensor. The yields were almost the same. The orange yellow ClO_4^- salt of ruthenium bipyridine-5-oxygen complex was recrystallized from water solution in the presence of small portion of acetone. The complete crystal structure of this sensor was obtained using x-ray crystallography. The yield was 60%.

Ruthenium Bipyridyl-6-Oxygen Crown Sensor

The preparation method and purification procedures of previous ruthenium bipyridyl crown sensors were used without significant modifications except that acetone was used as eluent. The yield was 50%.

The Investigation of Physical and Photophysical Properties of the Ruthenium Bipyridyl Crown Sensor Systems

Determination of Molar Absorption Coefficients for Ruthenium Bipyridyl Crown Sensors

The absorption data of three ruthenium sensors were determined in DMSO/H₂O solution at room temperature. The molar extinction coefficients were calculated using Beer's law.

$$A = \epsilon bc. \quad (1)$$

Determination of Quantum Yields for Ruthenium Sensors

The emission spectra of three sensors in DMSO/H₂O solution were measured by exciting the DMSO/H₂O solutions of these sensors at 450nm at room temperature and at 77K.

Sample Preparation and Data Collection

A Ru(bpy)₃²⁺ solution in DMSO/H₂O was prepared with an absorbance between 0.2 and 0.1. Then solutions of three sensors in DMSO/H₂O with the absorbance matching that of

$\text{Ru}(\text{bpy})_3^{2+}$ solution were prepared. All four solutions were degassed with N_2 or Ar at 77K. The solutions were then put in emission spectroscopic meter and emission data (emission integral areas) were collected. The solutions were warmed back to room temperature and the emission data and spectra were again collected. The de-oxygenation step was important because the diffusion of O_2 may quench the emission of the sensors.

The Calculation of Quantum Yields

The quantum yield of ruthenium sensor was calculated by comparing with the quantum yield of $\text{Ru}(\text{bpy})_3^{2+}$ at same temperature and absorbance employing equation (2)

$$\Phi_{\text{sensor}} = \Phi_{\text{rubpy}} * (\text{Area of sensor} / \text{Area of rubpy}) \quad (2)$$

Φ_{sensor} is the quantum yield of the sensor. Φ_{rubpy} is the quantum yield of $\text{Ru}(\text{bpy})_3^{2+}$ and rubpy represents $\text{Ru}(\text{bpy})_3^{2+}$.

The Solvent Polarity Effects On the Photophysical Properties of the Sensor Systems

CH_2Cl_2 , THF, MeOH, and CH_3CN were used to determine the solvent effects on the luminescent properties of three ruthenium sensors.

NMR Determination of the Metal Ion Coordination of Free Ligands and Ruthenium Sensor Systems

NMR methods are often used to examine metal ion coordination behavior and the resulting conformational

change of the coordinated molecule³⁴. The effects of K^+ , Na^+ , Pb^{2+} and Cd^{2+} on NMR spectra of free ligands and the corresponding sensors were examined in $CDCl_3$. The salts used in this examination were $K(CF_3SO_3)$, $Na(CF_3SO_3)$, $Pb(CF_3SO_3)_2$ and $Cd(CF_3SO_3)_2$. The general preparation procedure of $Pb(CF_3SO_3)$ is given below as an example.

0.1 moles of $PbCO_3$ were added to a long and clean graduate cylinder. 18 ~ 20ml of triflic acid was then added drop wise with great care. Triflic acid ($H_2CF_3SO_3$) is volatile and extremely corrosive to human skin. Hot MeOH was added to the mixture and then it was filtered. Caution: The reaction of triflic acid with $PbCO_3$ generated large quantity of CO_2 and heat therefore care should be taken when adding hot methanol to the reaction mixture. The filtrate was cooled overnight and then ether was added. The final product was collected by filtration.

The Absorption and Emission of the Sensor Systems in the Presence of IA Metal, Pb^{2+} , Cd^{2+} Ions in Different Solvents

The photophysical behavior of the sensor systems in the presence of the metal ions especially Pb^{2+} were systematically examined in different solvents as well as at different temperature.

In order to quantitatively analyze the effect of metal ions on the absorption and emission of the sensors in different solvents. A series of solutions, which have

the same ruthenium sensor concentration and different metal ion concentrations, were prepared as described below. 100ml solutions of ruthenium bipyridyl-4-oxygen, 5-oxygen, 6-oxygen crown sensor in DMSO/H₂O were prepared with the absorbance between 0.2 and 0.1 as stock solutions. To 10ml of the stock solutions a calculated amount of Pb(NO₃)₂, Cd(NO₃)₂, KNO₃, and NaNO₃ salts were added to make the concentration of the metal ions equal to 0.5M respectively. These 0.5M metal ion solutions were then systematically dilute to 0.25M, 0.1M, 0.05M, 0.01M and 0.001M solutions using ruthenium sensor DMSO/H₂O solutions as solvent. The same procedures were used to prepare THF, CHCl₃, MeOH, and CH₃CN sensor solutions with different metal ions and different concentrations. In stead of nitrate salts the triflix salts were used in the preparation of THF, CHCl₃, MeOH, and CH₃CN solutions.

RESULTS

Synthesis

Binicotinic Acid

The melting point of this compound was 261°C and this value agrees with literature³² value very well. The IR spectrum of the synthesized binicotinic acid showed a sharp peak between 1700cm^{-1} and 1750cm^{-1} . The sharp peak is a typical C=O stretch vibration band. The broad band centered at 2900cm^{-1} was assigned to the -OH group.

3,3'-Dicarbomethoxy-2,2'-Bipyridine

The melting point of new made 3,3-dicarbomethoxy-2,2'-bipyridine was 150°C , which agrees with literature value³⁴ very well. The proton NMR data in CDCl_3 is the followings: δ 8.80(d,2), 8.40(d,2), 7.49(m,2), 3.78(s,6). Three peaks in the range of 7.49 and 8.80 represent three different hydrogen atoms on the bipyridine ring and the singlet peak at 3.78 was assigned to the hydrogen atoms of $-\text{CH}_2$ group on the diester. The integration shows 1:1 ratio and fits the calculation value very well.

3,3'-Dimethylol-2,2'-Bipyridine

The melting point of the diol was 144°C . IR spectrum

showing a strong board band at 3260cm^{-1} indicated the typical -OH group of alcohol. In the range of 1650cm^{-1} to 1750cm^{-1} there was no absorption and this is due to the disappearance of C=O group. The proton and carbon NMR data are present in Table 1.

Table 1

Proton and Carbon NMR Data of 3,3'-Dimethylol-2,2'-Bipyridine in CDCl_3

^1H NMR	(δ_{H})	^{13}C NMR	(δ_{C})
8.58	(d, 2)	157.22	
7.90	(d, 2)	147.14	
7.41	(m, 2)	140.28	
4.40	(s, 4)	137.06	
		124.12	
		63.52	

The proton NMR data indicated that three peaks in the range of 7.41ppm to 8.58ppm were of three different H atoms on the bipyridine ring. The singlet peak at 4.4ppm represented the H atom form $-\text{CH}_2$ group. ^{13}C NMR further conformed the correctness of this compound. Between 120 and 160 five peaks appeared. These five peaks were assigned to the five different carbon atoms on the bipyridine ring and at 63.52 a singlet peak account for

the carbon atom of $-\text{CH}_2$ group.

Bipyridine-4-Oxygen, 5-Oxygen, and 6-Oxygen Crown Ethers

The NMR data for Bipyridine-4-oxygen crown ether is present in Table 2.

Table 2
Proton and Carbon NMR Data for Bipyridine-4-Oxygen Crown Ether

^1H NMR	(δ_{H})	^{13}C NMR	(δ_{C})
8.45	(d, 2)	156.38	
7.85	(d, 2)	147.43	
7.25	(m, 2)	136.58	
4.40	(m, 4)	133.29	
3.15 ~ 3.70	(m, 12)	123.14	
		69.99 ~ 70.57	(5)

Three peaks between 7.25ppm and 8.45ppm in proton NMR spectrum indicated three different H atoms from bipyridine ring and at 4.40ppm a multiple peak represent H atoms from $-\text{CH}_2$ group. The carbon NMR also showed 5 expected peaks between 120 and 160 and 5 peaks between 69 and 71. Similar results for bipyridine-5-oxygen crown ether was obtained. The NMR data for six-oxygen crown is

summarized in Table 3.

