

Dinuclear Ruthenium Complexes as Photosensitizers

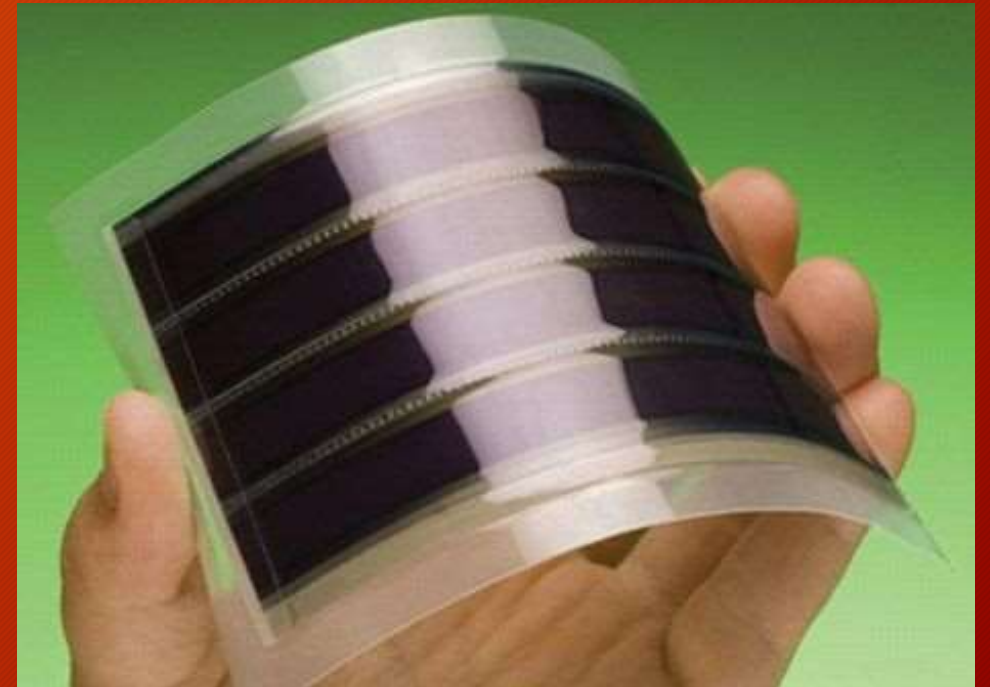
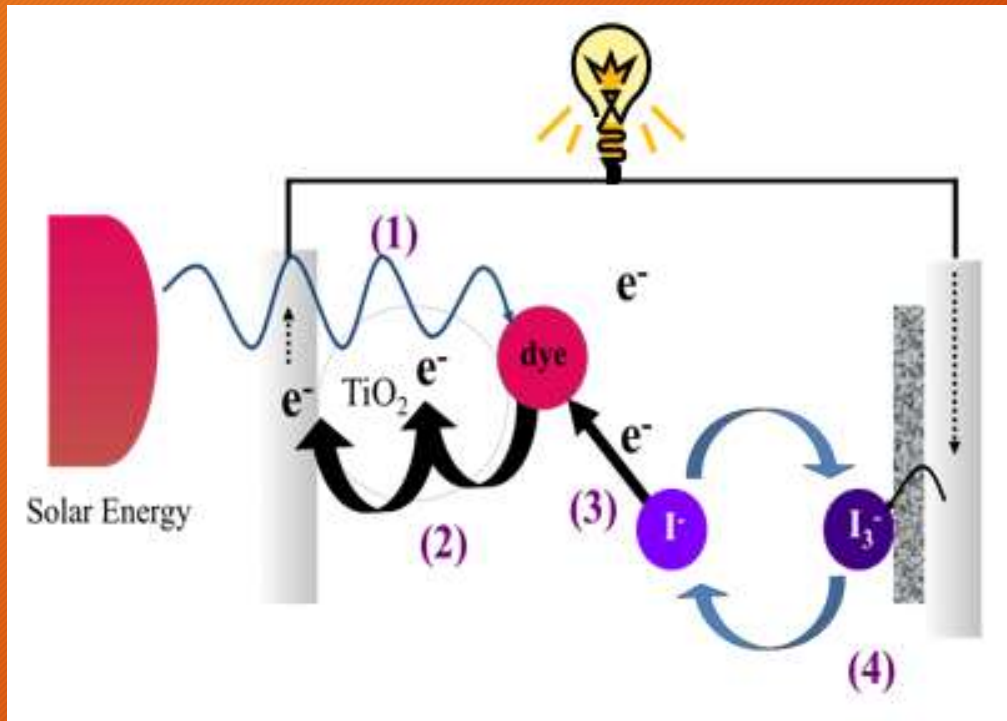
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Background

- Harvesting solar energy is a major research effort
- Grätzel cell is a great idea in the solar energy conversion
 - Easy to fabricate
 - Uses low cost materials
 - But suffers from poor efficiency (< 12%)
- Important components of Grätzel cell are:
 - TiO₂ nanoparticle semiconductor
 - Ru(II)-bpy dyes as photosensitizers, and
 - Triiodide electrolyte

