

Microscale preparation of the N3 dye

cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) and photophysical characterization 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 (high visible absorption molar extinction coefficients; rapid singlet-triplet intersystem crossing; long-lived $^3\text{MLCT}$ excited state; relatively high phosphorescent quantum yield). These unique properties have led to its importance in the study of fundamental electron-transfer (e.g. Marcus theory), 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 *pseudooctahedral* $[\text{Ru}(\text{bpy})_3]^{2+}$ complex via a *chemiluminescence* experiment. Building upon this knowledge you will then prepare the $\text{Ru}(4,4'-dicarboxy-2,2'-bipyridyl) $_2(\text{NCS})_2$ complex (commonly known as the “N3 dye”) 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 DSC devices has now been realized.² 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).$

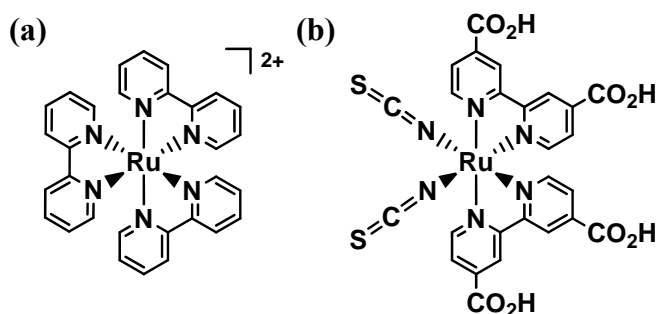
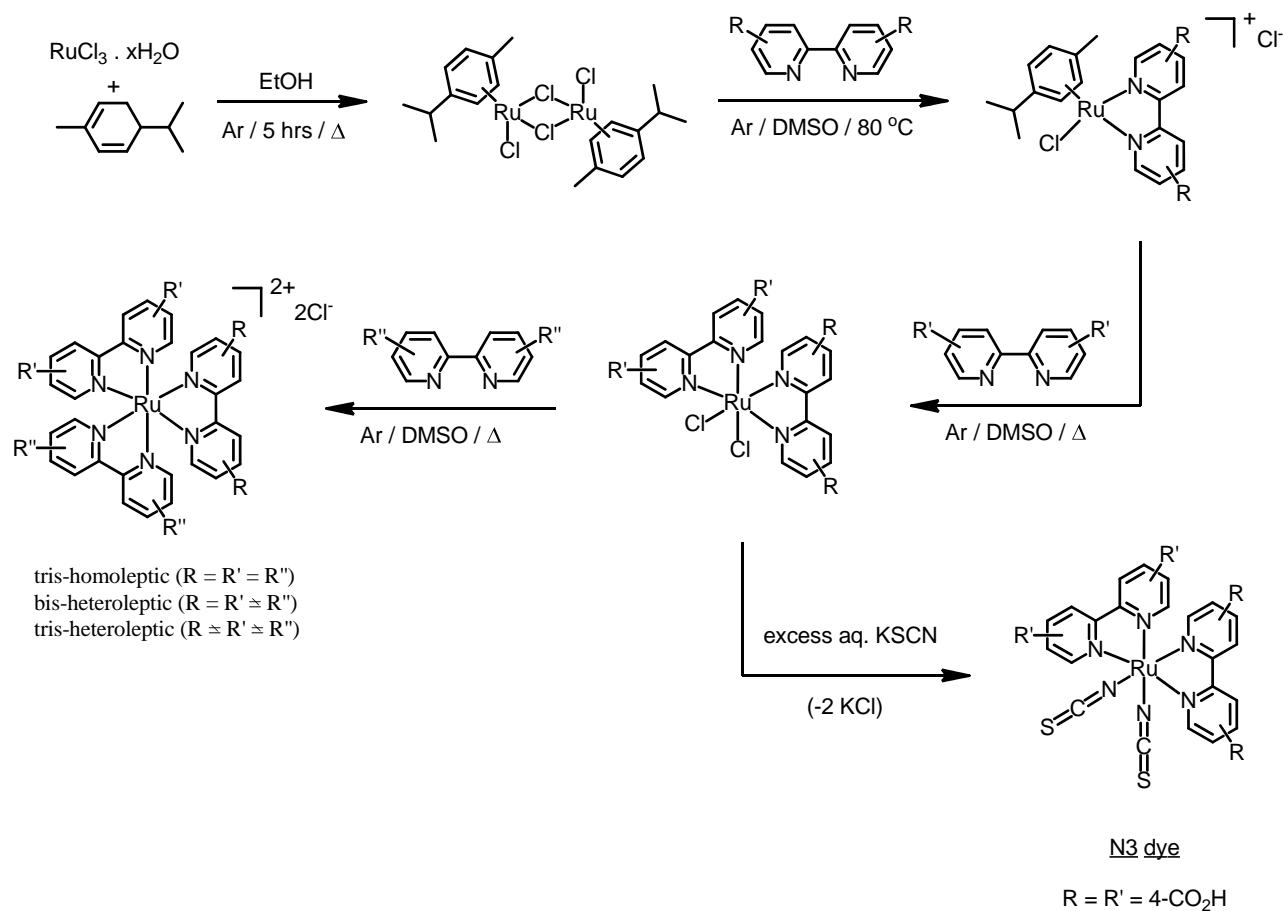


Figure 1. Structures of (a) $[\text{Ru}(\text{bpy})_3]^{2+}$ and (b) N3.

