Ruthenium Polypyridyl Photochemistry
2,2'-Bipyridine

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

- The \([\text{Ru(bpy)}_3]^{2+}\) complex 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 $\Delta_0$ values and smaller $P$ values.

• Also, bpy is a strong-field ligand, which tends to produce large $\Delta_0$ values.

• As a result, [Ru(bpy)₃]²⁺ is a $d^6$ low-spin case, which is diamagnetic.

• [Ru(bpy)₃]²⁺ has two absorption bands at 428 nm and 454 nm with high extinction coefficients which have been assigned to *metal-ligand charge-transfer* (MLCT) transitions.

• 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*. 
Scheme 1. Stepwise synthesis of a tris-heteroleptic ruthenium(II) polypyridyl complex using the dichloro(p-cymene)ruthenium(II) dimer precursor.
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 ($m = 2S + 1$ where $S = 0$).

  \[ ^1M + h\nu \rightarrow ^1M^* \rightarrow ^1M + h\nu \]

- $^1M^*$ 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.

\[ ^1M + h\nu \rightarrow ^1M^* \rightarrow ^3M^* \rightarrow ^1M + h\nu' \]
Molecular Orbitals of $[\text{Ru(bpy)}_3]^{2+}$
Experimental and Computational UV-vis spectra for \([\text{Ru(bpy)}_3]^{2+}\)

- H-1 \rightarrow L+1 (28%)
- H-1 \rightarrow L+5 (40%)
- H-2 \rightarrow L+2 (30%)
- H-2 \rightarrow L+1 (28%)
- H-1 \rightarrow L+2 (26%)
- H-1/H-2 \rightarrow L (39%/40%)

Oscillator strength vs. Wavelength (nm)
Non-Innocent Ligand Architectures for Dye Sensitized Solar Cell Applications

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Splitting of $d$ orbital degeneracies: $O_h \rightarrow D_{4h}$

- From the correlation table that links the groups $O_h$ and $D_{4h}$ we see that the two $e_g$ orbitals of the octahedral field become non-degenerate as $a_{1g}$ and $b_{1g}$ in the tetragonal field.

- From the direct product listings in the $D_{4h}$ character table we see

  $a_{1g} = d2z^2-x^2-y^2 \quad (= dz^2)$

  $b_{1g} = dx^2-y^2$

- The degeneracy among the $t_{2g}$ orbitals in $O_h$ is partially lifted to become $b_{2g}$ and $e_g$ in the $D_{4h}$ tetragonal field.

- From the direct product listings in the $D_{4h}$ character table we see

  $b_{2g} = dxy$

  $e_g = (dxz, dyz)$
Relative Energies of $d$ orbitals in $D_{4h}$

- The relative energy ordering of the orbitals depends on the direction and magnitude of the tetragonal distortion.

- A distortion in which the two M-L bonds along $z$ are progressively stretched is an interesting case to consider, because at its limit the two ligands would be removed, resulting in a square planar ML$_4$ complex.

- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in $d$ orbitals that have substantial electron distribution along $z$.

- Thus the energies of the $dxz$, $dyz$, and $dz^2$ orbitals are lowered.

- If we assume that the stretch along $z$ is accompanied by a counterbalancing contraction in the $xy$ plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the $xy$ plane will experience increased repulsions.

- Thus, the $dxy$ and $dx^2$-$y^2$ orbitals rise in energy.
Orbital splitting from stretching tetragonal distortion

- The upper $e_g$ orbitals of the perfect octahedron split equally by an amount $\delta_1$, with the $dx^2-y^2$ orbital ($b_{1g}$ in $D_{4h}$) rising by $+\delta_1/2$ and the $dz^2$ orbital ($a_{1g}$ in $D_{4h}$) falling by $-\delta_1/2$.

- The lower $t_{2g}$ orbitals of the perfect octahedron split by an amount $\delta_2$, with the $dxy$ orbital ($b_{2g}$ in $D_{4h}$) rising by $+2\delta_2/3$, and the degenerate $dxz$ and $dyz$ orbitals ($e_g$ in $D_{4h}$) falling by $-\delta_2/3$. 

Increasing stretch along $z$