Grätzel Cell



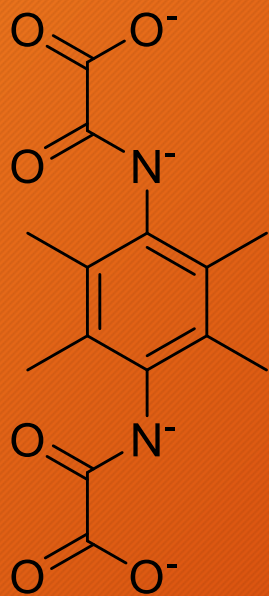
Grätzel Cell

- Ruthenium(II)-bipyridyl compounds are the first and most widely studied photosensitizers
- $[\text{Ru}(\text{bpy})_3]^{2+}$ complex cation has favorable electronic levels
- Better photosensitizers must have similar electronic levels but must absorb most of the sunlight and have higher excited state lifetimes
- Towards achieving these goals, we wanted to synthesize and study **dinuclear ruthenium(II) complexes with electronically-communicative bridging-ligands**

Bridging ligands

- Derivatives of tetramethyl-1,4-phenylenediamine are well-known for their **electron-exchange** and **electron-transfer** properties
- These aromatic bridges have suitably oriented carbon and nitrogen p-orbitals that they are known to **connect** two metal centers electronically
- Metal-Metal coupling or interaction facilitated by such ligands leads to very useful reduction and oxidation (redox) properties
- The electronically-communicative bridges can give or take electrons from the metal centers
- We chose three types of ligands for this research which contain such bridge

