$$\left[\cdots \right]^{2+}$$

Facile One Pot Preparation of $[Ru(bpy)_2PVP_{10}]^{2+}$ (RuPVP) Metallopolymer

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Introduction:

Many previous literature reports generated from the Rusling[1] and Forster[2] groups have pointed to other previous literature reports that should be followed in order to obtain electrochemiluminescence (ECL) generating cis-$[Ru(bpy)_2PVP_{10}](ClO_4)_2$ (RuPVP) polymer. The literature train that one delves into when attempting to elucidate the preparation steps involved includes various reports describing isolation and purification of many precursor materials. However, it is possible to purchase precursor chemicals and synthesize this material in several mini-steps in one vessel (or one pot) eliminating the tediousness of isolating every precursor substance. In addition, upon careful stoichiometric addition of counter ions to the solution, one can tailor solubility characteristics of the resulting polymer. In this fashion, one accumulates an appreciation of inorganic polymer synthesis concurrent to making economical use of valuable research time.

Background:

Upon following the citations from previous Rusling papers in addition to following the circulating lab prep written by Dr. Minjeong So, one finds that the synthesis of cis-Bis(2-2'-bipyridne)dichloro ruthenium(II) (cis-$Ru(bpy)_2Cl_2$) can be performed employing $RuCl_3$ starting material following the equation[3]:

$$RuCl_3 + 2 \text{ equiv. } 2,2\text{'-bipyridine} + \text{excess LiCl} \rightarrow \text{cis-}Ru(bpy)_2Cl_2$$
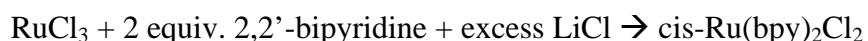
The above reaction is performed in DMF, followed by acetone isolation/purification. The isolated di-chloro material is then reacted with water to create the bis-aquo complex following the reaction[4]:

$$Ru(bpy)_2Cl_2 + 2H_2O \text{ (excess solvent)} \rightarrow Ru(bpy)_2(H_2O)_2$$
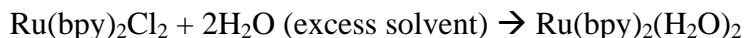
The bis-aquo complex can be precipitated from solution using an excess of $LiClO_4$ and recrystallized with an acetone mixture.[5] This complex would then be refluxed (80:20 ethanol:water) in the presence of 10 fold (pyridine monomer units) polyvinylpyridine (PVP) and 5 fold excess of $LiClO_4$ to produce RuPVP:

$$Ru(bpy)_2(H2O)_2 + PVP + LiClO_4 \rightarrow \text{cis-}[Ru(bpy)_2PVP_{10}](ClO_4)_2$$
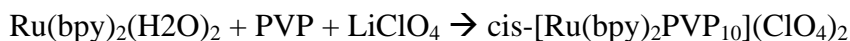
The RuPVP can be isolated by precipitation from the ethanol solution using ethyl-ether, dried, and tested for content.

While one learns the ropes of inorganic synthesis and purification methods (or how to operate a high vacuum pump at least) following this protocol, the prep did not always work as described. The preparation of the di-chloro complex is not as easy as is described in literature, with various steps missing or altered since the report in the literature since 1978.[6] One readily finds inconsistencies in reading the seminal inorganic preps in the literature.[4,7,8] Finally, upon mixing the di-chloro (then bis-aquo) complex with PVP with the prescribed amount of $LiClO_4$, an insoluble polymer was often the result, which was eventually discarded.