Table 3
Proton and Carbon NMR Data of Bipyridine-6-Oxygen Crown
in CDCl₃

¹ H NMR	(δ_H)	¹³ C NMR	(δ_C)
8.54	(d, 2)	156.15	
7.95	(d, 2)	147.58	
7.34	(m, 2)	136.87	
4.49~ 4.67	(m, 4)	133.32	
3.30~ 3.82	(m, 20)	123.24	
		70.75	(m)

Ruthenium Bipyridyl-4-Oxygen Sensor System

The proton NMR spectrum of this sensor in acetone is much more complicated than that of free ligand. This was reasonable due to the more complicated structure. The free ligand has one bipyridine moiety while the ruthenium sensor has two additional bipyridine rings and a ruthenium attached to the free ligand fragment. The ¹³C NMR of the ruthenium complex in acetone also showed significant position change compared to that of the free ligand. The mass spectroscopy in acetone and H₂O (50:50)

as depicted in Figure 2 further confirmed the correctness of the complex. As showing in Figure 2 there was a base molecular ion peak at 372m/z. It agreed with calculated value perfectly. Crystal structure of the ClO_4^- salt of this molecule was obtained. The NMR and mass spectroscopy data are present in Table 4.

Table 4

The NMR and MS Data of Ruthenium Bipyridyl-4-Oxygen Crown Sensor in Acetone Solution

^1H NMR (δ_{H})	^{13}C NMR (δ_{C})	Mass spectrum m/z
8.78 (d)	152.18	157
8.20 (m)	138.08	242
7.97 (s)	138.01	371
7.54 (m)	127.84	372
3.78 (m)	124.46	373
3.76 (d)	72.07	651
2.82 (d)	70.42	764
2.59 (s)	70.18	889
	69.51	932

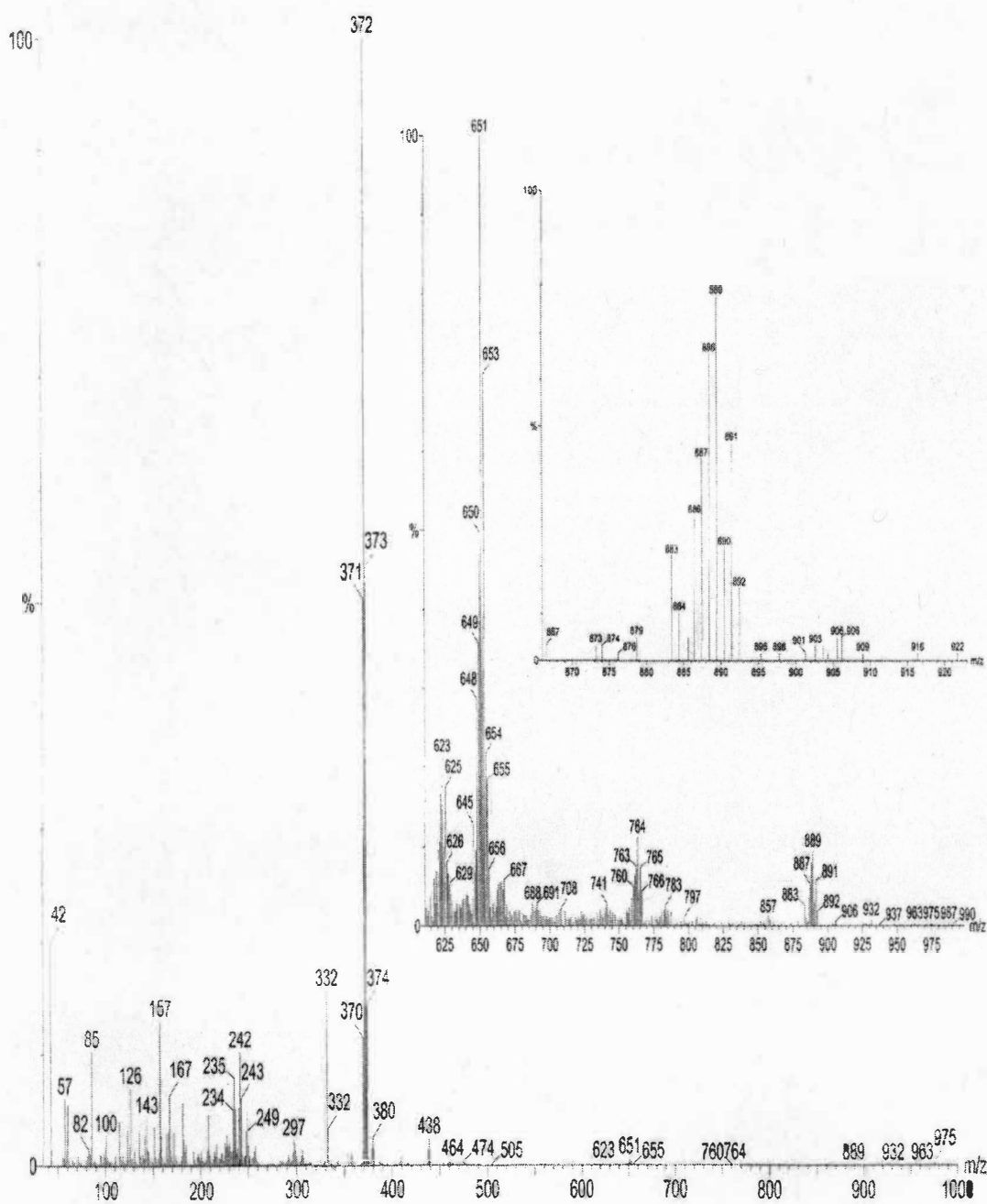


Figure 2. Mass Spectrum of Ruthenium Bipyridyl-4-Oxygen Crown Sensor in Acetone Water.

Ruthenium Bipyridyl-5-Oxygen Crown Sensor System

The proton and carbon NMR of ruthenium bipyridine-5-oxygen crown sensor is very similar to that of ruthenium-4-oxygen crown ether. A complete ClO_4^- salt crystal structure of this complex was obtained. The ^1H and ^{13}C NMR data in acetone solution and MS data in acetone water mixture were summarized in Table 5. The mass spectrum of this compound in acetone and water mixture is shown in Figure 3. As indicated in Table 5 and Figure 3 there is a base peak at 395m/z and this is the molecular ion peak.

Table 5

Proton and Carbon NMR and MS Data of Ruthenium Bipyridyl-5-oxygen Crown Sensor

^1H NMR (δ_{H})	^{13}C NMR (δ_{C})	MS (m/z)
8.79(d)	152.2	181
8.20(m)	137.8	242
7.98(s)	127.6	395
7.55(m)	126.8	669
3.61(s)	71.1~ 69.2 (m)	695
2.83(m)		

