

# Journal of the Arkansas Academy of Science

---

Volume 65

Article 6

---

2011

## Synthesis, Characterization, and Properties of Homometallic Dinuclear Ruthenium Complex Containing Chloro-Phenanthroline and Bipyridine

A. A. Bhuiyan

Arkansas Tech University, [abhuiyan@atu.edu](mailto:abhuiyan@atu.edu)

S. Kudo

Arkansas Tech University

Follow this and additional works at: <http://scholarworks.uark.edu/jaas>

 Part of the [Organic Chemistry Commons](#)

---

### Recommended Citation

Bhuiyan, A. A. and Kudo, S. (2011) "Synthesis, Characterization, and Properties of Homometallic Dinuclear Ruthenium Complex Containing Chloro-Phenanthroline and Bipyridine," *Journal of the Arkansas Academy of Science*: Vol. 65 , Article 6.  
Available at: <http://scholarworks.uark.edu/jaas/vol65/iss1/6>

This article is available for use under the Creative Commons license: Attribution-NoDerivatives 4.0 International (CC BY-ND 4.0). Users are able to read, download, copy, print, distribute, search, link to the full texts of these articles, or use them for any other lawful purpose, without asking prior permission from the publisher or the author.

This Article is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in Journal of the Arkansas Academy of Science by an authorized editor of ScholarWorks@UARK. For more information, please contact [scholar@uark.edu](mailto:scholar@uark.edu).

# Synthesis, Characterization, and Properties of Homometallic Dinuclear Ruthenium Complex Containing Chloro-Phenanthroline and Bipyridine

A.A. Bhuiyan<sup>1,2</sup> and S. Kudo<sup>1</sup>

<sup>1</sup>*Department of Physical Sciences, Arkansas Tech University, Russellville, AR 72801*

<sup>2</sup>Correspondence: abhuiyan@atu.edu

## Abstract

This paper deals with the synthesis and spectroscopic investigation of homometallic dinuclear ruthenium(II) complex containing chloro-phenanthroline and bipyridine ligands. This bimetallic ruthenium polypyridine complex may be useful for biological electron transfer studies. Heteroleptic ruthenium monomer complex Ru(bpy)<sub>2</sub>(Cl-phen) (where bpy = 2,2'-bipyridine and Cl-phen = 5-chloro-1,10-phenanthroline) was prepared in a two step procedure previously developed in our laboratory. This monomer complex was used to prepare the ruthenium dimer complex, (bpy)<sub>2</sub>Ru(phen-phen)Ru(bpy)<sub>2</sub>, by utilizing the Ni-catalyzed coupling reaction. Both the complexes were purified by column chromatography. The identity and the integrity of the complexes were confirmed by elemental analysis as well as mass spectroscopy. The calculated and the experimental values for the elemental analysis were in good agreement. The calculated and experimental molar masses of the dimer complex were also identical. UV/Vis absorption, emission spectroscopic method, and cyclic voltammetric method were used to investigate the properties of the dimer complex.

## Introduction

The study of the photophysical and photochemical properties of transition metal complexes is of great interest for a variety of fundamental and practical reasons (Kalyanasundaram 1987). In the past few years most of the attention in this field has been focused on the polypyridine complexes of ruthenium(II) as components of solar energy conversion schemes (Jures et al. 1988, Kalyanasundaram 1982). These complexes offer desirable redox potential, excited state properties, photophysical properties, and excited state lifetimes. Ruthenium polypyridine complexes have been investigated for use in artificial photosynthesis and many biological electron transfer processes. Electron transfer reactions play essential roles in numerous

important biological processes such as photosynthesis, mitochondrial respiration, and intermediary metabolism. It has been documented that ruthenium polypyridine complexes have potential use as efficient photoinitiators in electron transfer studies (Winkler et al. 1982). This has prompted us to investigate the properties of such complexes.