The N3 dye is a far superior chromophore 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, i.e. *bathochromically shifted*, due to the electron rich nature of the two monodentate isothiocyanate ligands (NCS^-) which destabilize 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 between both dye molecules (note: carboxylic acid groups are essential for anchoring the N3 dye at the semiconducting metal oxide nanoparticle electrode surface via monolayer self-assembly in the DSSC device).

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 the N3 dye.



Scheme 1. Stepwise synthesis of a tris-heteroleptic ruthenium(II) polypyridyl complex using the dichloro(*p*-cymene)ruthenium(II) dimer precursor.

Procedure

1. Synthesis of Ru(4,4'-dicarboxy-2,2'-bipyridyl)₂(NCS)₂

Take a 5-ml microscale reflux vial charged with 64 mg of [Ru(η^6 -*p*-cymene)Cl]₂(μ -Cl₂) and 98 mg of 4,4'-dicarboxy-2,2'-bipyridine (provided by the instructor). Add 2 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-N₂ purge process three times finishing with the N₂ 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 N₂ balloon attached for pressure equilibration) proceed to reflux for 1 hr duration. After 1 hour, inject 0.2 ml of 10 M aqueous potassium isothiocyanate solution via syringe through the rubber septum. Maintain reflux for a further 30 min. and then 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 hydrochloric acid 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. Check sample purity by recording the UV-vis spectrum in methanol: λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 314 (27,900); 393 (13,000); 469 (9,300); 539 (11,400).

[Note: during the one hour reflux time conduct part 2 of the experiment but observe the reflux intermittently for any characteristic color changes].

2. Chemiluminescence of [Ru(bpy)₃]Cl₂ · 3H₂O

Weigh out approximately 5 mg of [Ru(bpy)₃]Cl₂·6H₂O into a 10 mL reaction tube. Add 1 mL of 0.2 M aqueous KH₂PO₄ buffer solution and 60 mg of K₂S₂O₈ to the flask. To this solution add 5 mL of acetonitrile, stopper and shake carefully until all of the solid has dissolved. Now, in a darkened room, add approximately 4-5 small pieces of elemental magnesium to the stirred solution. Shake carefully and report your observations?

3. UV-vis absorption and phosphorescence emission spectrum of [Ru(bpy)₃]²⁺

Prepare *ca.* 1 ml of a dilute [Ru(bpy)₃]Cl₂·6H₂O methanolic solution. Add 1-2 drops to a fluorimeter cell containing 2 ml of methanol such that its absorption maximum at 453 nm is between 0.1 – 0.2 units. Now purge the solution gently with a steady flow of N₂ for at least 3 min. Stopper the cuvette and record its emission spectra on a fluorimeter over a 500 – 800 nm range using 453 nm excitation wavelength.

[Note: In the interest of time this step may be conducted as single cohort as opposed to independent groups]

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 $[\text{Ru}(\text{bpy})_3]^{2+}$. 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ 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. Explain the chemiluminescence reaction.
5. Suggest point group assignments for both the $[\text{Ru}(\text{bpy})_3]^{2+}$ and N3 dye complexes.
6. Comment on the purity of N3 dye via UV-vis qualitative analysis. Overlay this spectrum with that of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. Correct both spectral baselines. Convert both absorption data to "molar extinction coefficient" units using reported values (below) and comment on the *light-harvesting* properties of each dye.

$$[\text{Ru}(\text{bpy})_3]^{2+} \lambda_{\text{max}} \text{MLCT in MeOH} = 453 \text{ nm } (\epsilon = 14,700 \text{ M}^{-1} \text{ cm}^{-1})$$

$$\text{N3 dye } \lambda_{\text{max}} \text{MLCT in MeOH} = 539 \text{ nm } (\epsilon = 11,400 \text{ M}^{-1} \text{ cm}^{-1})$$

References

1. Vlachopoulos, N.; Liska, P.; Augustynski, J.; Gratzel, M., *J. Am. Chem. Soc.* **1988**, *110*, 1216-1220.
2. (a) www.dyesol.com; (b) www.g24i.com; (c) www.heliatek.com; (d) www.hydrogensolar.com.
3. Bolton, E.; Richter, M. M., *Journal of Chemical Education* **2001**, *78*, 47.