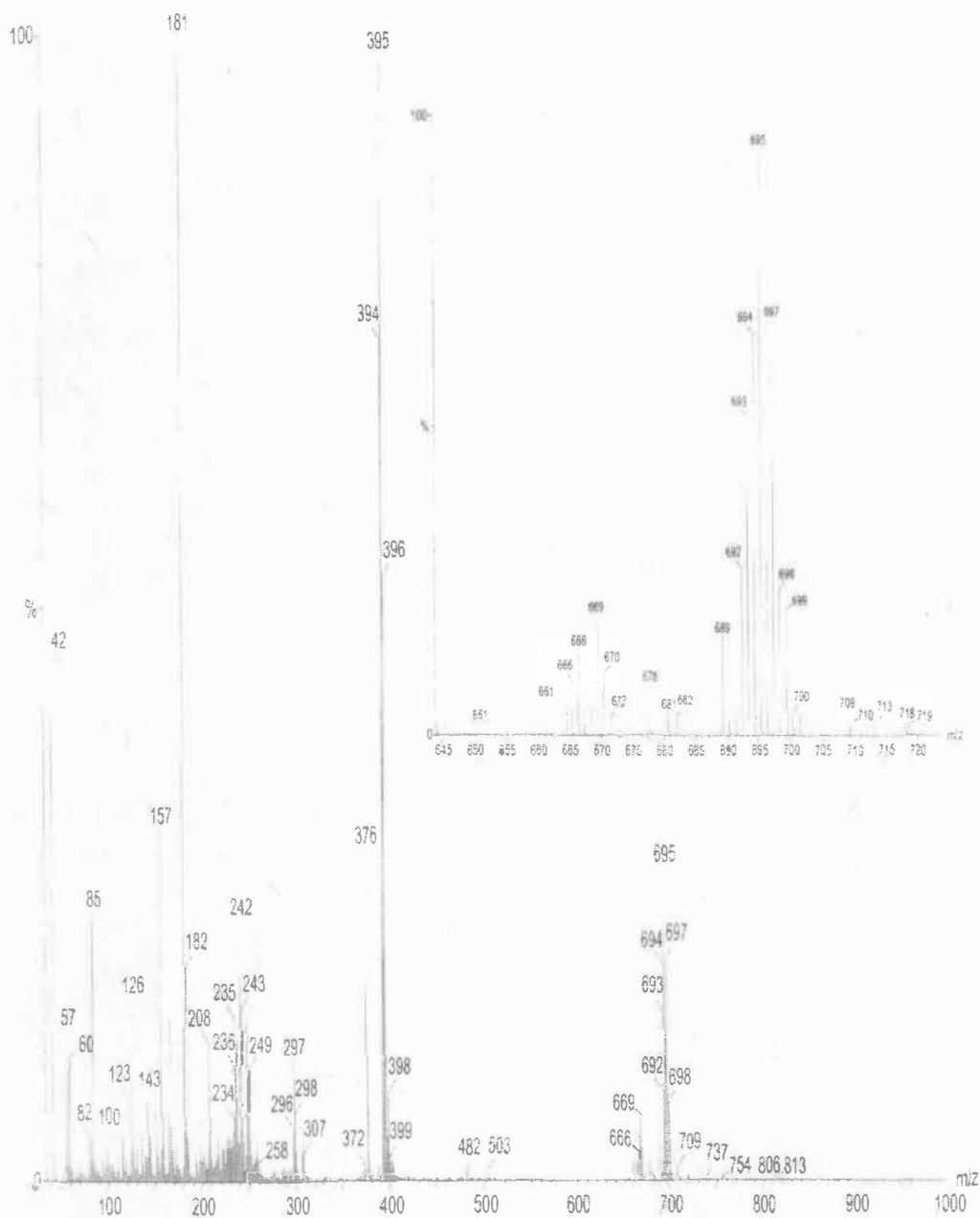


Figure 3. Mass Spectrum of Ruthenium Bipyridyl-5-Oxygen Crown Sensor in Acetone Water.

Ruthenium Bipyridyl-6-Oxygen Crown Sensor System

The orange yellow needle of ruthenium bipyridyl-6-oxygen crown sensor was characterized using ^1H NMR and ^{13}C NMR in acetonitrile and mass spectroscopy. We were unable to obtain the crystal structure of this complex that may due to the relatively large and complicate structure of this compound. The mass spectrum as shown in Figure 4 in pure ethanol solution clearly proved that the complex was the right product with the appearance of expected peaks especially the base peak at 417m/z.

Table 6

Proton and Carbon NMR and Mass Spectrum Data of Ruthenium Bipyridyl-6-Oxygen Crown Sensor

^1H NMR (δ_{H})	^{13}C NMR (δ_{C})	MS	m/z
8.50 (d)	152.3		236
8.26 (m)	138.5 (d)		371
8.06 (m)	127.8		416
7.36 (m)	124.3		417
3.58	68.1~ 70.05 (m)		738
2.56 (m)			764

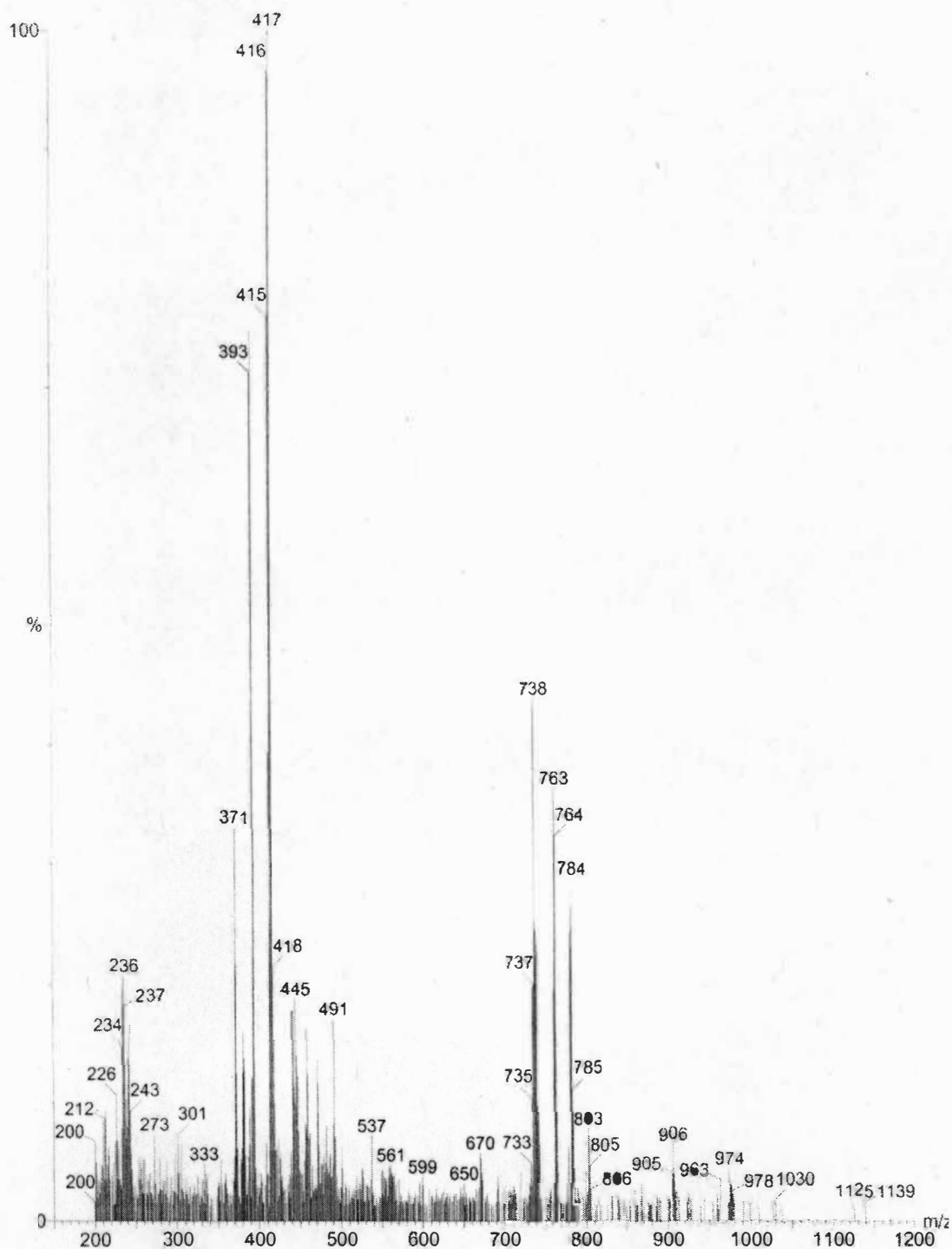


Figure 4. Mass Spectrum of Ruthenium Bipyridyl-6-Oxygen Crown Sensor in Methanol.

