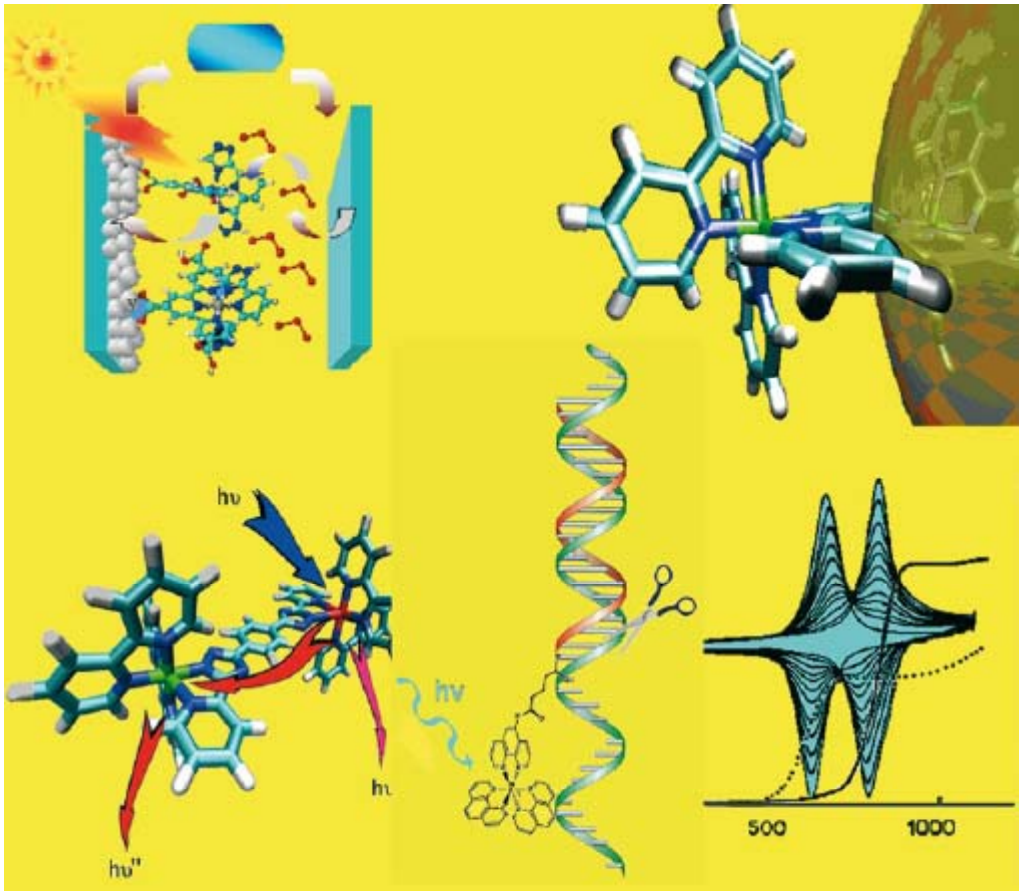
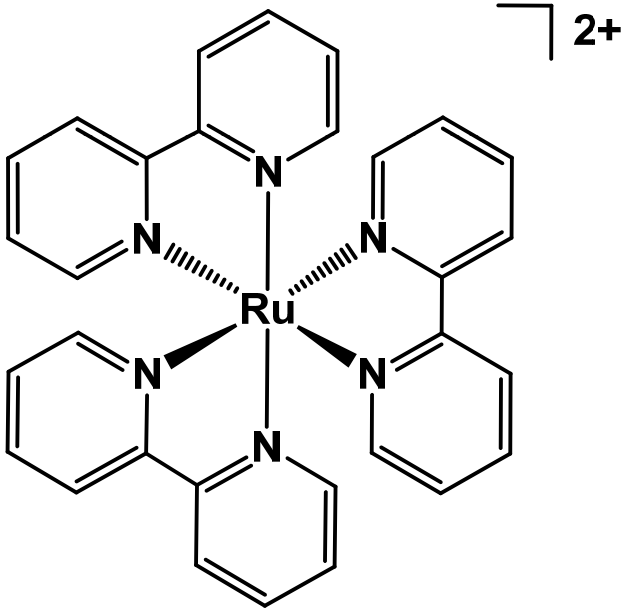
Tris(2,2'-bipyridine)ruthenium(II) Dichloride Hexahydrate

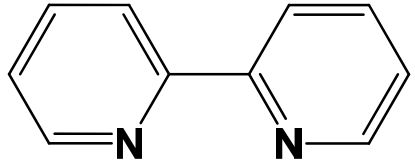




$[Ru(bpy)_3]Cl_2.6H_2O$

2,2'-Bipyridine

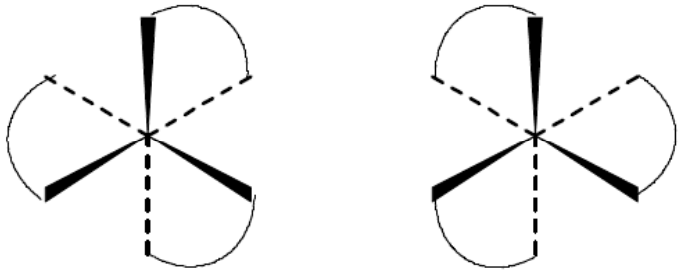
- 2,2'-bipyridine, commonly abbreviated as *bpy*, functions as a bidentate chelating ligand.