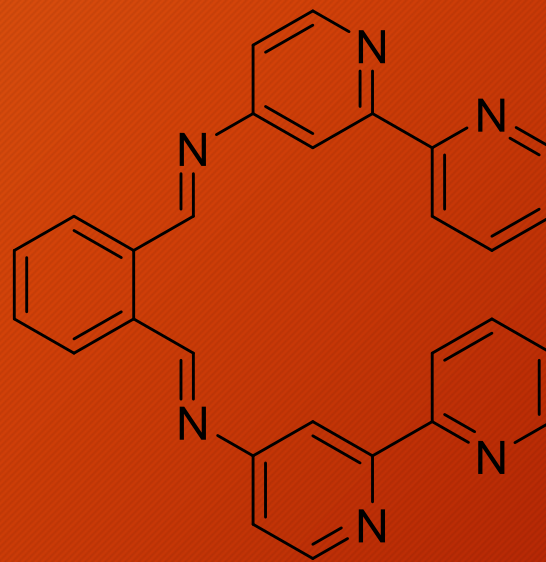
Bridging ligands



Me₄L1



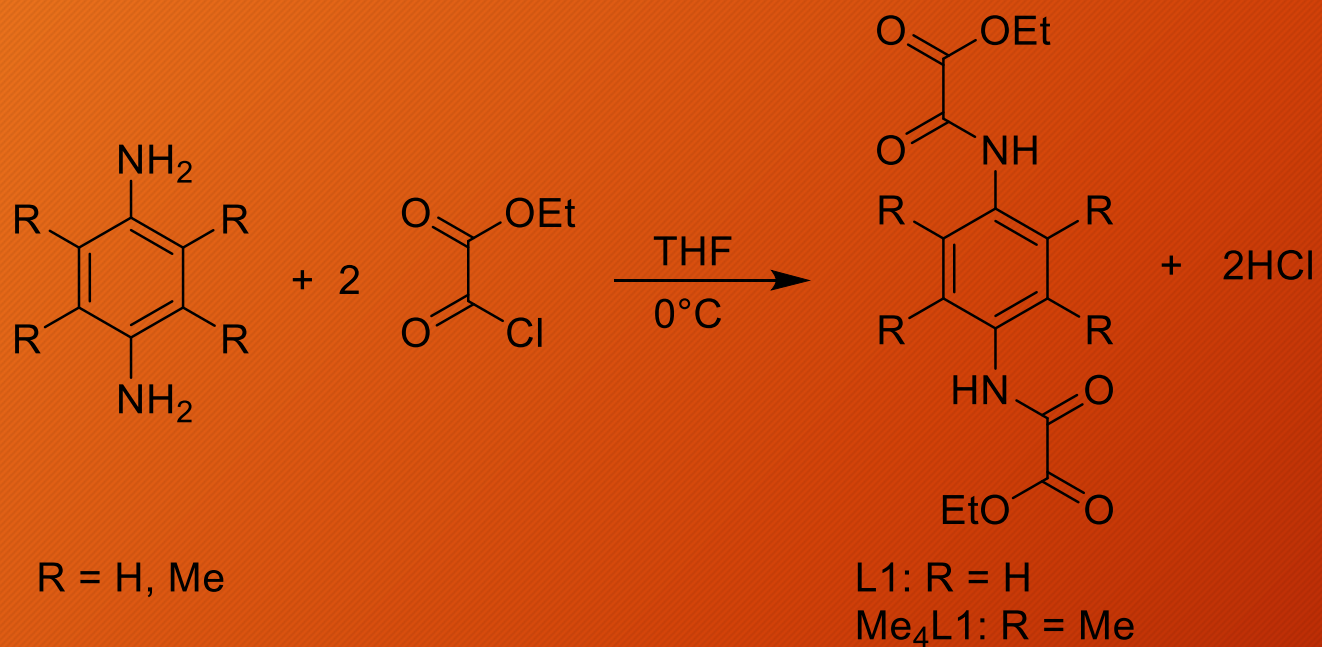
L2: R = H
Me₄L2: R = CH₃



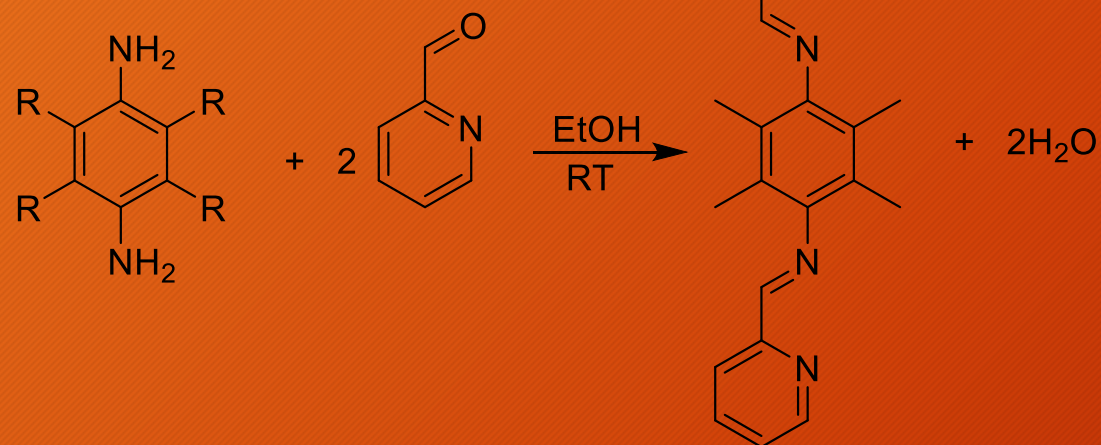
cis-L3

Ligand Synthesis

- The L1 type ligands are synthesized by a known method



Ligand Synthesis



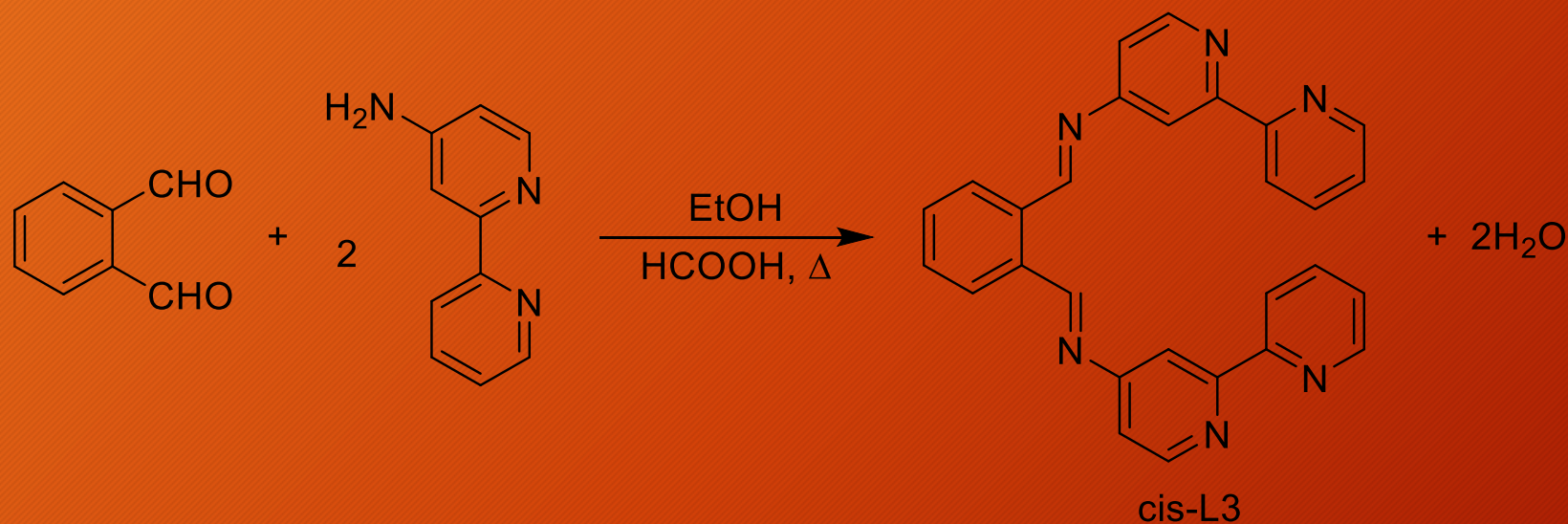
R = H, Me

L2: R = H
Me₄L2: R = Me

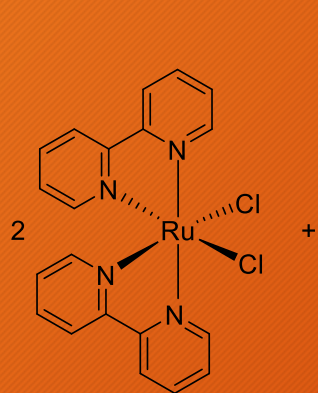
- L2 ligands are synthesized from the condensation of 2-pyridinecarboxaldehyde and phenylenediamines