Photophysical Investigation

Extinction Coefficients

Absorption at wavelength lower than 250nm were not calculated because the absorption were too intense to measure. There was no solvent dependence observed in experiment. The extinction coefficients of three sensors in DMSO/H₂O mixture are presented in Table 7.

Table 7

The Extinction Coefficients ϵ (mol⁻¹.cm⁻¹) of Three Sensors in DMSO/H₂O Solution at 298K

Wavelength	Sensor	ϵ (mol ⁻¹ .cm ⁻¹)
450nm	Ruthenium-4-Oxygen Sensor	13950
290nm	Ruthenium-4-Oxygen Sensor	69714
450nm	Ruthenium-5-Oxygen Sensor	16026
290nm	Ruthenium-5-Oxygen Sensor	94853
236nm	Ruthenium-5-Oxygen Sensor	78126
450nm	Ruthenium-6-Oxygen Sensor	6460
290nm	Ruthenium-6-Oxygen Sensor	40660
252nm	Ruthenium-6-Oxygen Sensor	18622

The Quantum Yields of Three Sensors

The emission spectra of three sensors in DMSO/H₂O solution were collected at 77K and 298K. The quantum yields were then calculated by equation (2). The quantum yields of all three sensors at 77K were one magnitude of that of 298K because less dynamic quenching at 77K than that at 298K. All three had similar quantum yields at both 77K and 298K. The results were tabled in Table 8.

Table 8

Quantum Yields (Φ) of Three Sensors in DMSO/H₂O

Sensor	Φ (77K)	Φ (298K)
Ruthenium-4-Oxygen Sensor	0.0332	0.0138
Ruthenium-5-Oxygen Sensor	0.0321	0.0198
Ruthenium-6-Oxygen Sensor	0.0399	0.0174

The Solvent Polarity Effects on the Photophysical Properties of the Sensor Systems

The solvent effects were examined using THF, CHCl₃, MeOH and CH₃CN at 77K and 298K. The absorption of these three sensors did not display any significant changes in either absorption intensity or wavelength when the

solvents were changed. However the emission spectra of the sensor systems in CH_2Cl_2 at 298K displayed significant wavelength changes compared with those of THF and CH_3CN as shown in Figure 5. The data is present in table 9. The emission spectra of these sensors did not shift at 77K. Emission intensities depend on the choice of solvent especially at room temperature. The luminescent intensity increases as the solvent change to CH_2Cl_2 .

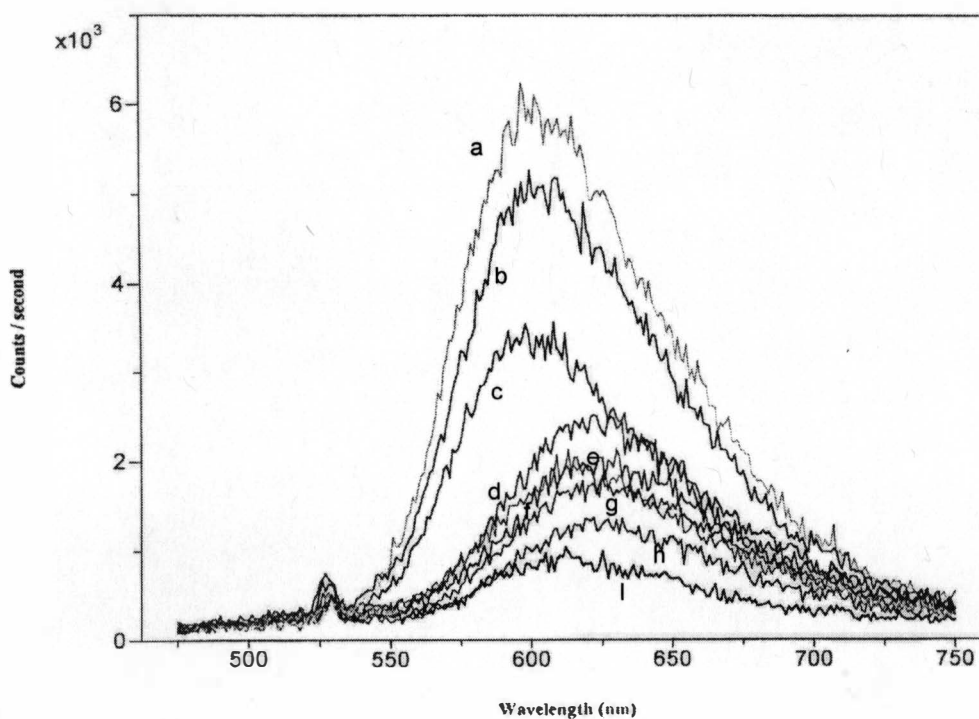


Figure 5. The Solvent Effects on the Emission of Three Sensor Systems at 298K.

Curves c, H, and I are ruthenium bipyridyl-4-oxygen, spectra in CH_2Cl_2 , THF, and CH_3CN . Curves, a, f, and I are ruthenium bipyridyl-5-oxygen sensor spectra in CH_2Cl_2 ,

THF, and CH_3CN . Curves b, g, and e are spectra of ruthenium bipyridyl-6-oxygen sensor in CH_2Cl_2 , THF, and CH_3CN .

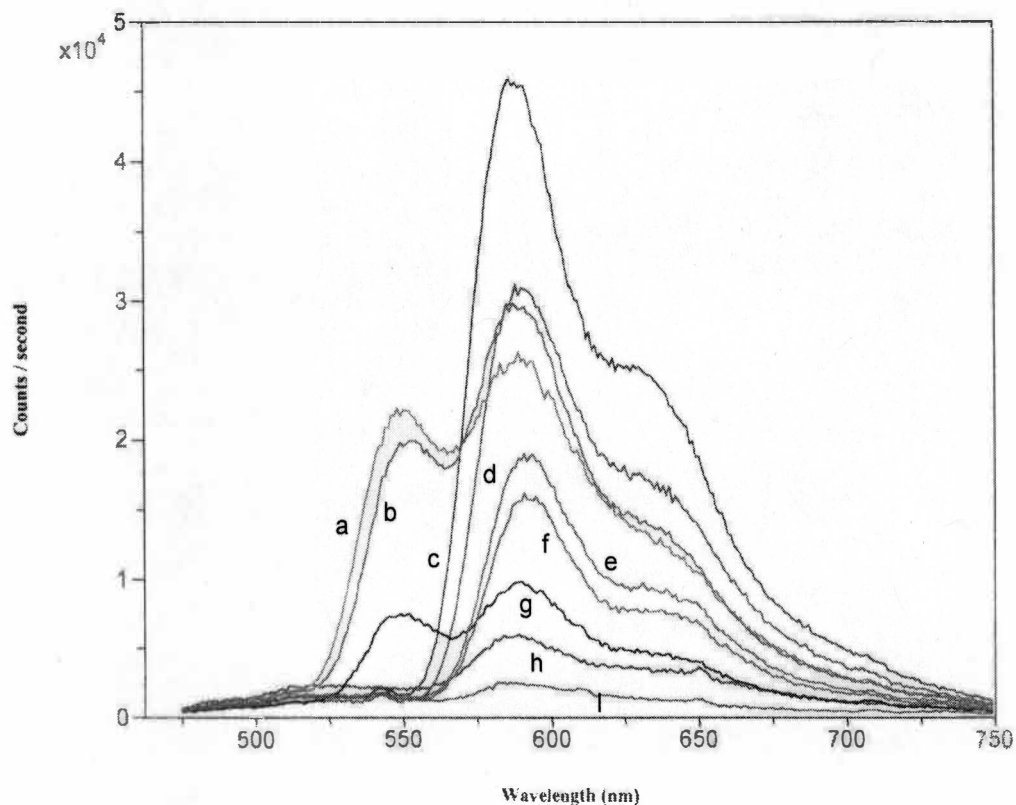


Figure 6. Solvent Effects on the Emission of Three Sensor Systems at 77K.