Alternate Method:

Through perusing the vast ruthenium synthesis literature, one finds that the purification of the di-chloro ruthenium material is performed in many different ways, but it is never seemingly straight forward.[7-9] In fact, some of our reports from our laboratory point to one paper that makes the complex in one way, which varies from the currently accepted lab protocol in one way or another.[1,10] From conversations with a colleague who obtained his PhD from B.P. Sullivan, a central figure who with Forster obtained his PhD from Tom Meyer (U. North Carolina) *via* the initial preparation of these complexes in the 70's, it was learned that diffuse information exists on the preparation of the Ru-chloro complex. The comment was also made, "why don't you just purchase this material from Strem or Aldrich?" That is, even tried and true synthetic chemists are purchasing the precursor materials for these syntheses. To this end, the di-chloro compound was obtained ca. 2006 (cis-Bis(2-2'-bipyridine)dichlororuthemium(II)hydrate; item# 288128-5g, Aldrich). Despite some initial discussion on the purity of this compound, UV-analysis and comparative qualitative studies performed with it and a crystallized form from a previous prep showed similar characteristics and solubility behavior, and it can be used without any reservation.

The use of this material significantly enhances the synthesis process and allows one not to get bogged down in the intricacies of inorganic synthesis when there is a higher analytical goal to be achieved. The important aspects are to learn and know the steps involved outlined above in preparing such material for future reference.
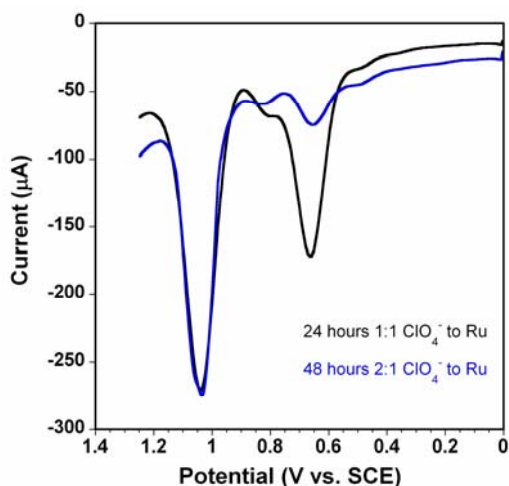
To start the polymer prep, a useable amount of this ruthenium di-chloro complex (λ_{max} = 530 nm in ethanol) (~0.2g) is added to a 50 mL round bottom or three necked flask with ~5 mL of water. The flask is attached to the *large* condenser (24/40 size) and sealed using silicon grease to preclude any solvent leakage. A needle hooked into the house N_2 line can be inserted into a rubber stopper at the top of the condenser or into a rubber stopper on the three-necked flask to gently purge with nitrogen throughout the reaction. A second needle must be inserted at the top of the condenser to release any excess pressure that develops and to avoid an explosion. The flask is placed in a preheated silicon oil or paraffin oil bath (simply preference, some like sand, but others believe it does not provide a homogenous heat), and the water solution is refluxed (~100°C) for 30 mins. to 1 hr. This corresponds to at most a "1" setting on the Corning PC 351 old heat plate (from Prof. Tanaka). The reaction can be monitored using UV-Vis

noting the shift of λ_{max} to 503 nm (use a couple of drops of the aqueous reaction in ethanol).

After sufficient time to displace the chlorines from the ruthenium center, a 10x excess in pyridine sub-units can be added in the form of polyvinylpyridine (PVP, avg. mw = 60,000; Aldrich #47,234-4). Typically, if 0.2 g ruthenium di-chloro compound was initially used, this corresponds to approximately 413 µmoles of ruthenium (mw = 484 g mol^{-1}). Some error will enter into the calculation due to the hydrated nature of the compound, but the spec. sheet details that this is no more than 11% of the total mass; therefore, for these purposes, this calculation will suffice. The average PVP molar mass is 60,000 Da; therefore, this equates to approximately 520 pyridine units per PVP strand (unit mw = 115 g mol^{-1}). By calculating a 1:10 molar ratio of ruthenium to pyridine units and multiplying through to obtain the amount of total PVP, a value of 7.9 µmoles of PVP, or 0.475 g of PVP is needed for the reaction at this scale.