Ligand Synthesis

- Cis-L3 is synthesized from phthalaldehyde and 4-amino-2,2'-bipyridine



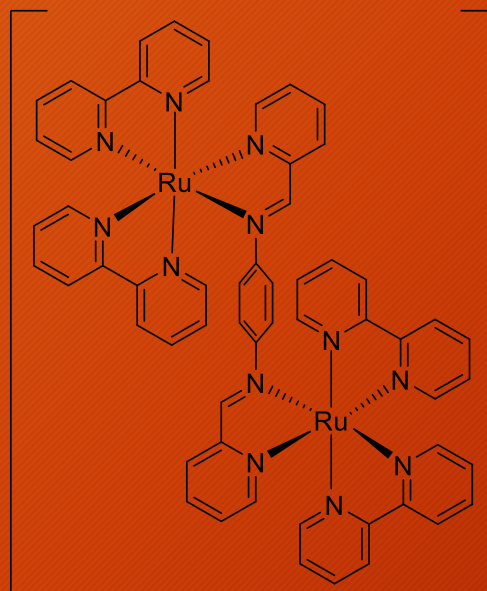
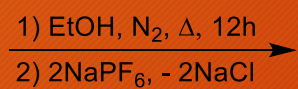
Diruthenium Complexes



$\text{RuCl}_2(\text{bpy})_2$

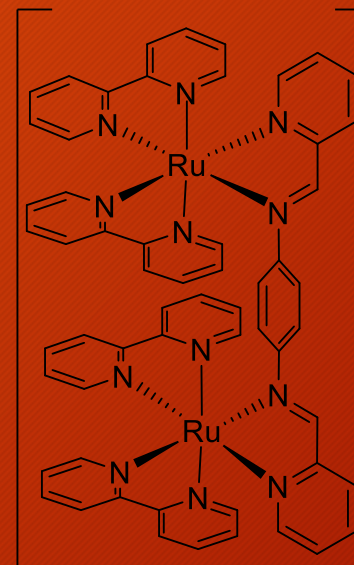


L2



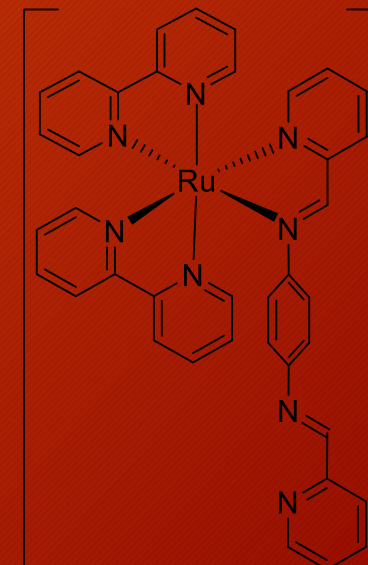
$\text{trans}-\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-L2})\}(\text{PF}_6)_4$

$(\text{PF}_6)_4$ +



$\text{cis}-\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-L2})\}(\text{PF}_6)_4$