Curves g, d, and H are ruthenium bipyridyl-4-oxygen sensor spectra in THF, CH_2Cl_2 and CH_3CN , respectively. Curves a, e, and I are ruthenium bipyridyl-5-oxygen sensor spectra in THF, CH_2Cl_2 and CH_3CN , respectively. Curves b, c, and f are ruthenium bipyridyl-6-oxygen sensor spectra in THF, CH_2Cl_2 and CH_3CN , respectively.

Table 9

Maximum Emission Wavelength of Three Sensors in Different Solvents

Temp	Sensors	λ_{max}			
		DMSO/H ₂ O	THF	CH ₂ Cl ₂	CH ₃ CN
77K	Ru-4-O Sensor	589	587.1	591.7	588.8
	Ru-5-O Sensor	588	587.9	592.2	588.8
	Ru-6-O Sensor	585	589.2	589.2	588.8
298K	Ru-4-O Sensor	615	620.8	600.4	613.8
	Ru-5-O Sensor	616.7	620.6	601.7	622.5
	Ru-6-O Sensor	622.1	620.8	600.4	615.6

Ru-4-O sensor, Ru-5-O sensor, and Ru-6-O sensor are abbreviations of ruthenium bipyridyl-4-oxygen, ruthenium bipyridyl-5-oxygen and ruthenium bipyridyl-6-oxygen crown sensors, respectively.

NMR Determination of the Metal Ion Coordination toward free Ligands and the Sensor Systems

The proton NMR spectra of the free ligands and sensors in the presence of different metal ions were examined. The aromatic region of the free ligands remained undisturbed while the signals in the macrocycle

were affected by the addition of K^+ , and Na^+ ions. In the presence of K^+ the singlet peak of three ligands at 4.4ppm was splitted to doublet and a new doublet appeared at about 5.0ppm. In the presence of Na^+ bipyridine-4-oxygen and bipyridine-5-oxygen crowns displayed similar NMR patterns as that of K^+ . But bipyridine-6-oxygen crown ligand showed significant peak diminishment at 4.5ppm compared to that of the ligand without the sodium ion present. The spectrum is depicted in Figure 7. There was no change when added Pb^{2+} and Cd^{2+} ions to three ligands solutions.

Ruthenium bipyridyl sensors showed no appreciable change in peak pattern and positions when IA metal ions and Pb^{2+} and Cd^{2+} ions were added.

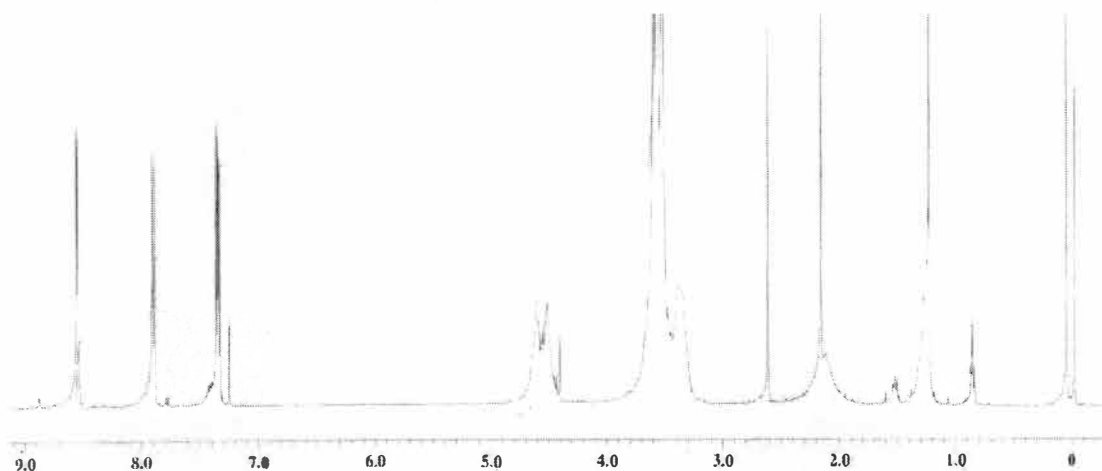


Figure 7. The Na^+ Effects on the Bipyridine-6-Oxygen Crown Ether in $CDCl_3$.

The Metal Ion Effects on the Spectroscopy Properties of Three Sensors

The absorption of the sensors did not display any appreciable changes in both absorption intensity and absorption bands when a series of sensor solutions with different metal ions at different concentrations were examined.

The emission of the sensor solutions with different concentrations of metal ions was also examined at both room temperature and at 77K. At room temperature the emission spectra of the sensor solutions did not exhibit any appreciable changes in the presence of K^+ , Na^+ and Pb^{2+} ions. The spectra were shown in Figure 8, Figure 9, and Figure 10, respectively. The emission spectra of three sensors in THF, CH_3CN , and MeOH with K, Na, and Pb were collected. There was no solvent dependence observed.

However, in DMSO/ H_2O solutions at 77K, all three sensors did display considerable luminescence changes in the presence of different metal ions but the emission changes did not show any concentration dependence in the range studied. The emission spectra of three sensors in the presence of different metal ions were shown in Figure 11, Figure 12, and Figure 13, respectively. For ruthenium bipyridyl-4-oxygen crown sensor the presence of K^+ increases luminescent intensity while the presence of Na^+ and Pb^{2+} ions exhibit luminescence quenching effects on

the sensors. For ruthenium bipyridyl-5-oxygen crown sensor the effects of Na^+ and K^+ were opposite while Pb^{2+} still acted as a quencher although not very significant. The luminescent behavior of ruthenium-6-oxygen crown sensor showed dramatic changes in the addition of the metal ions. Pb^{2+} greatly increased the luminescent intensity of the sensor but K^+ has no effect. The presence of Na^+ decreased the luminescence of the sensor.

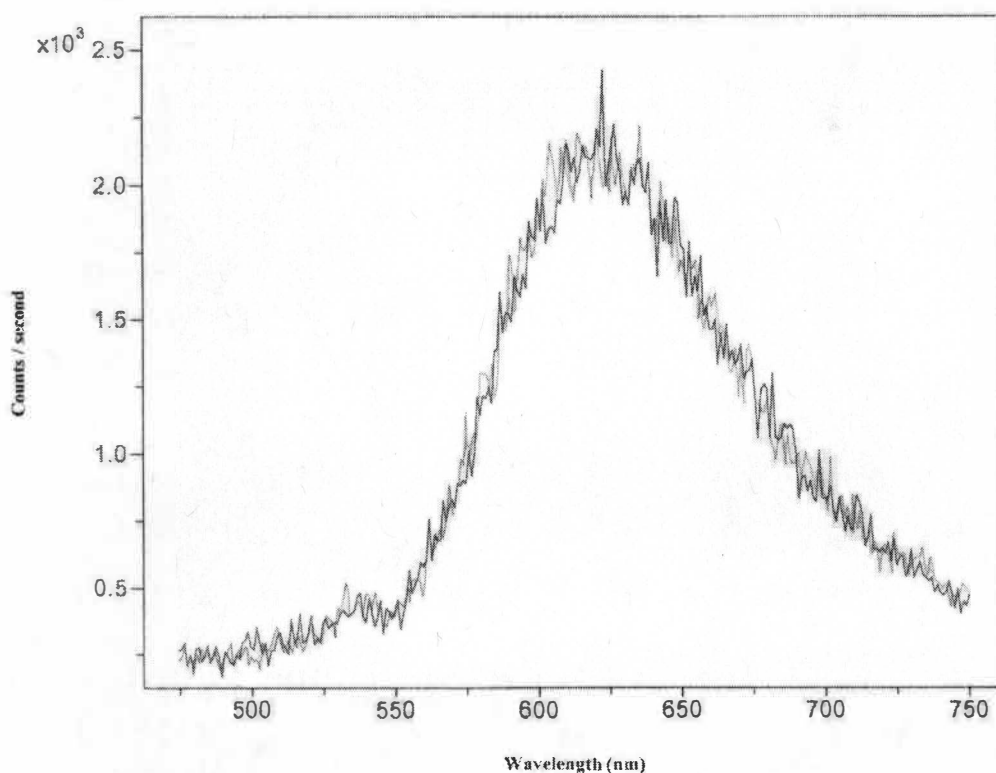


Figure 8. Emission Spectrum of Ruthenium Bipyridyl-4-Oxygen Sensor with and without Pb^{2+} in $\text{DMSO}/\text{H}_2\text{O}$ at 298K.