The PVP should be dissolved in approximately 25 ml of ethanol in a separate flask and slowly added to the refluxing ruthenium water solution. It will be necessary to allow several hours of stirring for the PVP to be completely dissolved. It was found that if this is allowed to mix together at reflux (~80 ^{o}C, setting "warm") for a short period of time (at most an hour), the reaction proceeded more smoothly. Upon monitoring with UV-Vis, one notices very little change taking place – i.e. no reaction is occurring between the ruthenium center and the polymer. At this stage, LiClO$_4$ is added to the reaction vessel. This is done by calculating the stoichiometric amount desired, dissolving the Li salt in 1 ml of water, and adding this solution to the reaction. For experimental purposes, we added the salt in phases, starting with a 1:1 ratio of ClO$_4^-$ to each ruthenium unit (mw LiClO$_4$ = 106 g mol^{-1}; for this scale 1:1 = 43 mg). After addition of the LiClO$_4$, the reaction is allowed to progress for a few hours refluxing the ethanol/water solution at around 80°C.

After this period of time, a few drops of the ruthenium solution can be extracted from the reaction vessel, and UV-Vis in addition to electrochemical studies can be performed to ascertain the extent of the metallopolymerization. UV-Vis signatures for this polymer (in ethanol) show a $\lambda_{max} = 465$ with a shoulder at 435nm. This spectrum will occur with a mix of ruthenium coordination of 5 or 6; however, so it is not 100% indicative that the ECL polymer has been formed. The better test is to place a ~30 µl drop of the ethanolic ruthenium reaction solution on a cleanly polished PG electrode and allow the solvent to evaporate in the dark (casting). The electrode is then placed in an electrochemical cell with *0.1 M H$_2$SO$_4$* and the proper counter (Pt) and reference electrodes (SCE or Ag/AgCl). The acid nature is very important, as HCl will strip the polymer off of the electrode and give no electrochemical response. A standard SWV is the easier experiment to run, and an example of one is shown below. An oxidation wave at ~+1.05 to +1.10 V vs. SCE (or Ag/AgCl) demonstrates the presence of the ECL polymer. An oxidation

24 hours 1:1 ClO$_4^-$ to Ru

48 hours 2:1 ClO$_4^-$ to Ru

wave at ~+0.70 V vs. SCE (or Ag/AgCl) indicates the presence of the non-ECL mono-chloro ruthenium polymer, with 5 pyridinyl coordination. The electron transfer is facilitated by proton presence; therefore, there is a shift toward more negative potentials (easier to oxidize) in the acid – i.e. deviation from +1.15 V seen in neutral media.

If the stoichiometric amount of $LiClO_4$ is less than 2 ClO_4^- to 1 Ru, there will be a significant presence of penta-coordinated ruthenium polymer present (black line in figure). However, this "impurity" can be removed by addition of more $LiClO_4$ and reacting a little longer with a total $LiClO_4$ excess not exceeding ~2.5 times the amount of Ru. This is demonstrated in the SWV figure to the left where the proportion of 5-coordinated Ru to 6-coordinated RuPVP shows significant decrease upon increasing the $LiClO_4$ in the reaction. Eventually, the proportion was increased to ~2.5x and the +0.7V peak disappeared. The reaction can be turned off when an electrochemical experiment shows a significantly muted presence of the 5 coordinated Ru polymer. The important aspect to remember here is that the addition of the $LiClO_4$ is the key step in this reaction, and adding it to the reaction with no attention to stoichiometric detail will usually ruin the reaction leaving one with a sloppy, insoluble polymer mess.

After the reaction is turned off, the ethanol/water solvent needs to be removed either by rotovap or high vacuum creating a dry polymer. To clean the polymer, it needs to be re-dissolved in ethanol (~20 ml, solvent stripping), and allowed to completely enter into solution. This might take several minutes. The polymer is then precipitated with addition of ~5 ml ethyl ether. The precipitate is filtered and rinsed with cold water and ethyl ether.

Discussion:

The theoretical yield of this reaction is approximately 550 mg on this scale. Expected % yields can be in the range of 50-75% with losses due to unreacted ruthenium that is rinsed away in the isolation steps. However, this yields one with at least 300 mg of usable metallopolymer that can be used for sensor construction. To demonstrate how long this would last, in Feb 2005, a RuPVP prep yielded approx. 300 mg of product, and this has still not been exhausted in Jan. 2008 after the construction of several thousand LbL sensors resulting in the publication of several high quality papers.