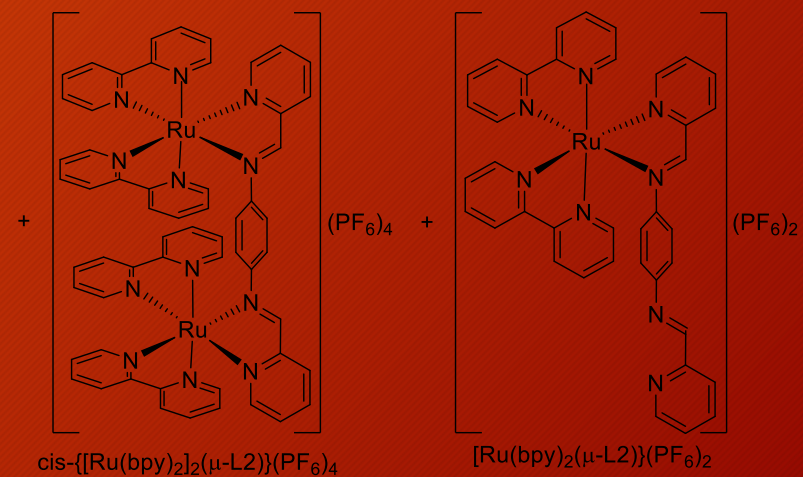
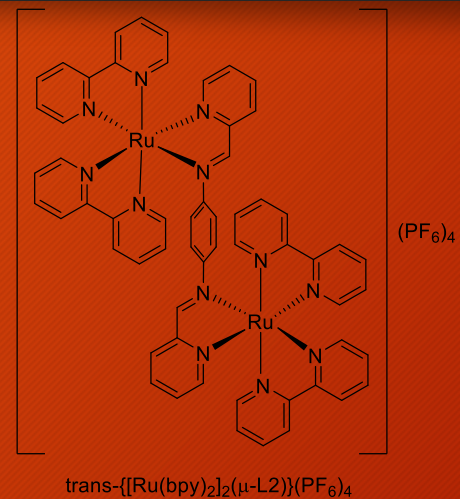
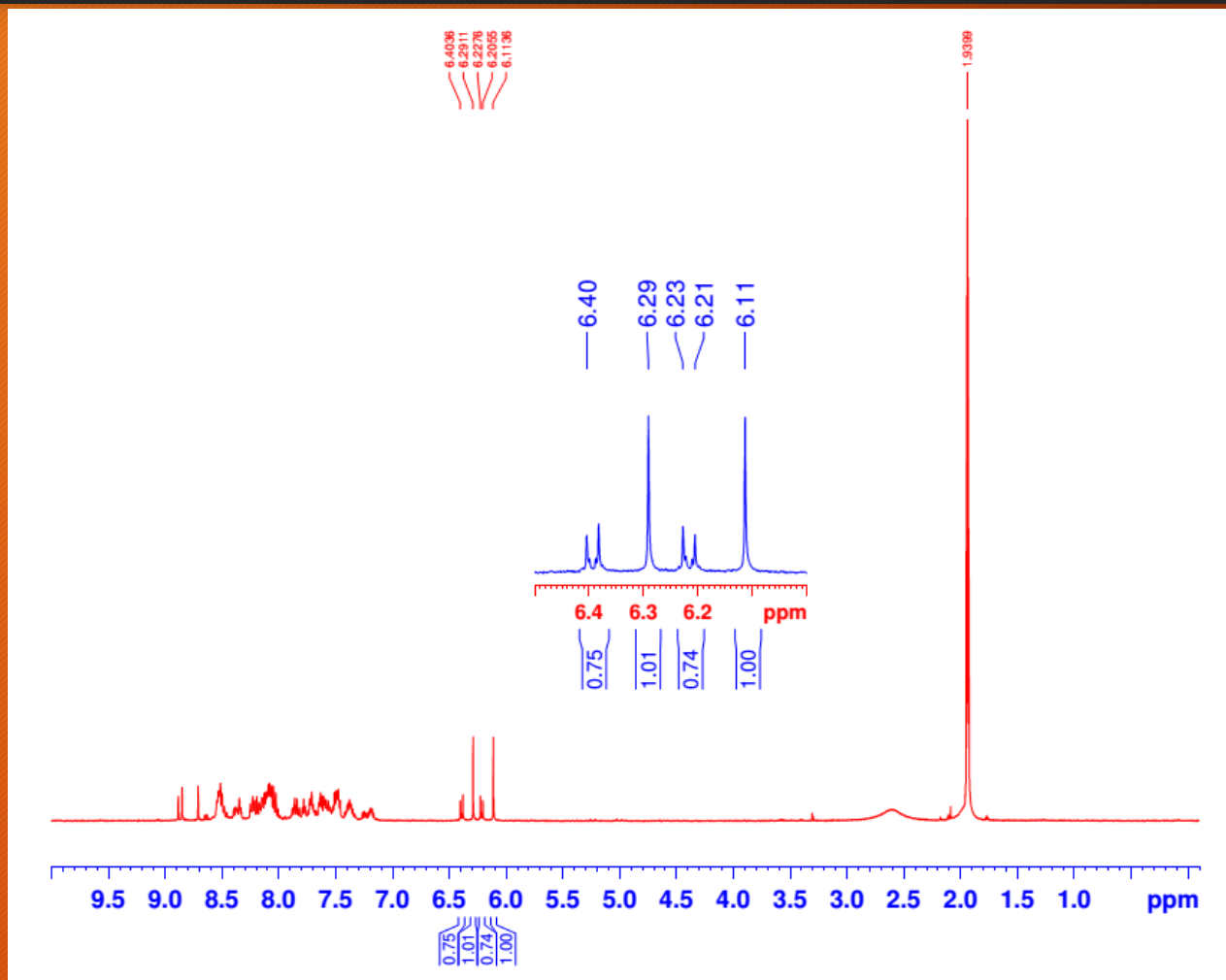
$(\text{PF}_6)_4$ +

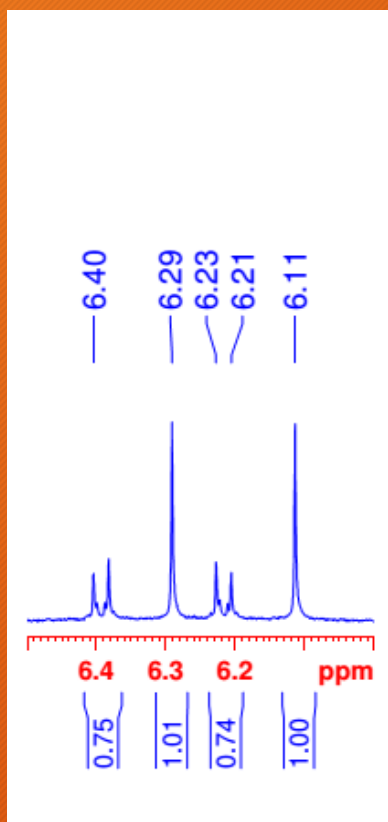
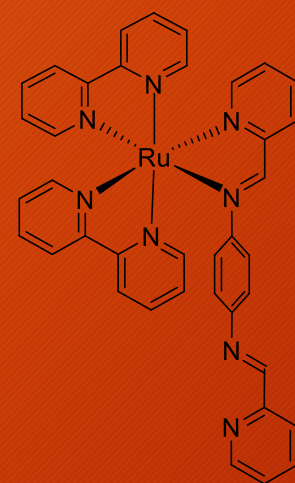
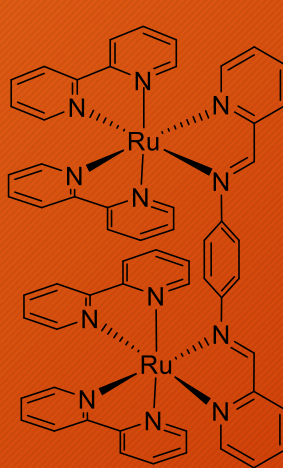
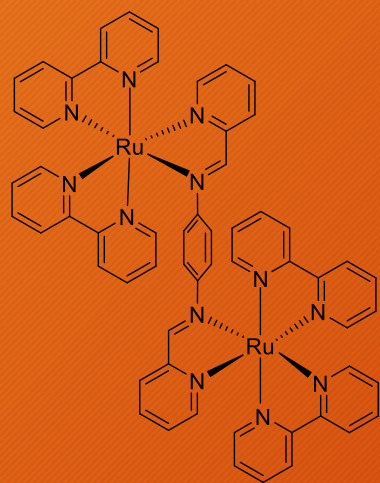


