

Synthesis and Photophysical Analysis of of Ru(II) polypyridyl complexes

For a number of decades the tris-homoleptic polypyridyl complex $[\text{Ru}(\text{bpy})_3]^{2+}$ (where bpy = 2,2'-bipyridyl) has been extensively studied due to its facile redox chemistry and its unique photophysical properties: large, $^1\text{MLCT}$ absorption, molar extinction coefficient (λ_{max} MLCT in MeOH = 453 nm, $\epsilon = 14,700 \text{ M}^{-1} \text{ cm}^{-1}$); rapid singlet-triplet intersystem crossing and long-lived $^3\text{MLCT}$ excited state (890 ns); reasonable phosphorescent quantum yield ($\Phi_{\text{Ph}} = 0.06$). These unique properties have led to its importance in the study and advancement of many fundamental and applied chemical systems, e.g. Marcus theory of electron-transfer, UV-vis-NIR spectro-electrochemistry and electron spin resonance (ESR), electroluminescence and LEDs, solar-to-electric energy conversion and photocatalysis. In this experiment you will be introduced to the unique properties of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex – the archetypical ruthenium(II) polypyridyl reference compound. Building upon this knowledge you will then prepare the $[\text{Ru}(\text{bpy})_2(\text{dcbpy})](\text{PF}_6)_2$ complex for later application in a dye-sensitized solar cell (DSSC) device. Introduced over 20 years ago by Michael Grätzel and co-workers,¹ DSSC technology has stimulated vast interest from the academic, federal and private sectors. Such is the demand for clean, renewable sources of energy that large scale fabrication of DSSC devices has now been realized.²⁻⁵ Commercialization has been made possible by advances in engineering and cell stability, and is driven by the major advantages of DSSC devices over the current state-of-the-art silicon or gallium based devices such as their lower cost of production, compatibility and substrate flexibility, aesthetic color tuning and performance under low-Sun conditions (1 Sun = 1000 W m^{-2}).

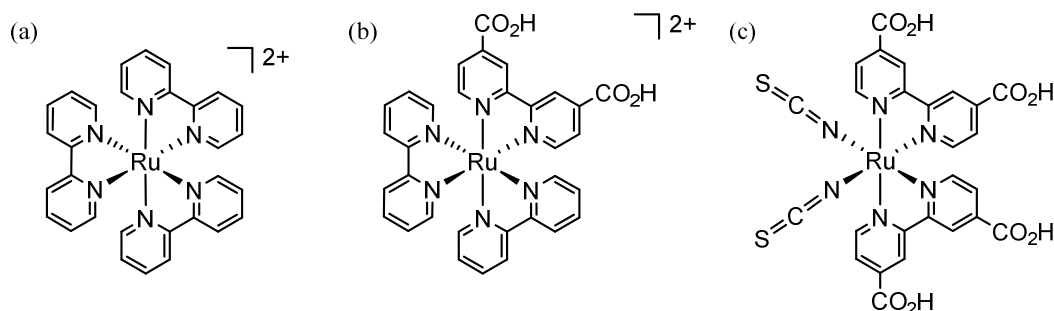
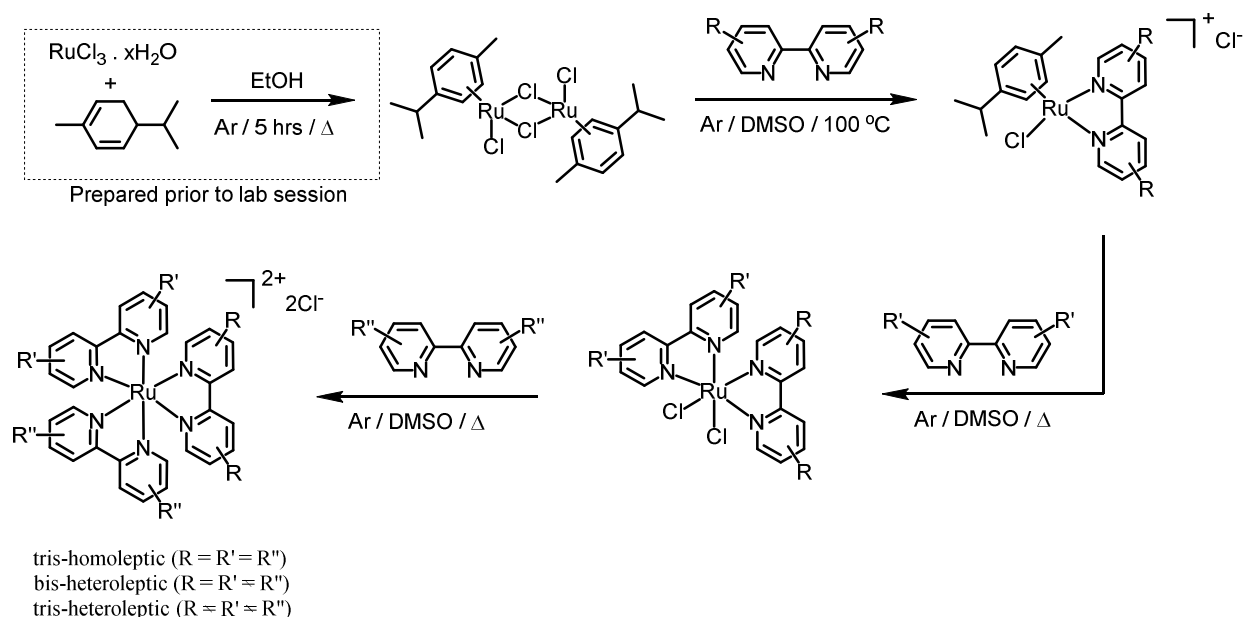