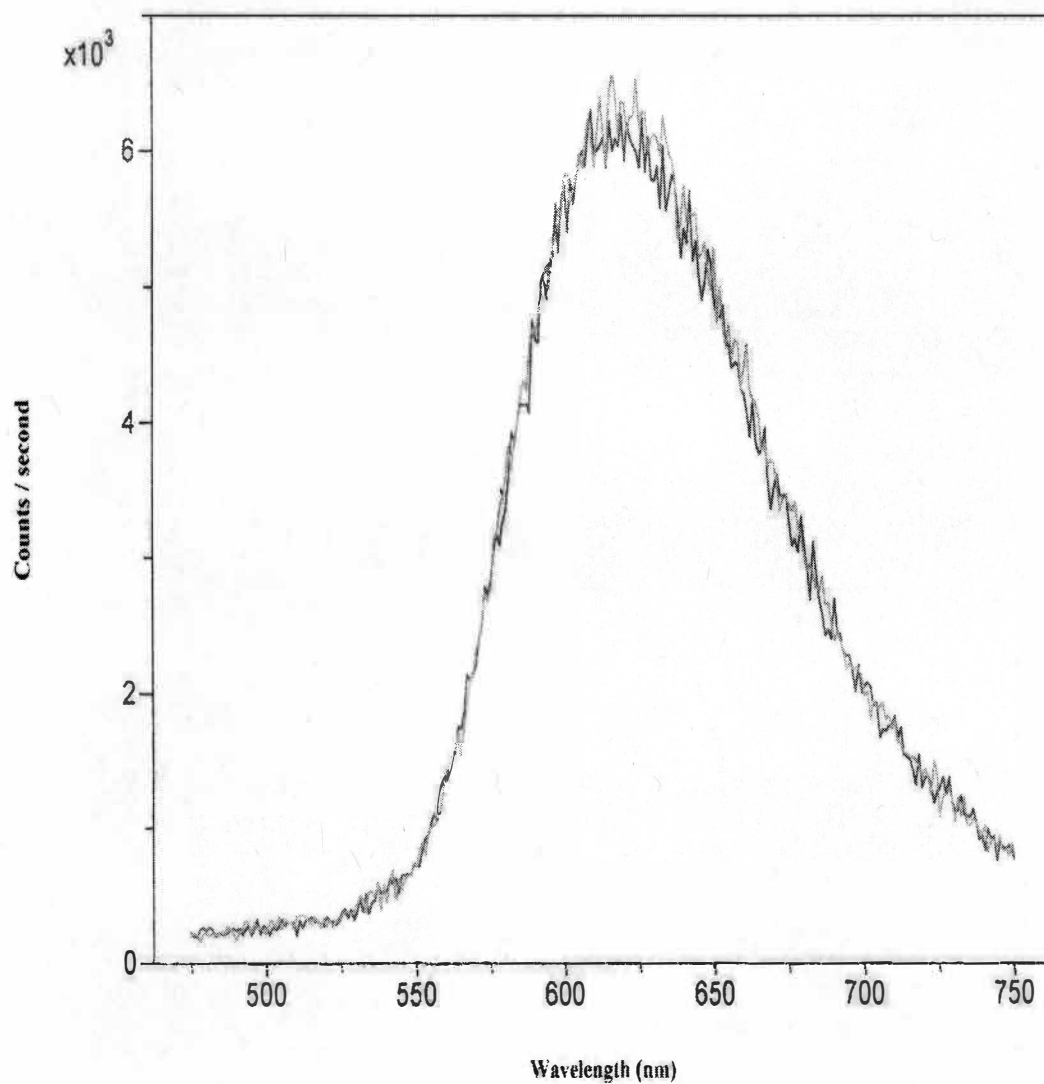


Figure 9. Emission Spectrum of Ruthenium Bipyridyl-5-Oxygen Sensor with and without Pb^{2+} in $\text{DMSO}/\text{H}_2\text{O}$ at 298K.

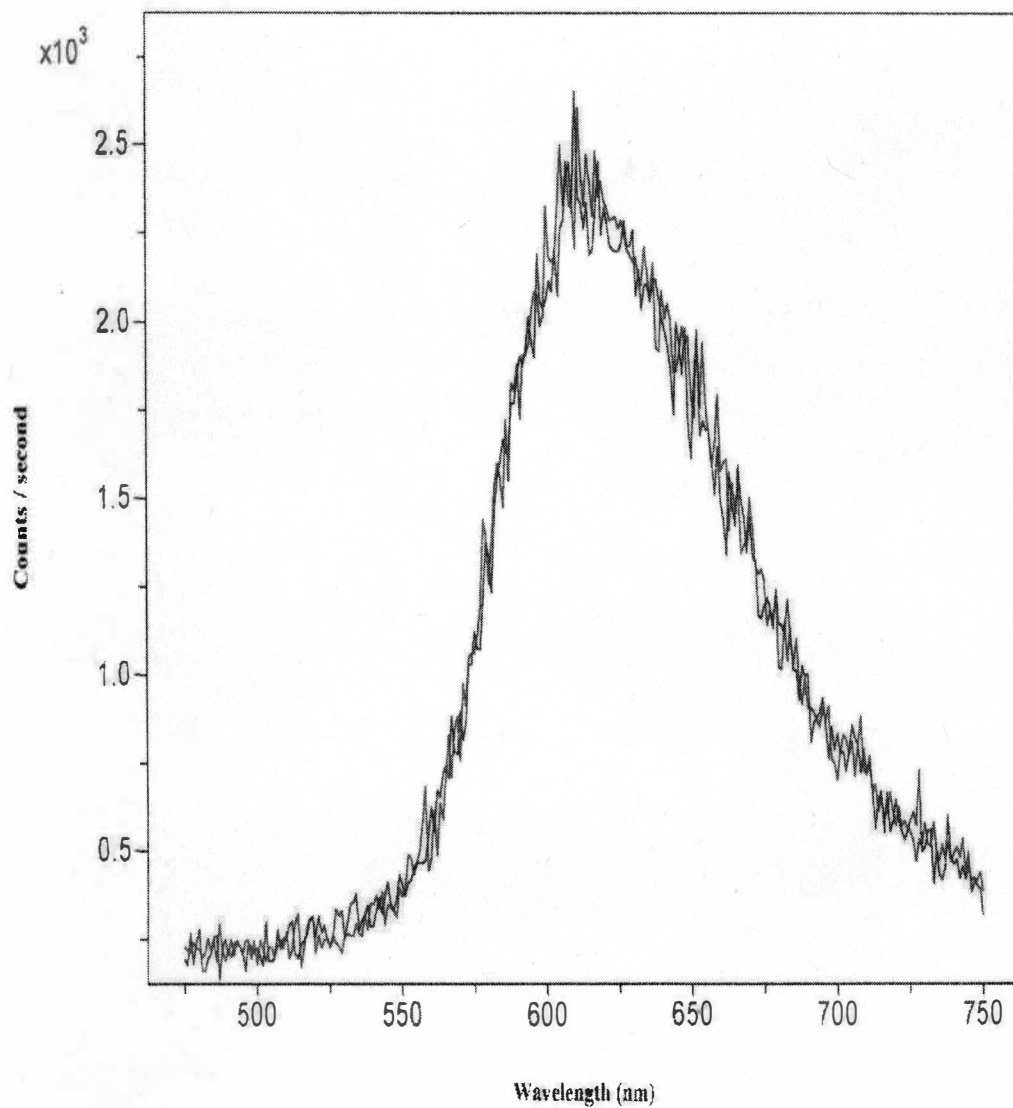


Figure 10. Emission Spectrum of Ruthenium Bipyridyl-6-Oxygen Sensor with and without Pb^{2+} in DMSO/ H_2O at 298K.

