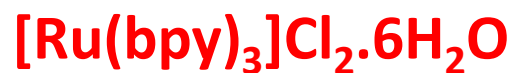
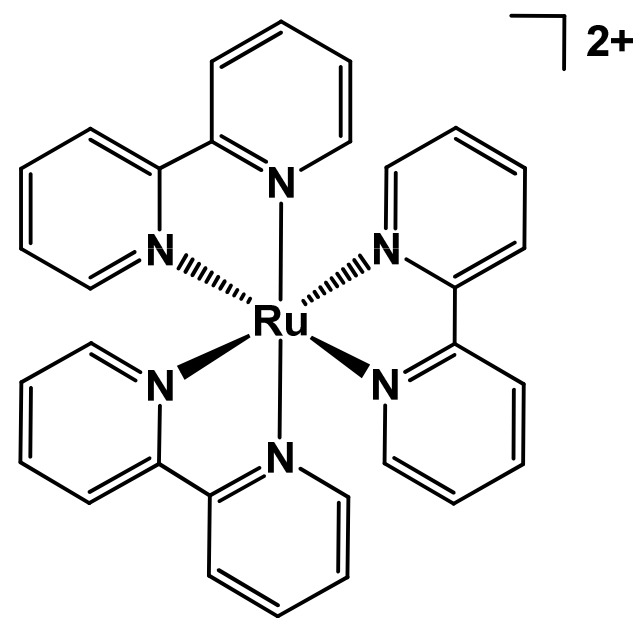
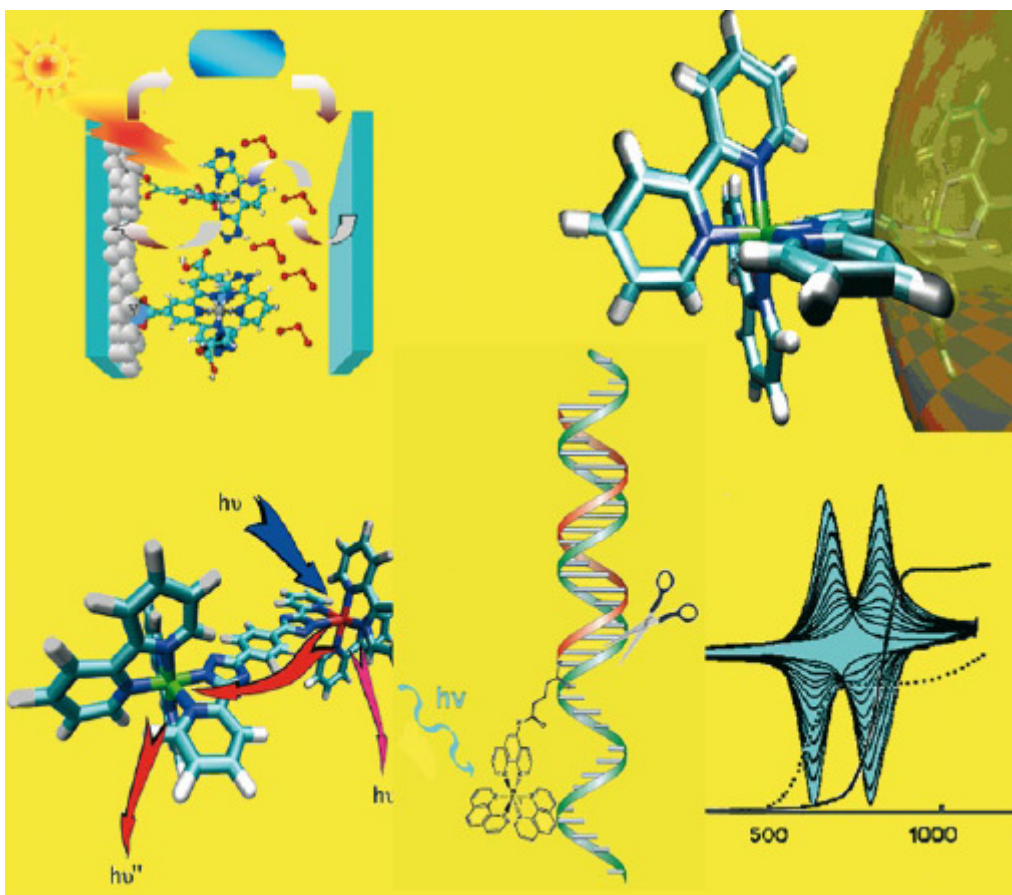
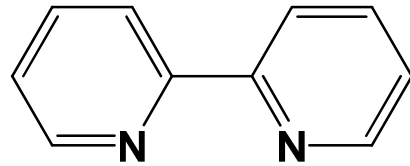