Figure 1. Structures of (a) $[\text{Ru}(\text{bpy})_3]^{2+}$ and (b) $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ (c) N3 dyes

The $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ dye is similar in most respects to its tris-homoleptic $[\text{Ru}(\text{bpy})_3]^{2+}$ analogue apart from having functionalized one bpy ligand with *para* carboxylic acid substituents. The presence of these carboxy groups impart a minor perturbation of its electronic structure due to the lower lying π^* orbital of the dcbpy ligand relative to the unsubstituted bpy ligands. This is observed in a bathochromically shifted visible absorption spectrum and an anodic shift in its first reduction potential by cyclic voltammetry. The principal purpose of functionalizing the complex with carboxy groups here, however, is for covalent attachment to the surface of a TiO_2

nanoparticle based mesoporous electrode towards fabrication of a solar cell device. It should be stated that the N3 dye is a far superior chromophore for application in DSSCs due to its reduced symmetry relative to the reference $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. This imparts additional bands in its electronic absorption spectrum improving its light-harvesting properties. These transitions occur further to the red of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the visible region due to the electron rich nature of the two anionic isothiocyanate ligands which destabilizes the HOMO orbital reducing the band-gap of the molecule. In a later DSSC experiment we will also discuss the electrochemical implications of this major electronic difference when comparing dye molecules.

Traditionally, preparation of ruthenium(II) polypyridyl complexes has involved the direct reaction of ruthenium(III) chloride with a stoichiometric amount of the appropriate ligand and the excess alcoholic solvent playing a dual role as the one-electron reductant (alternatively sodium phosphinate may be used as a reductant in aqueous solvent). A major progression in ruthenium chemistry was introduction of the dichloro(*p*-cymene)ruthenium(II) dimer complex $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}]_2(\mu\text{-Cl}_2)$ as a synthetic intermediate (Scheme 1). This procedure allows stepwise introduction of ligands towards the preparation of bis- and tris-heteroleptic polypyridyl systems. Such synthetic diversity has allowed chemists to gain access to a wider variety of ruthenium polypyridyl systems while fine tuning their optical and electrochemical properties and optimizing performance and durability towards a variety of applications. We will take advantage of this procedure for an efficient and convenient one-pot synthesis of $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$.