An interesting aspect of this reaction is the careful addition of the $LiClO_4$, which seems to be the reason that this reaction did not work most researchers in the 2006-2008 time frame. The perchlorate ion affects the approach and reaction of the ruthenium with the PVP polymer, and in too high excess, it is speculated that there is significant crosslinking of the Ru center with multiple PVP segments resulting in a highly insoluble, unusable complex.[11] Therefore, most of the detail in this reaction needs to be centered on the proper stoiciometric addition of the lithium salt for proper coordination of the ruthenium to the PVP.

In addition, it seems that by altering the amount of $LiClO_4$ in the reaction, one can tailor the aqueous solubility of the resulting polymer. For instance, the first prep done by an indigenous lab member (not from Ireland) was that performed by Minjeong So. Her polymer was famously insoluble if water was added, a point of contention in discussions of how to properly form LbL sensor films. The polymer synthesized in Feb. 2005 (EH) was slightly, but not totally, soluble in water to the point where 50% water could be

added if the RuPVP concentration was kept at or below ~2 mg/ml. In both of these preps, the Forster protocol was followed that proposed heavy excess of $LiClO_4$. It can be speculated that useable polymer was obtained from these preps because a) we serendipitously added less $LiClO_4$ than for what was called, or b) we were not starting with the hydrated form of the $Ru(bpy)_2Cl_2$, and so further calculations were not skewed resulting in addition of too much $LiClO_4$. In the Jensen prep (2008), approximately 2.2x excess was added, and the resulting polymer is soluble in almost all proportions of water/ethanol – i.e. much more water soluble than the other two preps. In fact, at 100% ethanol, the polymer is not completely soluble, where it was for the former preps. Therefore, if water solubility of the resulting complex is desired, lower concentration of $LiClO_4$ should be added, yet if a higher organic/ethanol solubility is desired; then the proportion of $LiClO_4$ needs to be increased. Too much $LiClO_4$ yields a polymer that is insoluble in ethanol, or pretty much any other tested solvent, and therefore pretty much unusable. All three successful preps yield polymer that gives sufficient ECL upon electro-oxidation; however, and that is the eventual characteristic with which we are most concerned.[12]

Conclusions:

Too often in this lab, we do things according to a published report or a piece of paper that someone gave us without thinking of the steps involved in what we are doing. This could be the formation of electrode sensors or the synthesis of compounds we need to perform our research. Sometimes the established protocol is a very good one or even the best, but other times it is not, and has been done in such a way because "that's just the way things were always done." At times, we need to stand back and ask, "why?"

The drone mode of thinking was definitely exhibited in this synthesis situation where several synthesis attempts were made at this prep and no one (including myself) ever stood back to think why it would not or did not work. The established protocol was tedious involving many steps that yielded the same product as the easier prep. If the one pot method was attempted, it was done in an identical fashion, yet we were surprised to find the same unusable product in the end! This is Einstein's definition of insanity. In addition, through personal communication with one of the primary authors on the seminal work in this area, the "established" protocols still generate plenty of conversation and controversy[6,11] – i.e. no protocol is set in stone.

Overall, following this easy one pot reaction using an easily obtainable precursor ruthenium compound should yield the researcher enough RuPVP to last throughout his or her graduate/postdoctoral career. The researcher can tailor the solubility characteristics of the RuPVP through the careful addition of $LiClO_4$ to the reaction. By understanding the underlying reactions that lead to the eventual product, the researcher becomes acquainted with important inorganic synthesis protocols, yet avoids the dangerous trap of becoming immersed in a time-consuming side project and neglecting the more important analytical goals of the lab.

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12. ECL can be tested by casting on the Cu-PG chip electrode, placing the electrode into the ECL cell with either Tris buffer or oxalate ions and acquiring light with gel doc CCD camera upon excitation at +1.25 V vs. Ag/AgCl.