Tris(2,2'-bipyridine)ruthenium(II) Dichloride Hexahydrate

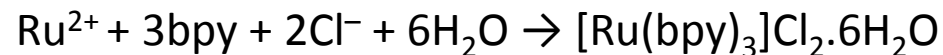


2,2'-Bipyridine

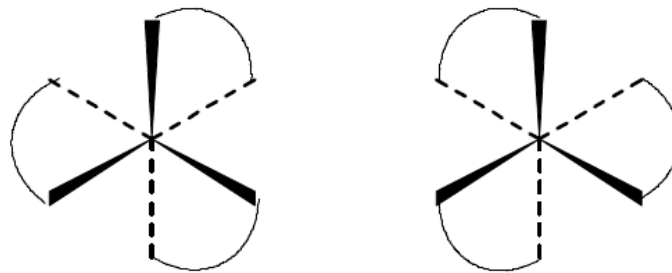
- 2,2'-bipyridine, commonly abbreviated as *bpy*, functions as a bidentate chelating ligand.



- The *bpy* in the phosphinic acid/ruthenium chloride solution complexes with the Ru^{2+} produced by the redox reaction, and the complex is precipitated by adding excess Cl^- (as KCl), using the common ion effect:



- The $[\text{Ru}(\text{bpy})_3]^{2+}$ in the product is actually a mixture of two optical isomers with D_3 symmetry.



[Ru(bpy)₃]²⁺ Electronic Structure

- Second-row transition ions, like Ru²⁺ tend to have larger Δ_0 values and smaller P values.
- Also, bpy is a strong-field ligand, which tends to produce large Δ_0 values.
- As a result, [Ru(bpy)₃]²⁺ is a d^6 low-spin case, which is diamagnetic.
- [Ru(bpy)₃]²⁺ has two bands at 428 nm and 454 nm with high extinction coefficients have been assigned to *metal-ligand charge-transfer* (MLCT)
- The absorption of the blue end of the spectrum gives the complex its characteristic red color.
- [Ru(bpy)₃]²⁺ can be made to show *chemiluminescence*.

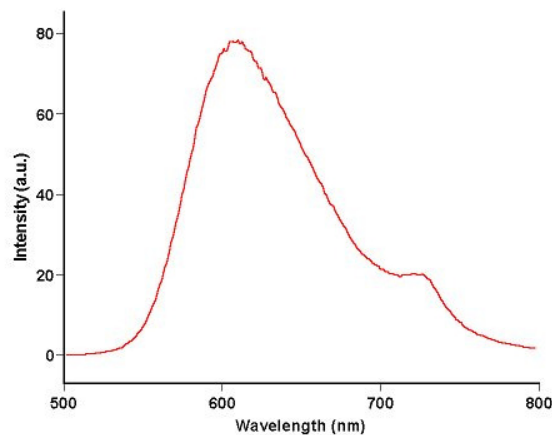
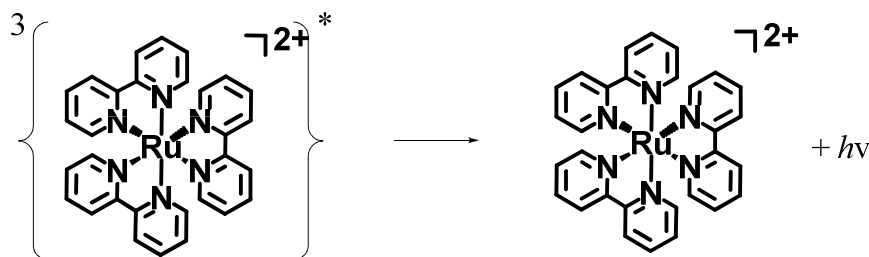
Chemiluminescence

- *Chemiluminescence* is the production of visible light through a *chemically induced excited state* of a molecule, which relaxes back to the ground state by photon emission.
- *Fluorescence* is a short lifetime *photoluminescence* process (0.5-20 ns) in which a molecule emits a photon from a singlet excited state, thus quickly decaying back to its singlet ground state.
- Both the ground and excited states are singlet states ($m = 2S + 1$).