Scheme 1. One pot stepwise synthesis of ruthenium(II) polypyridyl complexes using the dichloro(*p*-cymene)ruthenium(II) dimer precursor – applicable to mono-, bis- or tris-heteroleptic systems.

Procedure

1. Synthesis of $[\text{Ru}(\text{bpy})_2(\text{dcbpy})][\text{PF}_6]$

Take a 5-ml microscale reflux vial charged with 64 mg of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}]_2(\mu\text{-Cl}_2)$ and 49 mg of 4,4'-dicarboxy-2,2'-bipyridine (provided by the instructor). Add 3 ml of *N,N'*-dimethylformamide (DMF) solvent and a magnetic stirrer. Assemble the reflux apparatus with a rubber septum sealed condenser. Stir vigorously and degas the solution by attaching a vacuum line via rubber tubing-syringe-needle assembly through the septum. After 2-3 min of degassing swiftly replace the vacuum line with a nitrogen filled balloon-syringe-needle assembly. Repeat this degas- N_2 purge process three times finishing with the N_2 balloon-syringe-needle assembly still in place in the septum. Confident that the reaction mixture is now under an inert atmosphere (with dioxygen removed and the N_2 balloon attached for pressure equilibration) heat at $100\text{ }^\circ\text{C}$ for 30 minutes duration (your instructor will provide temperature probe to monitor reaction temperature). Making note of any color change, add 2 equivalents of 2,2'-bipyridyl and proceed to reflux for at least 1 hr duration. Allow the reaction to cool reaching room temperature. Transfer the reaction mixture to a 25 ml beaker (rinse with < 1 ml deionized water if necessary). Add 5 ml of 0.1 M aqueous H_2PF_6 to precipitate the solid product as a dark solid. Filter with a Hirsch funnel in vacuo and allow the solid to air dry for at least 10 min. Wash with diethyl ether and transfer to a pre-weighed vial to record the product yield.

[Note: during the initial 30 min heating step in part 1 conduct part 2 of the experiment but observe the reaction intermittently for any characteristic color changes].

2. UV-vis absorption and phosphorescence emission spectrum of $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$

Your instructor will aid in the preparation of mesoporous thin-films using TiO_2 (semiconductor) and ZrO_2 (insulator). Following completion of step 1, prepare *ca.* 5 ml of a 0.5 mM $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]\text{PF}_6$ in methanol. Substrates will be prepared consisting of

Cover glass slides : mesoporous nanoparticle film : dye-sensitizer

UV-vis and fluorescence emission spectra will be recorded of solutions and thin films prepared.

Laboratory Report

1. Give experimental details of all synthetic procedures and qualitative analysis conducted during the laboratory session. Note any deviations from the recommended procedure, report percentage yields and give details of any instrumentation (including instrumental parameters) used throughout.
2. Describe the difference between fluorescence and phosphorescence emission?
3. Overlay UV-vis absorption and emission spectra of $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$. Correct the spectral baselines and then normalize both the MLCT absorption maximum and the phosphorescence emission maximum. Using the normalized, overlaid plot calculate the E_{0-0} of $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ and report the Stoke's shift. Please comment on the importance of E_{0-0} Stoke's shift making reference to the Jablonski diagram discussed in lecture.
4. How can you describe a photoexcited state of a molecule as both a reductant and an oxidant? Give example from the literature where $[\text{Ru}(\text{bpy})_3]^{2+}$ is used as an oxidant and as a reductant (one example of each is sufficient).
5. What is the purpose of studying the absorption and emission properties of the dye following attachment to both TiO_2 and ZrO_2 nanoparticles? Compare observations for the dye when attached to TiO_2 and ZrO_2 and explain any differences observed.

References

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2. www.dyesol.com.
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