Despite the importance of biological electron transfer reactions to numerous processes, only few techniques are available to measure the actual rate of electron transfer between two redox partners in proteins. Many of these reactions are extremely fast with redox partners in nature (Sadoski et al. 2000). Accurate measurement of electron transfer rates of this magnitude is very difficult. Zaslavsky and coworkers (1998) introduced a new method to study biological electron transfer that utilizes a photoactive ruthenium(II) polypyridine complex which is covalently or electrostatically attached to a protein such as cytochrome c. Photoexcitation of Ru(II) to the metal-to-ligand charge-transfer state, Ru(II\*), a strong reductant, leads to rapid electron transfer to the ferric heme group in cytochrome c. Subsequent electron transfer from photoreduced heme c to redox center(s) in another protein can be measured on a time scale as fast as 50 nanoseconds (Pan et al. 1988).

It was found that the overall charge on the complex plays a critical role in protein binding and photoreduction or photooxidation efficiency. Ruthenium complexes with higher charge bind more tightly with the protein by electrostatic interaction. Dinuclear ruthenium complexes with an overall charge of +4 are capable of photoreducing protein with a 5-fold greater yield than mononuclear complexes (Sadoski et al. 2000). In this manuscript we report the efficient synthetic method, purification and characterization of (bpy)<sub>2</sub>Ru(phen-phen)Ru(bpy)<sub>2</sub> dimer complex. The dimer complex was synthesized from the monomer complex by the nickel-catalyzed direct coupling reaction shown in Figure 1. The phenanthroline moieties couple together producing about 75% yield of the dimer. The synthetic strategy

was based on the coupling reaction of 5-Cl-phen ligand developed by Toyota and coworkers (2005).

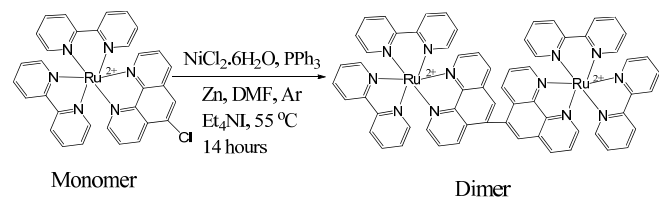


Figure 1: Synthetic scheme of ruthenium dimer,  $(\text{bpy})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{bpy})_2^{4+}$ , complex.

In this work, we report the efficient synthetic method for the preparation of the ruthenium dimer complex  $[(\text{bpy})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{bpy})_2]$  (where Cl-phen = 5-chloro-1,10 phenanthroline, phen = 1,10 phenanthroline and bpy = 2,2' bipyridine) from the monomer complex  $[\text{Ru}(\text{Cl-phen})(\text{bpy})_2(\text{PF}_6)_2]$  by the metal-catalyzed coupling reaction. The complexes were purified by repeated column chromatography. The identity and the integrity of the complexes were confirmed by elemental analysis as well as mass spectroscopy. UV/Vis absorption, emission spectroscopic method, and cyclic voltammetric method were used to investigate the properties of these complexes. Spectroscopic studies document that inherently favorable photophysical properties are not substantially altered by dimer formation.

## Materials and Methods

### Chemicals

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 5-chloro-1,10-phenanthroline (Cl-phen), 2,2'-bipyridine (bpy),  $\text{NH}_4\text{PF}_6$ , LiCl, N,N-dimethylformamide (DMF), tetraethyl ammonium iodide ( $\text{Et}_4\text{NI}$ ), Nickel(II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), triphenylphosphine ( $\text{PPh}_3$ ), alumina, and high-purity silica gel were purchased from the Aldrich Chemical Company. All the chemicals were used as purchased without further purification. All solvents used were reagent grade or better.

### Measurements

Elemental analysis was performed by Columbia Analytical Services, Tucson, AZ. Electrospray ionization mass-spectral (ESI-MS) measurements were performed with a Bruker Esquire LCMS by the Arkansas State Wide Mass Spectrometry Facility at the University of Arkansas, Fayetteville. The samples were dissolved in acetonitrile and were injected directly with nitrogen nebulizing gas at a flow rate of approximately  $50 \mu\text{L min}^{-1}$ . Electronic absorption spectra were