$[\text{Ru}(\text{bpy})_2(\mu\text{-L2})](\text{PF}_6)_2$

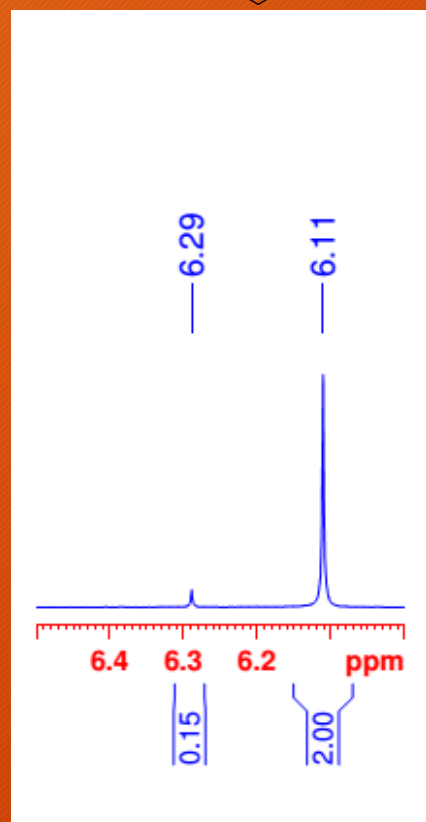
$(\text{PF}_6)_2$

^1H NMR for $\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-L2})\}(\text{PF}_6)_4$ Mixture