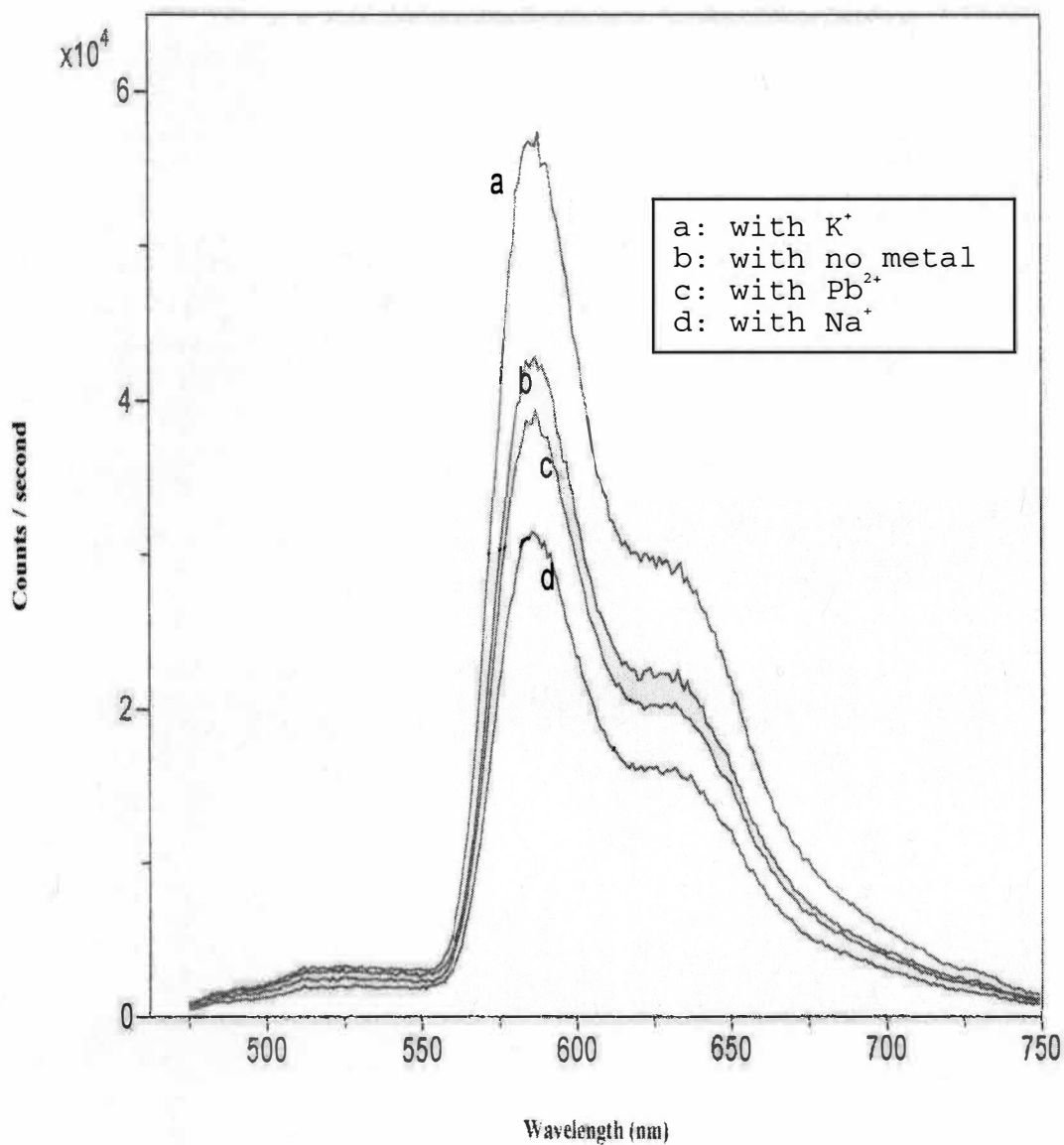


Figure 11. Emission Spectra of Ruthenium Bipyridyl-4-Oxygen Crown Sensor in the Presence of Different Metal Ions in DMSO/ H_2O at 77K.

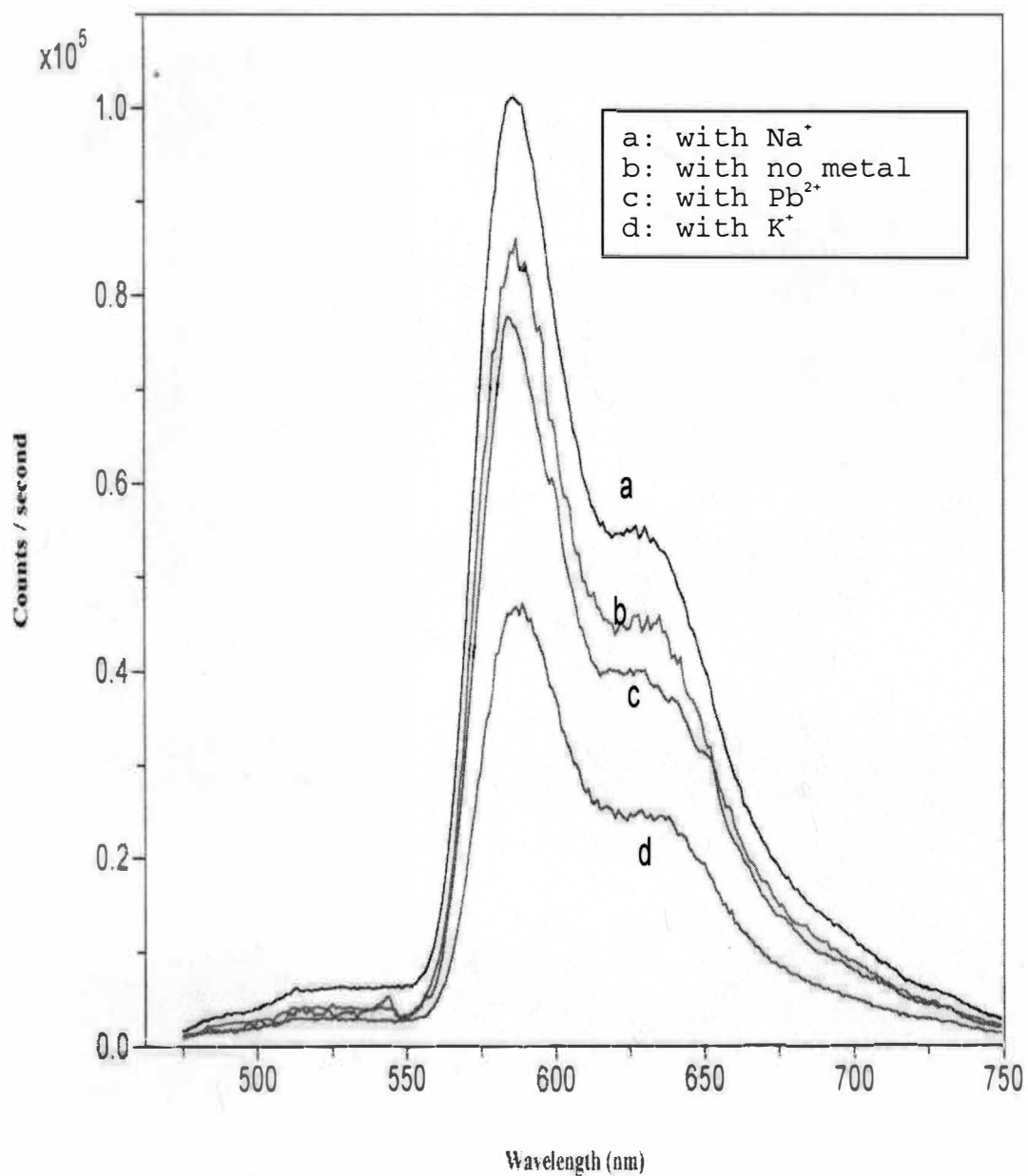


Figure 12. Emission Spectrum of Ruthenium Bipyridyl-5-Oxygen Crown Sensor in the Presence of Different Metal Ions in DMSO/ H_2O at 77K.