obtained with a Shimadzu model UV-2501 PC UV-Vis recording spectrophotometer using a 1-cm quartz cuvette. Spectra were obtained in the absorbance mode. The electronic absorption spectra of all the complexes were measured in acetonitrile solution. The electronic emission spectra were obtained with a PerkinElmer Model LS 55 luminescence spectrometer at  $450\text{nm } \lambda_{\text{exc}}$ . The emission spectra of the monomer and the dimer complexes were measured in acetonitrile solution at room temperature. Cyclic voltammetry was performed with an Epsilon BASi Instruments Electrochemical Analyzer. The working electrode was a 2-mm-diameter platinum-disk electrode, the auxiliary electrode was platinum wire and the reference electrode was a saturated calomel electrode from BASi Instruments. Cyclic voltammograms were recorded in 0.1 M  $(\text{Bu}_4\text{N})(\text{PF}_6)$  (tetrabutylammonium hexafluorophosphate) in  $\text{CH}_3\text{CN}$ .

### Preparation of Compounds

The monomer complex,  $\text{Ru}(\text{bpy})_2(\text{Cl-phen})(\text{PF}_6)_2$ , was prepared in a two step process by a method previously developed in our laboratory (Bhuiyan et al. 2010). The precursor complex,  $\text{cis-Ru}(\text{bpy})_2\text{Cl}_2$ , was prepared by following the literature method proposed by Sullivan et al. (1978). The identity of the prepared precursor complex was confirmed by absorption spectroscopy.  $\text{Ru}(\text{bpy})_2(\text{Cl-phen})(\text{PF}_6)_2$  was prepared from the reaction of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (0.5 mmol) and Cl-phen ligand (1.0 mmol) under reflux condition in aqueous solution. The solution was cooled to room temperature, filtered, and saturated aqueous  $\text{NH}_4\text{PF}_6$  was added to the filtrate to precipitate the product as a  $\text{PF}_6$  salt. The orange precipitate was collected by vacuum filtration and washed with cold water and diethyl ether. The product was purified by silica-gel column with  $\text{CH}_3\text{CN}$  as an eluent. The first band was collected and added dropwise to diethyl ether to reprecipitate. The typical yield was 65-75% (Bhuiyan et al. 2010). Elemental analysis calculated for  $\text{RuC}_{32}\text{H}_{23}\text{N}_6\text{ClPF}_6$ : C = 41.87%, H = 2.53%, N = 9.15%; experimentally found: C = 41.51%, H = 2.46%, N = 9.12%.

The dimer complex,  $(\text{bpy})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{bpy})_2^{4+}$ , was prepared from the precursor monomer complex,  $\text{Ru}(\text{bpy})_2(\text{Cl-phen})(\text{PF}_6)_2$ , by the metal-catalyzed direct coupling reaction, which is a modification of a method developed by Griffiths et al. (2000). Typically 0.076 g (0.321 mmol)  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 0.281g (1.07 mmol)  $\text{PPh}_3$  was taken in a dry three neck 100 mL round bottom flask. The flask and the sample was flushed with argon for few minutes and

## Synthesis, Characterization, and Properties of Homometallic Dinuclear Ruthenium Complex Containing Chloro-Phenanthroline and Bipyridine

then filled with argon. Then 10 mL dry DMF was added by syringe and the resulting blue solution was stirred and purged with argon for about 30 minutes. Zinc dust (0.021 g, 0.310 mmol) was added under strong flow of argon to the deep blue solution and then the reaction mixture was stirred under argon for 3 hours. During the first 30 minutes, the color of the reaction mixture changed from deep blue to green, then yellow, then orange, and finally reddish brown color. Ruthenium monomer complex (0.251 g, 0.534 mmol) and tetraethylammonium iodide (0.069 g, 0.534 mmol) were then added to the reaction mixture under a strong flow of argon. The resulting reaction mixture was stirred for 14 hours under argon at 55 °C. The resulting solution was then cooled to room temperature and filtered. The ruthenium dimer product was precipitated as a PF<sub>6</sub> salt by adding aqueous ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>). This mixture was refrigerated a few hours to enhance the precipitation, and the precipitate was collected by vacuum filtration. The precipitate was washed with cold water to remove excess NH<sub>4</sub>PF<sub>6</sub>, and was finally washed with diethyl ether. After the precipitate was dried in a desiccator, 0.245 g product was obtained. The crude compound was purified by column chromatography using a silica-gel stationary phase and acetonitrile as an eluent. The first band was collected and added dropwise to diethyl ether to reprecipitate and 0.187 g (75% yield) product was obtained. Elemental analysis calculated for Ru<sub>2</sub>C<sub>64</sub>H<sub>46</sub>N<sub>12</sub>P<sub>4</sub>F<sub>24</sub>: C = 43.55%, H = 2.63%, N = 9.52%; experimentally found: C = 41.86%, H = 2.56%, N = 9.00%.