- 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:

$$Ru^{2+} + 3bpy + 2Cl^- + 6H_2O \rightarrow [Ru(bpy)_3]Cl_2.6H_2O$$

- The $[Ru(bpy)_3]^{2+}$ 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 Ru^{2+} 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

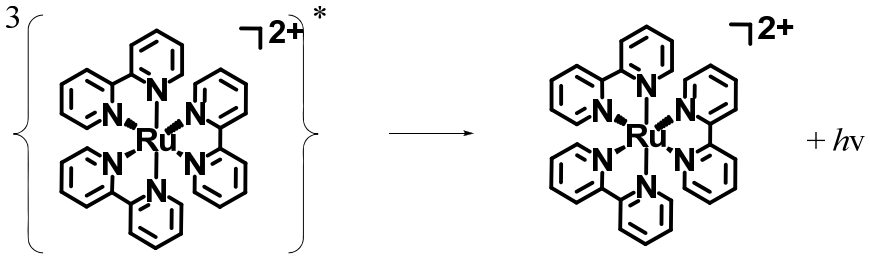
- *Chemiluminescence* is the production of visible light through a *chemically induced excited state* of a molecule, which relaxes back to the ground state by photon emission.
- *Fluorescence* is a short lifetime *photoluminescence* process (0.5-20 ns) in which a molecule emits a photon from a singlet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

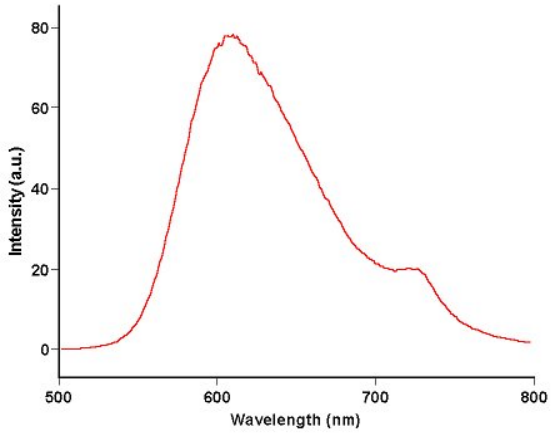
$$^{1}M + h\nu \rightarrow {}^{1}M^{*} \rightarrow {}^{1}M + h\nu$$