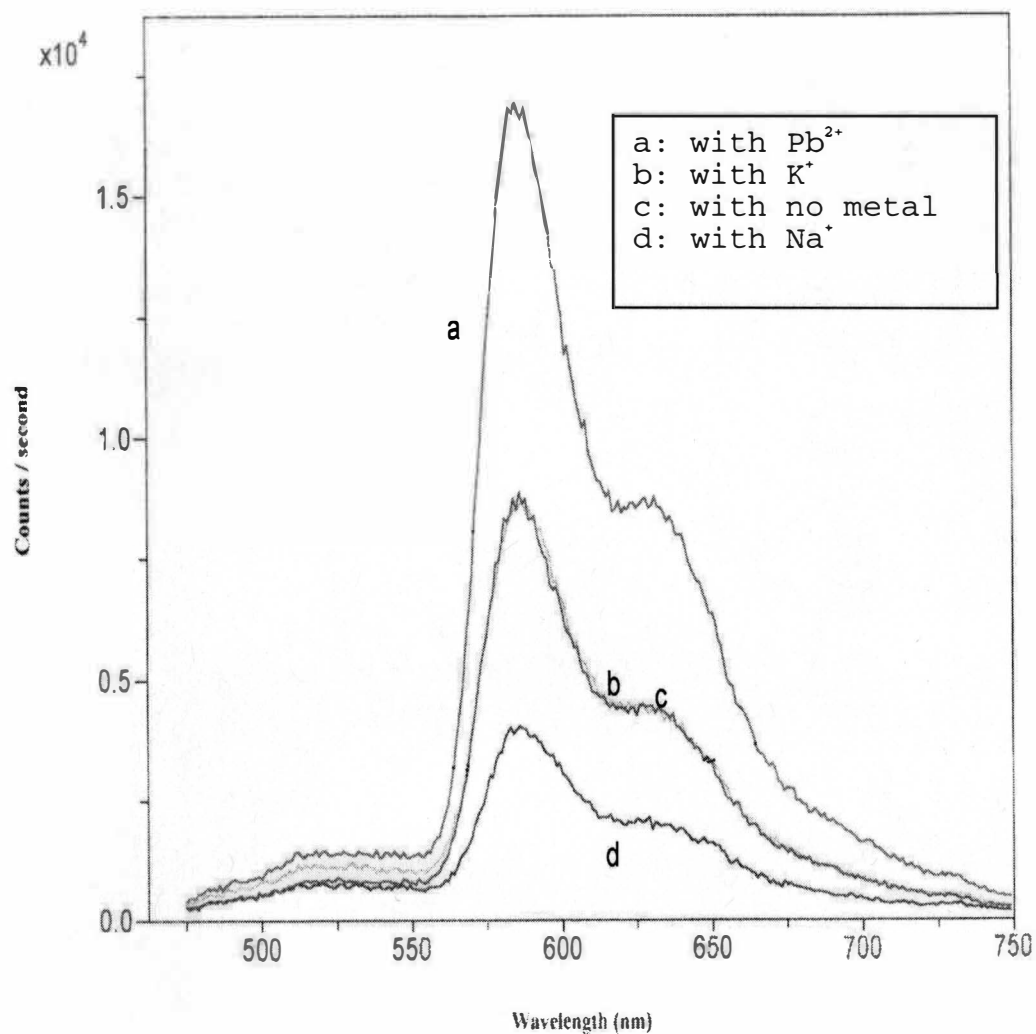


Figure 13. Emission Spectrum of Ruthenium Bipyridyl-6-Oxygen Crown Sensor in the Presence of Different Metal Ions in DMSO/ H_2O at 77K.

DISCUSSION

Several valuable results were obtained from this project. Solvents have important influences on the emission of the sensor systems. This is reasonable because of the non-identical ligand structures of three sensors. Usually sensors with identical ligands show less solvent dependence than do nonidentical ligand sensors and this is true in this study. The emission intensity increased when CH_2Cl_2 was used as solvent. The reason is that nonpolar solvent CH_2Cl_2 stabilizes the ground state of ruthenium sensor more than it does the excited state therefore the energy gap between ground and excited states becomes larger and results in strong emission intensity.

The free ligands exhibited significant changes in NMR spectra in the presence of IA metal ions but little change with Pb^{2+} , and Cd^{2+} ions. This result indicates that IA metal ions can coordinate into the crown ring but Pb^{2+} and Cd^{2+} could not. In contrast all ruthenium bipyridyl complexes essentially displayed no change in the presence of any metal ions and certainly no ion selectivity. This result indicates that metal ions could not effectively coordinate into the crown cavity of ruthenium sensor. The possible reasons are the followings. Chelating a

transition metal at the bipyridyl site forces the benzylic hydrogens toward each other and lowers the dihedral angle to near 0° . The consequence is that the benzylic oxygens are directed away from one another and they can not both be a part of the ether cavity. Space-filling molecular models indicate that, at best, only four of the oxygen atoms in the sensors may direct toward the center of the cavity³¹. Thus the ring size has little effect on the coordination of the metal ions. This results in the nonselectivity of the sensors with different ring sizes. The diminishment of the coordination ability is also proposed to relate to the conformation of the chelated system. Chelation at the bipyridyl function reduces the conformation availability of the crown ether and thereby limits the effective size of the cavity as well as the ability of guest complexation. As we know that the binding properties of crown ethers are sensitive to changes in conformations and 'effective size' of the host cavity.

The absorption and emission of the ruthenium sensor system demonstrated that the presence of the metal ions had little effect on the luminescent property of the sensor system. This may be attributed to two reasons. The main reason is that due to the allosteric effect the analyte ion could not effectively coordinate into the crown cavity thus little conformational and photophysical

property changes were expected. Another possible reason is that even analyte ion coordinated to the crown cavity, the result conformational change could not significantly change the luminescent behavior of the sensor. As noted earlier the excitation of the sensor transferred one electron to only one of the bpy ligand. The coordination of the crown ether would only be expected to change the luminescence of the sensor if the electron is transferred to the bpy ligand that was attached to the crown ether. So the attachment of a macrocyclic moiety to bpy ligand can only fine tune the luminescent behavior of $\text{Ru}(\text{bpy})_3^{2+}$ complex. The considerable luminescent intensity change of the sensor system at 77K may result from better coordination of the analyte ion into crown cavity and more opportunities that the electron was populated to the bpy ligand attached by crown ether. The detail reason is not well understood yet.

CONCLUSION

Supramolecules may provide suitable frameworks for the arrangement of several recognition sites in space, allowing the binding of several guest substrates.^{35, 36, 37, 38} Upon complexation these multisite receptors can act as models for studying different form of molecular behaviors such as cooperativity, allostery, and regulation. The design and synthesis of macrocyclic molecules possessing allosteric properties are of considerable current interest.^{39, 40}

Although the developed sensor systems were not ideal luminescent sensors systems in the sense of dramatic luminescence change and ion selectivity the research of this project is significant in several aspects. Former researchers almost all employed either ^1H NMR or ^{13}C NMR methods to examine the allosteric effects and usually in nonpolar solvent systems. In this project I used not only NMR but also absorption and emission methods to study the behavior of the sensor in the presence of cations. Aqueous and other polar solvents are mainly used in the study.

From the experimental results and the discussion it is convincible that allosteric effect imposes limitations on development of multiple binding site luminescent

sensors especially for those with short spacers and rigid structures. Similar results were obtained by P.D.Beer et al⁴¹. A prospective way to develop tunable sensor by the manipulation of conformation is to lower the allosteric effect and increase the flexibility of the whole system. Longer spacer and more macrocyclic moieties may be used to enhance the coordination and thus the luminescent recognition to the substrates.

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