### Results and Discussion

The monomer complex, Ru(bpy)<sub>2</sub>(Cl-phen)(PF<sub>6</sub>)<sub>2</sub>, was prepared by following the method previously developed in our laboratory (Bhuiyan et al. 2010). The heteroleptic monomer complex was prepared by a two-step process. In the first step, the precursor complex Ru(bpy)<sub>2</sub>Cl<sub>2</sub> was prepared according to published methods (Sullivan et al. 1978). Sufficiently pure precursor complex was obtained and no further purification was necessary. The second step involved the reaction of the previously prepared precursor complex and additional Cl-phen ligand. This type of procedure is common for mixed-ligand complexes (Bhuiyan 2008, Bhuiyan et al. 2008, Bhuiyan and Kincaid 1999, Bhuiyan et al. 2009). Thin-layer chromatography indicated that the monomer compound was slightly contaminated. We used the most common

purification method of column chromatography on silica with acetonitrile as an eluent for the complex (Bhuiyan et al. 2010).

The homometallic dinuclear ruthenium dimer complex, (bpy)<sub>2</sub>Ru(phen-phen)Ru(bpy)<sub>2</sub>, was formed by the nickel-catalyzed direct coupling of the monomer complex with a very satisfactory 75% yield. This synthetic strategy was based on the pioneering work of Toyota and coworkers (2005) on the coupling of free ligands. The yield was very low and it was very difficult to purify the coupled ligand. So we attempted to apply the nickel coupling reaction directly to the monomer complex, which is similar to the procedure mentioned in the literature for other complexes (Griffiths et al. 2000, Johansson et al. 2000). We would like to mention here that the requirement to maintain an inert atmosphere during the synthesis is very critical. This nickel catalyzed coupling reaction is very sensitive to traces of oxygen. The mass spectrum indicated that the product was contaminated with trace amount of monomer complex, which we then removed by column chromatography.

The calculated and experimental results of the elemental analysis of the monomer and the dimer complexes are shown in the Material and Method section. The experimental results are in close agreement with the calculated results for both the complexes, which confirms the identity of the prepared complexes.

The mass spectrum of the ruthenium dimer complex, (bpy)<sub>2</sub>Ru(phen-phen)Ru(bpy)<sub>2</sub>, is shown in Figure 2. The calculated molar mass of the dimer complex is 1185.27 g/mol [(bpy)<sub>2</sub>Ru(phen-phen)Ru(bpy)<sub>2</sub><sup>4+</sup>].

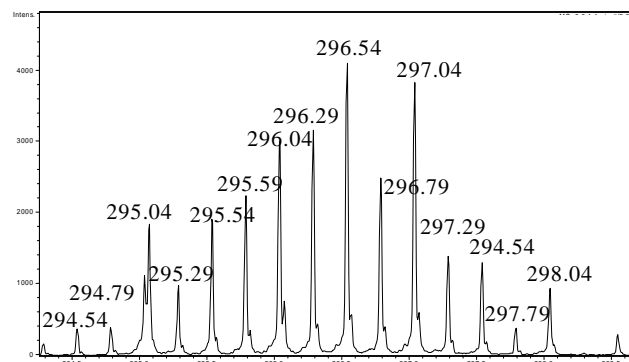


Figure 2. The electrospray mass spectrum of the prepared ruthenium dimer complex, showing the major fragment cluster.

The electrospray mass spectrometry of the complexes showed a consistent fragmentation pattern

(Figure 2). The experimental isotopic patterns are consistent with the calculated isotopic patterns. The mass spectrum showed that the molecular-ion peaks appear at  $m/z$  (mass/charge) = 296.29. From the isotopic patterns, it was confirmed that the molecular ion has an overall charge of 4+, so the experimental molar mass of the dimer complex is 1185.16 ( $4 \times 296.29$ ) g/mol. The experimental molar mass is in very good agreement with the calculated molar mass, which confirms the identity and the integrity of the prepared dimer complex.