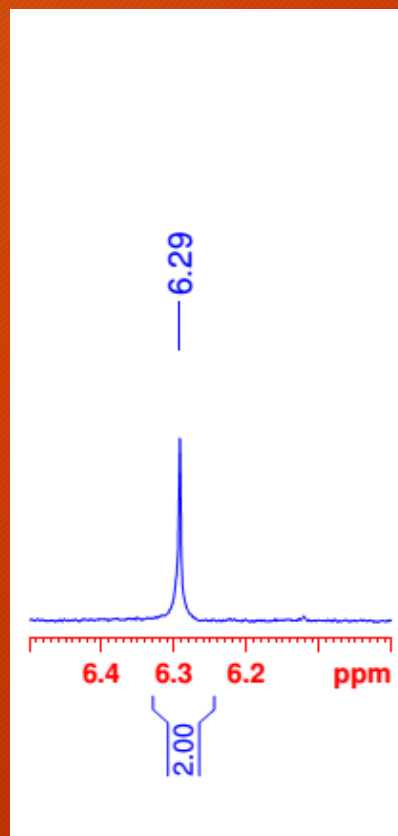




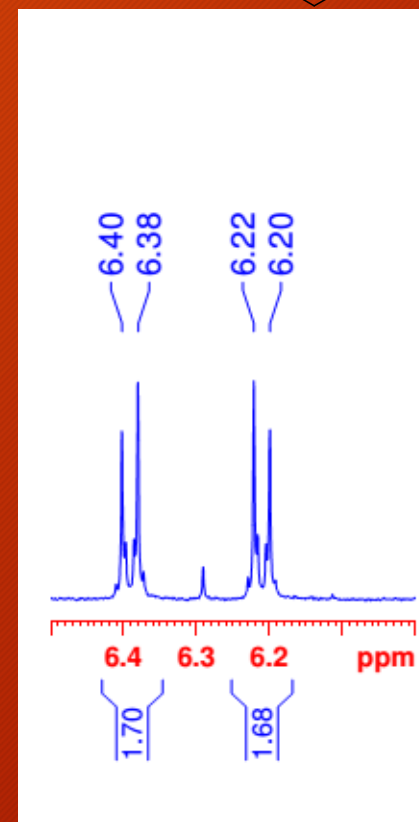
Mixture



trans dimer

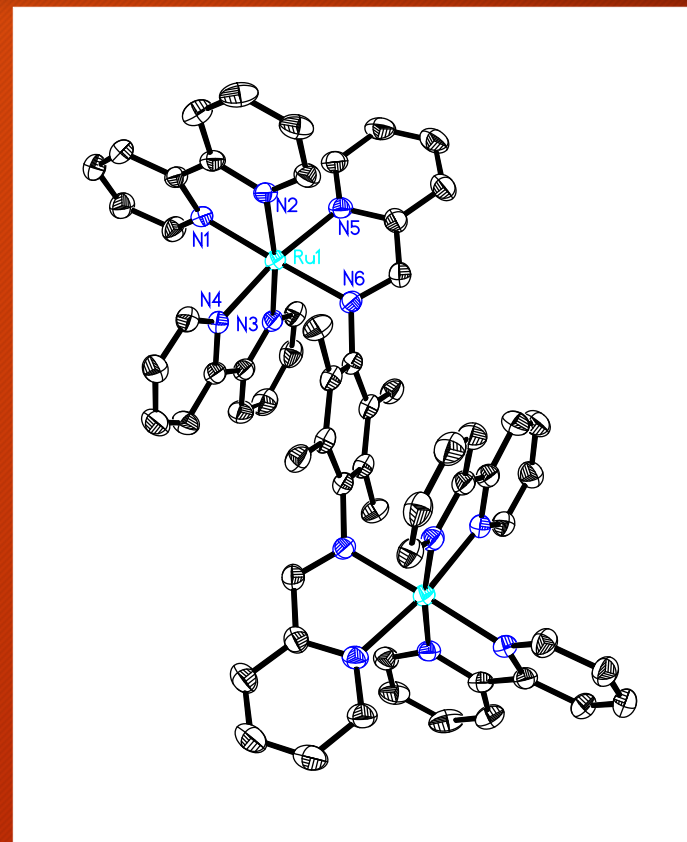
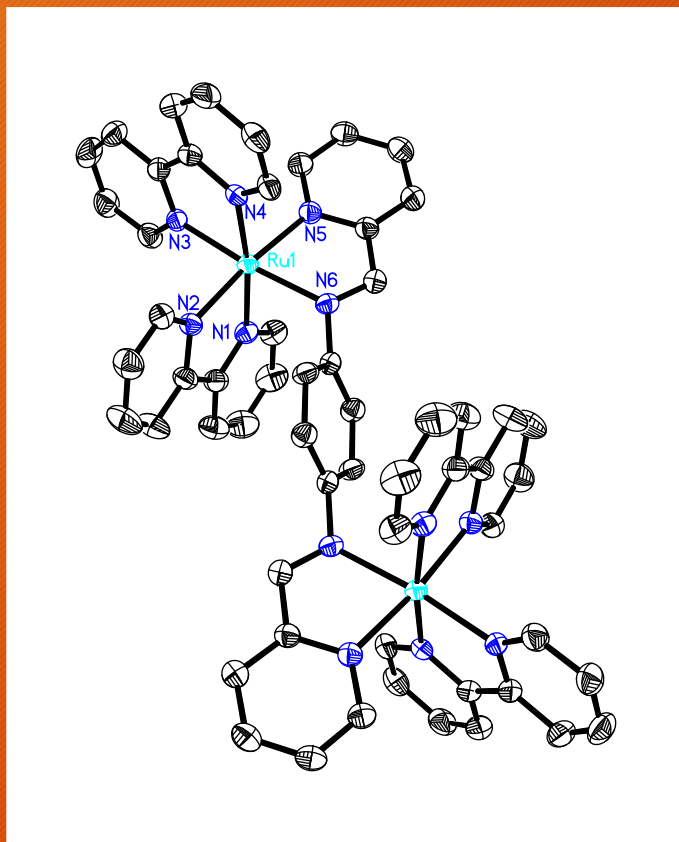


cis-dimer



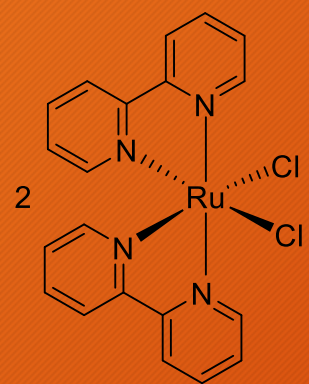
mono

Crystal Structures



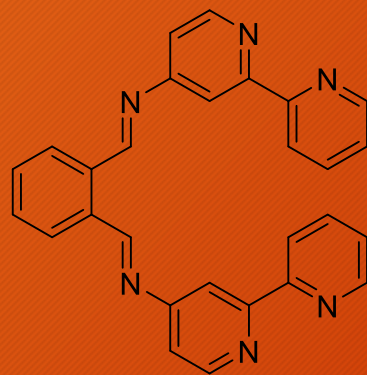
Views of $\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-L2})\}^{4+}$ and $\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-Me}_4\text{L2})\}^{4+}$ cations