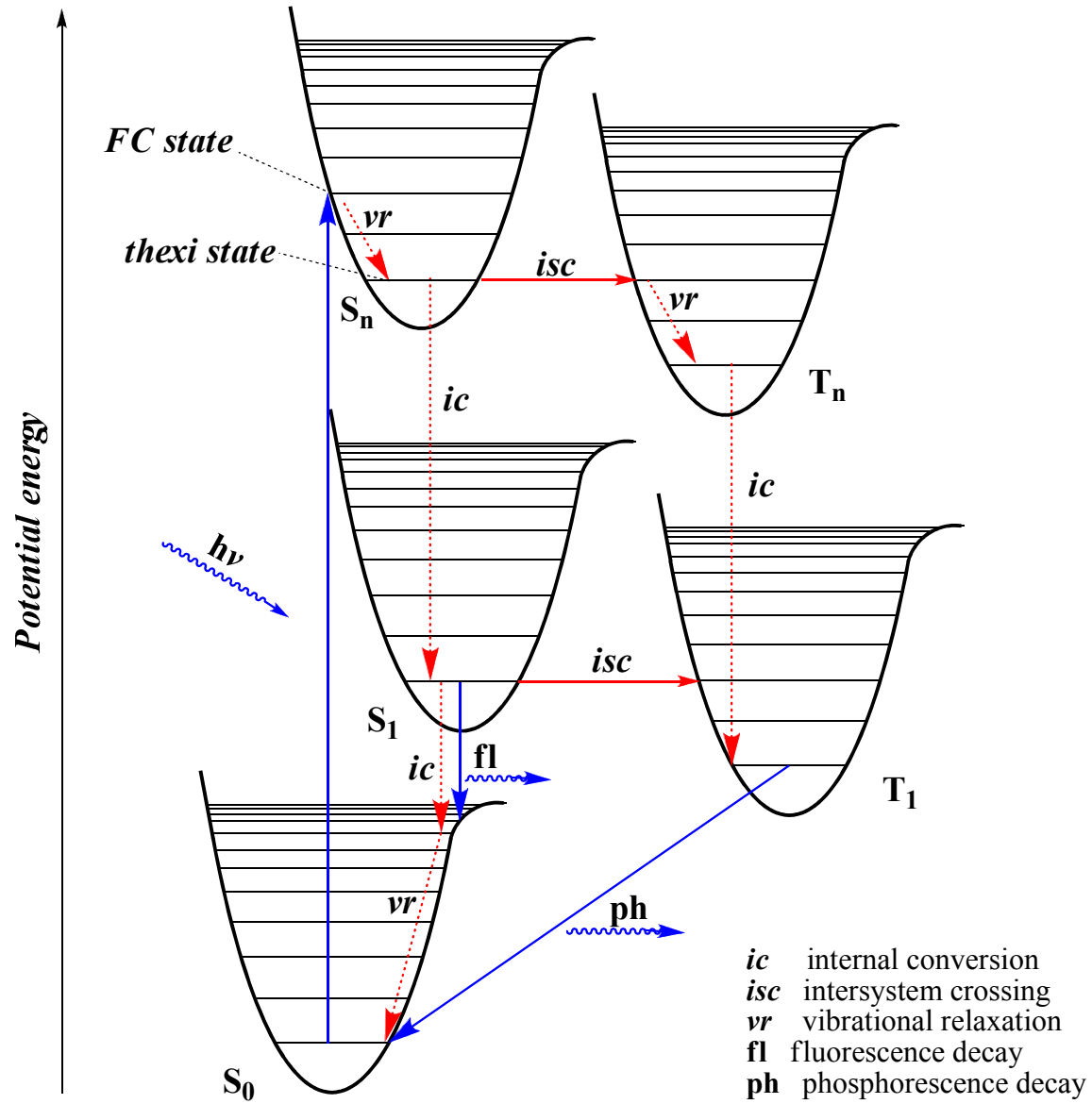


- ${}^1M^*$ can also lose energy by non-radiative processes (thermal motion, vibration, molecular quenching), resulting in no light emission, i.e. non-radiative decay.