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

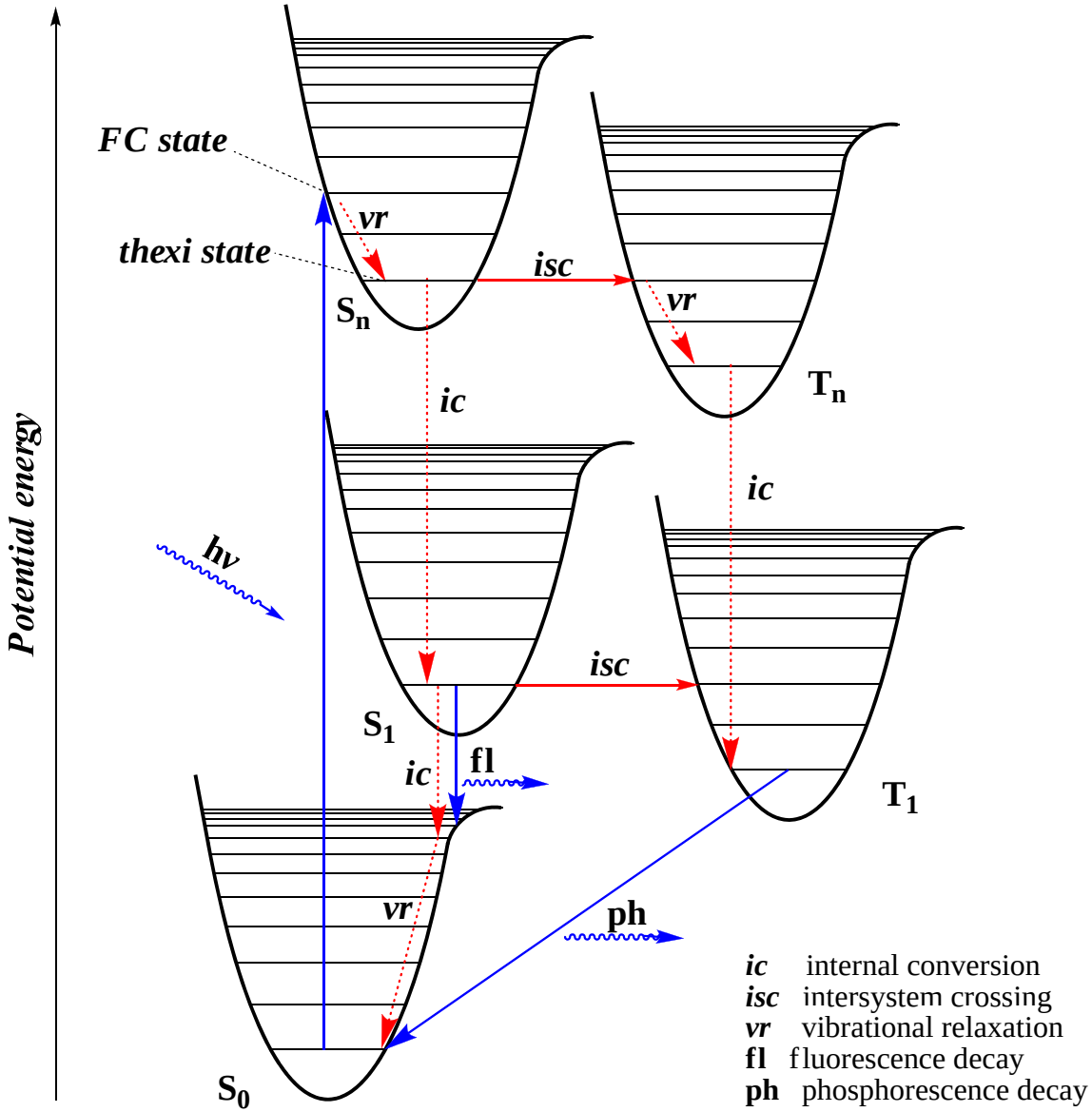
- *Phosphorescence* is a longer lifetime *photoluminescence* process (μs - hours) in which the excited molecule undergoes an intersystem crossing *(isc)* to a triplet excited state.
- Radiative transition from an excited triplet state to the singlet ground state is quantum mechanically "forbidden" but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

$$^1M + h\nu \rightarrow {}^1M^* \rightarrow {}^3M^* \rightarrow {}^1M + h\nu'$$





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 $[Ru(bpy)_3]^{2+}$. 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.

$$Ru^{o}\ (4d^{6}5s^{2}) - 2e^{-} \rightarrow Rn^{2+}\ (4d^{6}) - e^{-} \rightarrow Ru^{3+}\ (4d^{5})$$

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

$$Ru^{3+}\ (aq) + e^{-} \rightarrow Ru^{2+}\ (aq) \qquad E^{o} = +0.249\ V$$

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

$$H_3PO_2 + H_2O \rightarrow H_3PO_3 + 2H^{+} + 2e^{-} \qquad E^{o} = +0.499\ V$$

$$H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^{+} + 2e^{-} \qquad E^{o} = +0.276\ V$$

- This synthesis uses oven-dried $RuCl_3.xH_2O$, which is reduced with freshly prepared NaH_2PO_2, sodium phosphinate:

$$H_3PO_2(aq) + NaOH(aq) \rightarrow NaH_2PO_2(aq) + H_2O$$

$$H_2PO_2^{-} + 2H_2O \rightarrow H_2PO_4^{-} + 4H^{+} + 4e^{-}$$

$$4(Ru^{3+} + e^{-} \rightarrow Ru^{2+})$$

$$H_2PO_2^{-} + 2H_2O + 4Ru^{3+} \rightarrow H_2PO_4^{-} + 4H^{+} + 4Ru^{2+}$$

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

- In this experiment, $[Ru(bpy)_3]^{2+}$ is mixed with the strong oxidant $S_2O_8^{2-}$ and both are reduced by reaction with Mg(s).
- The reduction product of $S_2O_8^{2-}$ is the highly reactive species $SO_4^{\bullet-}$ which oxidizes $[Ru(bpy)_3]^{+}$ back up to $[Ru(bpy)_3]^{2+}$ in an excited state.

$$Mg \rightarrow Mg^{2+} + 2e^-$$

$$[Ru(bpy)_3]^{2+} + e^- \rightarrow [Ru(bpy)_3]^{+}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$

$$[Ru(bpy)_3]^{+} + SO_4^{\bullet-} \rightarrow \{[Ru(bpy)_3]^{2+}\}^* + SO_4^{2-}$$

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

$$\{[Ru(bpy)_3]^{2+}\}^* \rightarrow [Ru(bpy)_3]^{2+} + h\nu$$