Electronic absorption spectra of the prepared dimer and the monomer complexes are shown in Figure 3. The solid-line spectrum is for the dimer complex (trace A) and the dashed line is for the monomer complex (trace B). The absorption spectrum of the dimer complex is very similar to the monomer complex, which is also similar to the methyl-substituted complexes previously reported by Bhuiyan et al. (2009). Both the spectra consist of a series of absorption bands in the UV and visible regions. A very strong transition at 268 nm is assigned to a spin-allowed ligand-centered  $\pi-\pi^*$  transition of the Cl-phen ligand, and a 284 nm peak is assigned to a  $\pi-\pi^*$  transition of bpy ligand (Kalyanasundaram and Nazeeruddin 1990). In the dimer complex, the relative intensity of the 284 nm band increases in comparison with the 268 nm band. The broad, relatively intense visible band at 450 nm is assigned to a metal-to-ligand charge-transfer (MLCT) transition by comparing with other ruthenium(II) polypyridine complexes (Denti et al. 1990). The higher-energy shoulder observed is assigned to a second MLCT transition. It was observed that dimer formation did not affect the absorption pattern.

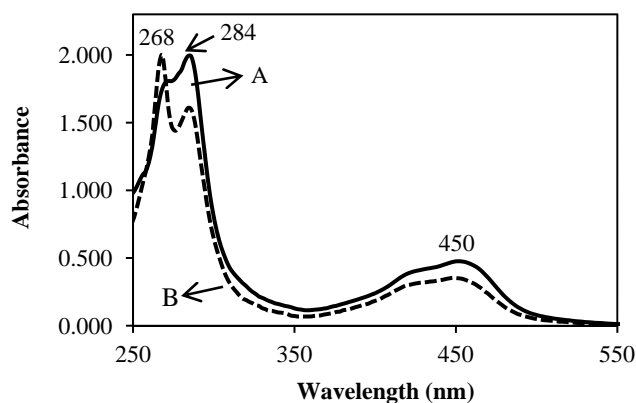


Figure 3. Electronic absorption spectra of the prepared complexes in acetonitrile: dimer (trace A) and monomer (trace B).

The room-temperature emission spectra of the dimer and the monomer complexes are shown in Figure 4. The excitation wavelength was determined by scanning the excitation spectra at a fixed emission wavelength. The excitation wavelength is 450 nm for both the complexes. The solid line is for the dimer complex (trace A) and the dashed line is for the monomer complex (trace B). The electronic emission spectra of the complexes exhibit strong emission bands at 608 nm for the dimer and 613 nm for the monomer. Both complexes exhibit a single emission band, which confirms the purity of the prepared complexes.

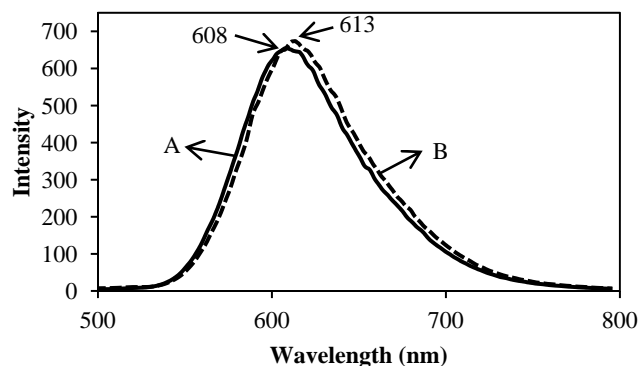


Figure 4. Electronic emission spectra of the prepared complexes in acetonitrile: dimer (trace A) and monomer (trace B).

The emission spectrum of the dimer complex is similar to the monomer complex which is also very similar to methyl-substituted complexes previously reported by Bhuiyan et al. (2009). As for other polypyridine complexes of Ru(II), these luminescence bands have been assigned as the phosphorescent process  $^3\text{MLCT}$  (triplet metal-to-ligand charge transfer)  $\rightarrow$   $^1\text{GS}$  (singlet ground state) (Lytle and Hercules 1969, Bhuiyan and Kincaid 2001). The emission band for the monomer compound is slightly red shifted from that observed for the dimer compound (613 nm vs 608 nm). This observation is consistent with the previously reported spectra of similar ruthenium(II) polypyridine complexes (Griffiths et al. 2000, Johansson et al. 2000).