- *Phosphorescence* is a longer lifetime *photoluminescence* process (μs - hours) in which the excited molecule undergoes an intersystem crossing (*isc*) to a triplet excited state.
- Radiative transition from an excited triplet state to the singlet ground state is quantum mechanically “forbidden” but occurs with low efficiency, resulting in longer lifetimes.



Jablonski diagram

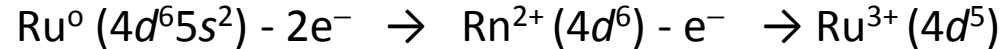


Procedure Notes

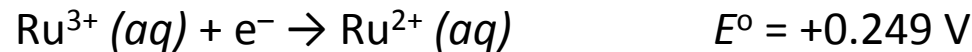
- Start by preparing the 10 % aqueous acetone solution needed for the first wash by chilling it on ice so that it will be ready when needed.
- A 31 % phosphinic acid solution has been prepared for use in making the NaH_2PO_2 solution.
- Converting 2 mL of the acid to a solution of the sodium salt should take about 6-7 NaOH pellets.
- Once the solution becomes slightly cloudy, add phosphinic acid dropwise until the precipitate just dissolves.
- We will not record a quantitative UV-Vis spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$. Just make up a solution, take a qualitative spectrum, and adjust the concentration if needed to obtain a decent spectrum to be submitted with your report.
- For point 1 of the write-up, simply comment on the purity of the compound on the basis of the number and positions of the bands, compared to the data given in the experimental procedure.
- For the chemiluminescence experiment, adjusting the pH using a 2 M HCl solution (pH indicator paper) and observe the chemiluminescence in the dark.

Redox Chemistry

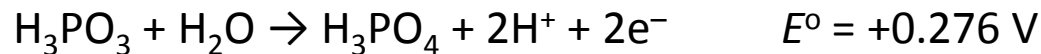
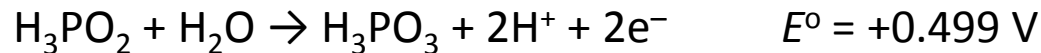
- Ruthenium is a second-row transition element, under iron in the periodic table.



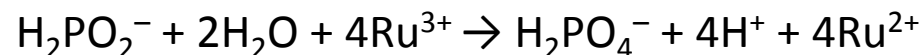
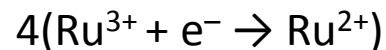
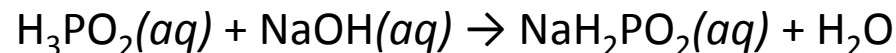
- $\text{Ru}^{3+} (aq)$ is a moderate oxidizing agent:



- In this synthesis Ru^{3+} is reduced with phosphinic acid:

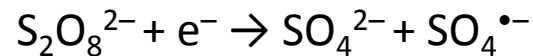
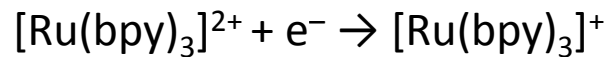


- This synthesis uses oven-dried $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, which is reduced with freshly prepared NaH_2PO_2 , sodium phosphinate:



Chemiluminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$

- In this experiment, $[\text{Ru}(\text{bpy})_3]^{2+}$ is mixed with the strong oxidant $\text{S}_2\text{O}_8^{2-}$ and both are reduced by reaction with $\text{Mg}(\text{s})$.
- The reduction product of $\text{S}_2\text{O}_8^{2-}$ is the highly reactive species $\text{SO}_4^{\bullet-}$ which oxidizes $[\text{Ru}(\text{bpy})_3]^+$ back up to $[\text{Ru}(\text{bpy})_3]^{2+}$ in an excited state.



- The excited state species phosphoresces, emitting bright orange light at 610 nm:

