Synthesis and Characterization of a Ruthenium Complex Dye for a Dye-Sensitized Solar Cell

(revised February 2024*)

SUMMARY: The ruthenium complex known as N719 will be synthesized and characterized. A TiO_2 nanoparticle-based Grätzel solar device will be prepared using this complex as the dye. The photovoltaic performance of this solar device will be evaluated.

INTRODUCTION

This study will be somewhat less guided than previous ones and will require some planning and creativity on your part. It will require some creativity and a significant amount of planning on your part. Your task will be to prepare a Grätzel or solar cell based on the *J. Chem. Ed.* paper by Michael Grätzel (Grätzel et al., *J. Chem. Ed.* **1998**, *75*, 752). This paper provides an excellent review of the technical aspects involved in preparing these solar cells and their functionality. Unlike most commercially available solar cells, which are silicon wafer-based, Grätzel cells are dye-sensitized solar cells, which rely on photoinjection of an electron into a nanocrystalline TiO_2 semiconductor matrix.

In addition to the *J. Chem. Ed.* paper indicated above, read the background papers below to get an idea of how solar cells work and how they are designed:

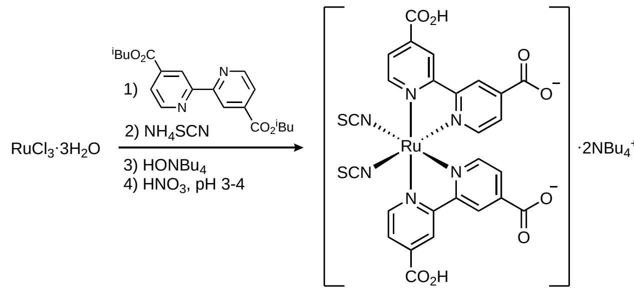
· Grätzel et al. *J. Am. Chem. Soc.* **1988,** *110*, 3686.

· Grätzel et al. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

Before engineering a solar cell, you need a photosensitive dye. The best dyes to date for Grätzel cells are often ruthenium complexes. For this project, you will synthesize the tetrabutylammonium salt of (*cis*-di(thiocyanato)- (2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium, an efficient photosensitive dye referred to as "N719". You will follow a modified version of the procedure reported by Vierucci et al. (*RSC Adv.* **2016**, *6*, 55768) for the preparation of ruthenium complex N719. Note: each article you are referencing is a full research paper and contains much more information than just an experimental procedure. You will need to look through the papers (including the experimental sections and supplementary information documents) and determine which parts are relevant to the chemical strategy outlined below. This process of planning an experiment by scanning through multiple papers and finding relevant sections mimics the process of designing and carrying out a synthetic procedure in scientific research.

EXPERIMENTAL PROCEDURES

Design a protocol for the synthesis of the ruthenium complex N719 based on the report by Vierucci indicated above. Scheme 1 shows a general scheme of the targeted process. (Note: the scheme you include in your report should contain more specific information based on the procedure that you use).



Scheme 1: Synthesis of ruthenium dye N719.

You should aim to conduct your ruthenium catalyst synthesis on ~120 mg scale, i.e. beginning with ~120 mg of the starting material. Note: this is smaller than the scale used in the paper. *You will need to scale down all reagents and solvents accordingly*.

As you plan out your procedures, pay particular attention to **any steps that take several hours or for any reasonable break points in your daily plans. You WILL need to plan your time as efficiently as possible.** Coordinate with your TA an instructor if any work needs to be done outside of the normal lab period, but you should be able to do everything in the allotted time.

It is often the case that a published procedure does not contain all of the specific details you are used to seeing in in undergraduate labs. It is also common to find that some modifications to the published procedure are required to accommodate the particular setup or preferred techniques of your lab. With this in mind, **the modifications to the original procedures and additional tips below should help you be successful in the aims of this experiment.**

Preparation of the ruthenium complex

Safety Note:* *Nitric acid reacts violently with organic compounds. Any waste containing nitric acid should be put in a separate waste bottle containing ONLY nitric acid and water (and any trace ruthenium and salts). DO NOT add acetone or any organics to this waste, as this could lead to pressure buildup and explosion.

The following modifications to the originally published experimental procedures and tips should help you be successful in carrying out these experiments:

*Contributions from Jennifer Monahan, Doug Crandell, and Jamie Neely. Troubleshooting by Travis LaPonsie, B.S. Biochemistry, SLU class of 2024.

1. Remember that you are working on a smaller scale compared to the published procedure. **Be sure to decrease amounts of reagents and solvents accordingly**.

2. Try to get as close as you can to the targeted weight of the starting material using chunks of ruthenium chloride, then recalculate the amount of ligand you need to add based on the actual weight (exact stoichiometry is important here).

3. Use a heating mantle to heat this reaction (you will need to get to a temperature above what a water bath can do).

4. Let the reaction flask cool before adding the NH_4SCN, then heat it back to reflux afterwards. Take care not to burn yourself on a hot flask!

5. Check the purity of the crude intermediate ruthenium complex (before addition of tetrabutylammonium hydroxide) by ^{1}H NMR in DMSO-d_6. It is likely that purification by column chromatography as suggested in the literature procedure will not be necessary.

6. Collect your final N719 product by gravity filtration through filter paper rather than by vacuum filtration through a fritted funnel (a coarse frit is too porous while a medium frit gets clogged). After cooling in the fridge, the precipitated solid should settle to the bottom of the flask. You can minimize filtration time by decanting some of the supernatant beforehand. Save this supernatant solution for rinsing out the flask during the filtration.

5. You will want to additionally wash your final product with cold isopropanol. Your filtrate at this point currently contains nitric acid, so **you must first switch to a separate collection flask**. Once you have an empty collection flask, rinse the filtered solid with several small volumes of cold isopropanol. (**This collecting vessel switch is to avoid mixing isopropanol, an organic compound, with nitric acid**).

6. After washing with isopropanol, transfer your final product to a tared round-bottom flask. Remove residual water *in vacuo* on the rotovap with heating before recording a yield and characterizing the product. This is better than drying under air, which allows more time for degradation.

7. Store your product when not in use under nitrogen, wrapped in foil, and in the fridge to help protect it from decomposition. Aim to characterize it as soon as possible after synthesis, in case it starts to degrade.

8. You should characterize your complex using the following spectroscopic techniques:

• FTIR (peak-pick all strong signals above 1500 cm^{-1})

• ^{1}H NMR (^{13}C NMR is not necessary as long as the ^{1}H NMR data are consistent with a previously reported spectrum, which should be cited)

• UV-vis absorption (make sure to choose a solvent that your complex is completely soluble in, as is necessary for quantitative analysis)

Grätzel cell assembly and testing

The *J. Chem. Ed.* paper by Grätzel uses natural dyes like chlorophyll or the anthocyanins present in berry juices as dye sensitizers for the solar cell. In contrast, you will use your synthesized ruthenium complex as the dye for your solar cell. Follow the steps described in this paper for:

· Depositing the titanium dioxide layer

· Staining the titanium dioxide with the dye (~0.3 mM solution of your ruthenium complex in EtOH)

Note: you will be provided with 2.5 cm × 2.5 cm ITO (indium tin oxide) transparent electrodes, so you do not need to make your own.

· Preparing the carbon-coated counter electrode

· Assembling the device and determining output characteristics and a full power curve (helpful video: https://www.youtube.com/watch?v=Jw3qCLOXmi0&t=1s)

· Comparing the performance of your cell to a commercial toy solar cell by constructing current-voltage (*I-V*) curves for each. This can be done inside, using a lamp or outside, if it is a consistently sunny day. The light intensity level may be measured using an appropriate sensor and recorded for a point of reference.

General Notes

You do not need to synthesize the ligand for your dye, as it was prepared for you.

You have more freedom with this project than others, and some steps warrant some work on days in the same week depending on your planning. **You will need to write up a full procedure and have it reviewed by the instructor before entering lab to start your synthetic work. This should include reagents and their exact amounts and a procedural plan that includes dates and times for the synthetic work. This is due before you start your synthetic work.** Note that the shorter amount of time from when you get started with the reaction to isolating the product, the more successful your synthesis will be. You have priority of using lab during your scheduled lab period over other students, but your out of lab work will have to be scheduled around limited glassware, space, other labs, and TA/instructor availability.

■ REPORT

Your report should be presented in the format of an Inorganic Chemistry journal article. All characterization data should be tabulated according to journal standards in the experimental section. Also include the following:

1. Detailed procedure and observations for the synthesis of the ruthenium complex in the experimental section. Details concerning the construction and evaluation of your solar cell should appear in the SI, though the results of these measurements should be discussed in the main text.

2. Reaction scheme with starting material, product, conditions (including equivalents), and yield of your ruthenium complex in the main text.

3. A master table summarizing all characterization data for your ruthenium complex, similar to the example given in Experiment 2. Do not include any NMR or IR spectra in the report, but make sure these are fully processed and labelled in your SI.

4. The UV-vis spectrum of the complex in an appropriate solvent plotted as molar absorption coefficient (ε, M^{-1} cm^{-1}) vs. wavelength (λ, nm) should appear in the report. What electronic transitions are responsible for the observed absorptions (specifically the lowest energy one)? How do the absorptions in the visible range relate to the color of the complex?

5. Discuss the structure and properties of TiO_2 that make it amenable as the electrolyte phase of a Grätzel cell. Why use nanoparticles instead of bulk TiO_2? What is the purpose of the I_2/I^- solution? What is the importance of the carboxylic acid groups of the complex dye with respect to TiO_2 layer?

9. Display and discuss the optoelectronic performance results of your Grätzel cell. This should include a plot of current density (mA/cm^2) versus voltage (*I-V* curve), obtained by measuring these values with different resistance loads using the provided resistor box. Construct *I-V* curves for both the ruthenium dye cell and the commercial toy cell (if the data are dramatically different, these curves can be presented in two separate figures). Does your solar cell work (i.e. does it produce current in the presence of light)? What are your measured open circuit voltage and short circuit current density? What is its approximate maximum power output? Discuss the performance of the ruthenium cell versus the toy cell, comparing performance numbers and *I-V* curve shape. What factors contribute to one being "better" than the other?

10. In your conclusion, discuss possible future directions in addition to summing up your results as usual. What changes could you make to the chemical structure of your complex dye to improve photovoltaic performance? How might you modify your physical solar cell to increase solar conversion?

Remember your introduction should NOT include general chemistry theory, like how photochemistry works (you can use references to point to that information). It should focus on and tie together some combination of dye sensitizer compounds and solar cells.

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