Cyclic voltammograms of the prepared monomer and dimer complexes are shown in Figure 5. The solid line is for the monomer complex and the dashed line is for the dimer complex. Both the complexes exhibit a single reversible electrochemical wave over the range examined. For each of the complexes, the potential corresponds to oxidation of ruthenium(II) to ruthenium(III). The potentials are  $E_{1/2} = +1.32$  V for the monomer complex and  $E_{1/2} = +1.36$  V for the dimer

## Synthesis, Characterization, and Properties of Homometallic Dinuclear Ruthenium Complex Containing Chloro-Phenanthroline and Bipyridine

complex. The single wave for each complex confirms the purity of the prepared complexes. The formation of dimer shifts the wave to slightly higher potential. This phenomenon indicates that the dimer formation did not change the energy levels significantly (Rillema et al. 1987).

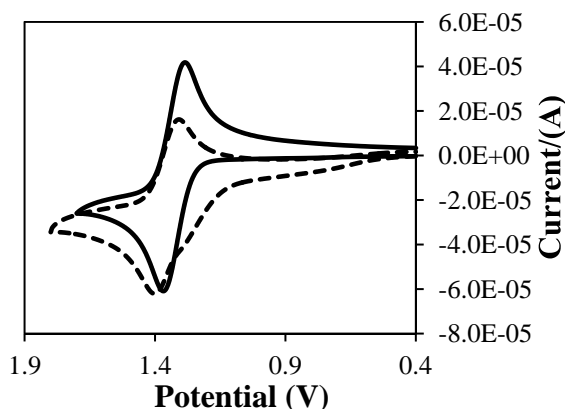


Figure 5. Cyclic voltammograms of the prepared complexes: solid line is for the monomer and the dashed line is for the dimer.

### Conclusions

The present report summarizes efficient synthetic procedures to construct a homometallic dinuclear ruthenium dimer complex,  $(bpy)_2Ru(\text{phen-phen})Ru(bpy)_2$ , containing chloro-phenanthroline and bipyridine. The dimer complex is formed by the nickel-catalyzed direct coupling of the monomer complex with a very good yield (75%). Elemental analysis and mass spectroscopy confirm the identity and structural integrity of the prepared monomer and the dimer complexes. Absorption, emission, and cyclic voltammetric results of the dimer complex were very comparable with the monomer complex. It was observed that the inherently favorable photophysical properties are not substantially altered by dimer formation. This high charge dimer complex can be used for metallo-protein electron transfer studies.

### Acknowledgments

The authors would like to thank the NASA-funded Arkansas Space Grant Consortium, Arkansas Tech University Undergraduate Research, and Arkansas Center for Energy, Natural Resources and Environmental Studies (ACENRES) for their financial support. We thank Dr. B. Durham of the University of

Arkansas and the Arkansas State-Wide Mass Spectrometry Facility for providing the mass spectra.