Diruthenium Complex of cis-L3



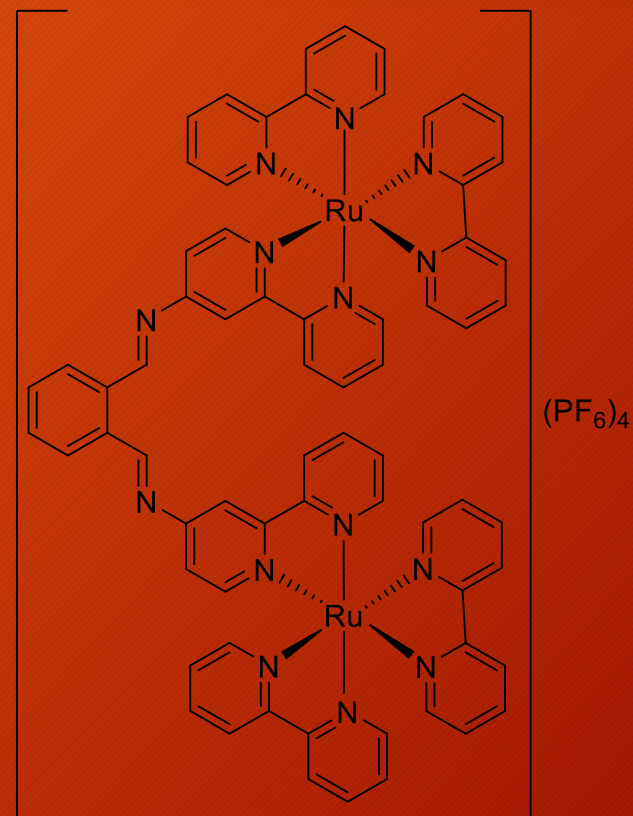
$\text{RuCl}_2(\text{bpy})_2$

+



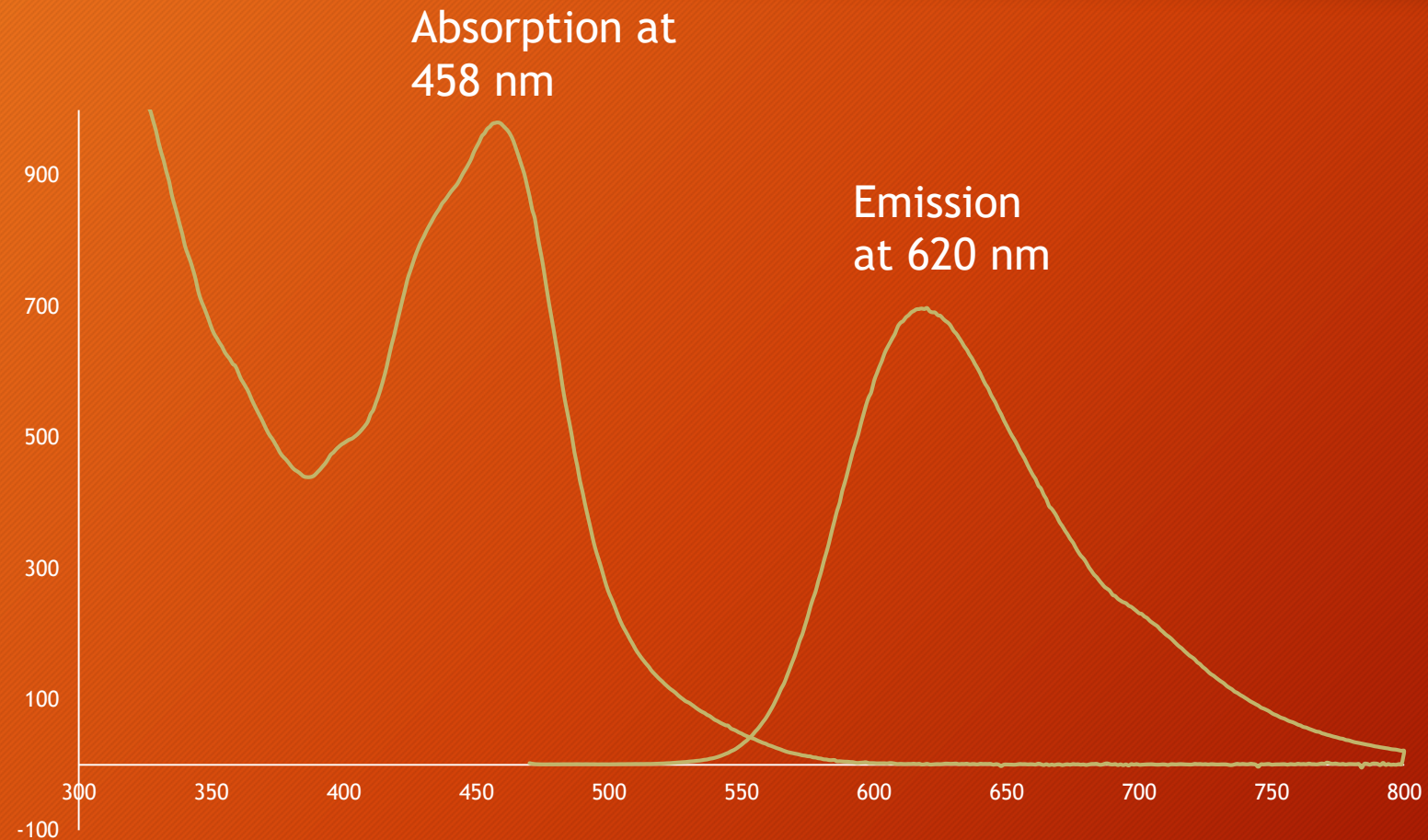
cis-L3

1) EtOH, N_2 , Δ , 12h
2) 4NaPF_6 , - 4NaCl



$\{[\text{Ru}(\text{bpy})_2]_2(\mu\text{-cis-L3})\}(\text{PF}_6)_4$

Absorption and Emission Spectra



Summary

- Three electronically communicative bridging ligands are used for the preparation of diruthenium compounds with two $[\text{Ru}(\text{bpy})_2]^{2+}$ chromophores
- The new diruthenium products are characterized by NMR spectra and in some cases by X-ray diffraction data
- One of the products is fluorescent
- Further studies will be needed to assess the photosensitizer properties of the new fluorescent product

Acknowledgement

- Wyoming NASA Space Grant Consortium
- Thank you for your attention