### Literature Cited

- Bhuiyan AA.** 2008. Resonance Raman spectroscopy for the investigation of heteroleptic ruthenium polypyridine complexes. *Journal of the Arkansas Academy of Science* 62:138-41.
- Bhuiyan AA, R Dossey, TJ Anderson, F Millett and B Durham.** 2008. Synthesis and characterization of ruthenium(II) phenanthroline complexes containing quaternary amine substituents. *Journal of Coordination Chemistry* 61:2009-16.
- Bhuiyan AA and JR Kincaid.** 1999. Synthesis and spectroscopic characterization of a zeolite-entrapped  $Ru(bpy)_2(dpp)^{2+}$  complex. *Inorganic Chemistry* 38:4759-64.
- Bhuiyan AA and JR Kincaid.** 2001. Zeolite-based organized molecular assemblies. Photophysical characterization and documentation of donor oxidation upon photosensitized charge separation. *Inorganic Chemistry* 40:4464-71.
- Bhuiyan AA, S Kudo and J Bartlett.** 2010. Synthesis and characterization of ruthenium complexes containing chlorophenanthroline and bipyridine. *Journal of the Arkansas Academy of Science* 64:33-40.
- Bhuiyan AA, S Kudo, C Wade and RF Davis.** 2009. Synthesis and characterization of homoleptic and heteroleptic ruthenium polypyridine complexes. *Journal of the Arkansas Academy of Science* 63:44-9.
- Denti G, S Campagna, L Sabatino, S Serroni, M Ciano and V Balzani.** 1990. Luminescent and redox-reactive building blocks for the design of photochemical molecular devices: mono-, di-, tri-, and tetranuclear ruthenium(II) polypyridine complexes. *Inorganic Chemistry* 29:4750-58.
- Griffiths PM, F Loiseau, F Puntoriero, S Serroni and S Campagna.** 2000. New luminescent and redox active homometallic dinuclear iridium(III), ruthenium (II) and osmium(II) complexes prepared by metal-catalysed coupling reactions. *Chemical Communication* 819-820.
- Johansson KO, JA Lotoski, CC Tong, and GS Hanan.** 2000. Toward high nuclearity ruthenium complexes: creating new binding sites in metal complexes. *Chemical Communication* 2297-2298.

- Juris A, V Balzani, F Barigelletti, S Campagna, P Belzer and AV Zelewsky.** 1988. Ru(II) polypyridine complexes: photophysics, photochemistry, electrochemistry, and chemiluminescence. *Coordination Chemistry Reviews* 84:85-277.
- Kalyanasundaram K.** 1987. *Photochemistry in Microheterogeneous Systems.* New York: Academic Press. 388 p.
- Kalyanasundaram K.** 1982. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogs. *Coordination Chemistry Reviews.* 46:219-44.
- Kalyanasundaram K and MK Nazeeruddin.** 1990. Photophysics and photoredox reactions of ligand-bridged binuclear polypyridyl complexes of ruthenium(II) and of their monomeric analogues. *Inorganic Chemistry* 29:1888-97.
- Lytle FE and DM Hercules.** 1969. The luminescence of tris(2,2'-bipyridine)ruthenium(II) dichloride. *Journal of the American Chemical Society* 91:253-7.
- Pan LP, B Durham, J Wolinska and F Millett.** 1988. Preparation and characterization of singly labeled ruthenium polypyridine cytochrome c derivatives. *Biochemistry* 27:7180-4.
- Rillema DP, DG Taghdiri, DS Jones, CD Keller, LA Worl, TJ Meyer and HA Levy.** 1987. Structure and redox and photophysical properties of a series of ruthenium heterocycles based on the ligand 2,3-bis(2-pyridyl)quinoxaline. *Inorganic Chemistry* 26:578-85.
- Sadoski RC, G Engstrom, H Tian, L Zhang, CA Yu, L Yu, B Durham and F Millett.** 2000. Use of a photoactivated ruthenium dimer complex to measure electron transfer between the rieske iron-sulfur protein and cytochrome c<sub>1</sub> in the cytochrome bc<sub>1</sub> complex. *Biochemistry* 39:4231-6.
- Sullivan BP, DJ Salmon and TJ Meyer.** 1978. Mixed phosphine 2,2'-bipyridine complexes of ruthenium. *Inorganic Chemistry* 17:3334-41.
- Toyota S, A Goto, K Kaneko and T Umetani.** 2005. Synthesis, spectroscopic properties, and Cu(I) complexes of all possible symmetric Bi-1,10-phenanthrolines. *Heterocycles* 65:551-562.
- Winkler JR, DG Nocera, KM Yocom, E Bordignon and HB Gray.** 1982. Electron transfer kinetics of Ru(NH<sub>3</sub>)<sub>5</sub>(III)(His-33)-Ferricytochrome c. *Journal of the American Chemical Society* 104:5798-800.
- Zaslavsky D, RC Sadoski, K Wang, B Durham, RB Gennis and F Millett.** 1998. Single electron reduction of cytochrome c oxidase compound F: resolution of partial steps by transient spectroscopy. *Biochemistry* 37:14910-6.