

Excited States in Organic Light-Emitting Diodes

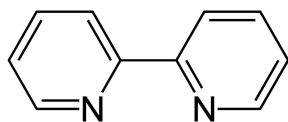
The metal-to-ligand charge transfer (MLCT) excited states of d_{π}^6 coordination compounds have emerged as the most efficient for solar harvesting and sensitization of wide-bandgap semiconductor materials.

Light absorption promotes an electron from the metal d orbitals to the Ligand (L_{π^*}) orbitals, $d_{\pi} - L_{\pi^*}$

A number of electric-dipole-allowed charge-transfer transitions are observed which give rise to intense absorption bands in the visible region with moderate extinction coefficients.

There is no formal spin for each excited state due to heavy-atom spinorbit coupling from the transition-metal center, especially for 4d and 5d metals.

The effects of spin-orbit coupling must be introduced in order to rationalize the relative oscillator strengths and absorption spectra of $[M(bpy)_3]^{2+}$ complexes, where $M = Fe(II), Ru(II)$ and $Os(II)$ transition metals, and bpy is the 2,2'-bipyridine ligand



bpy

The excited-state lifetime of $[Ru(III)(bpy)_2(bpy)]^{2+}$ is $\approx 1 \mu s$ in water. The radiative rate constant is typically about two orders-of-magnitude smaller than the non-radiative rate constant and hence the excited-state lifetime is controlled by the latter.

$Ru(II)$ - and $Os(II)$ -polypyridyl excited states have been shown to follow the **Energy Gap Law**, where the non-radiative rate constant increases exponentially with decreasing energy gap.

For this reason, it has proven to be difficult to prepare compounds that emit in the infrared region and have long-lived excited states.

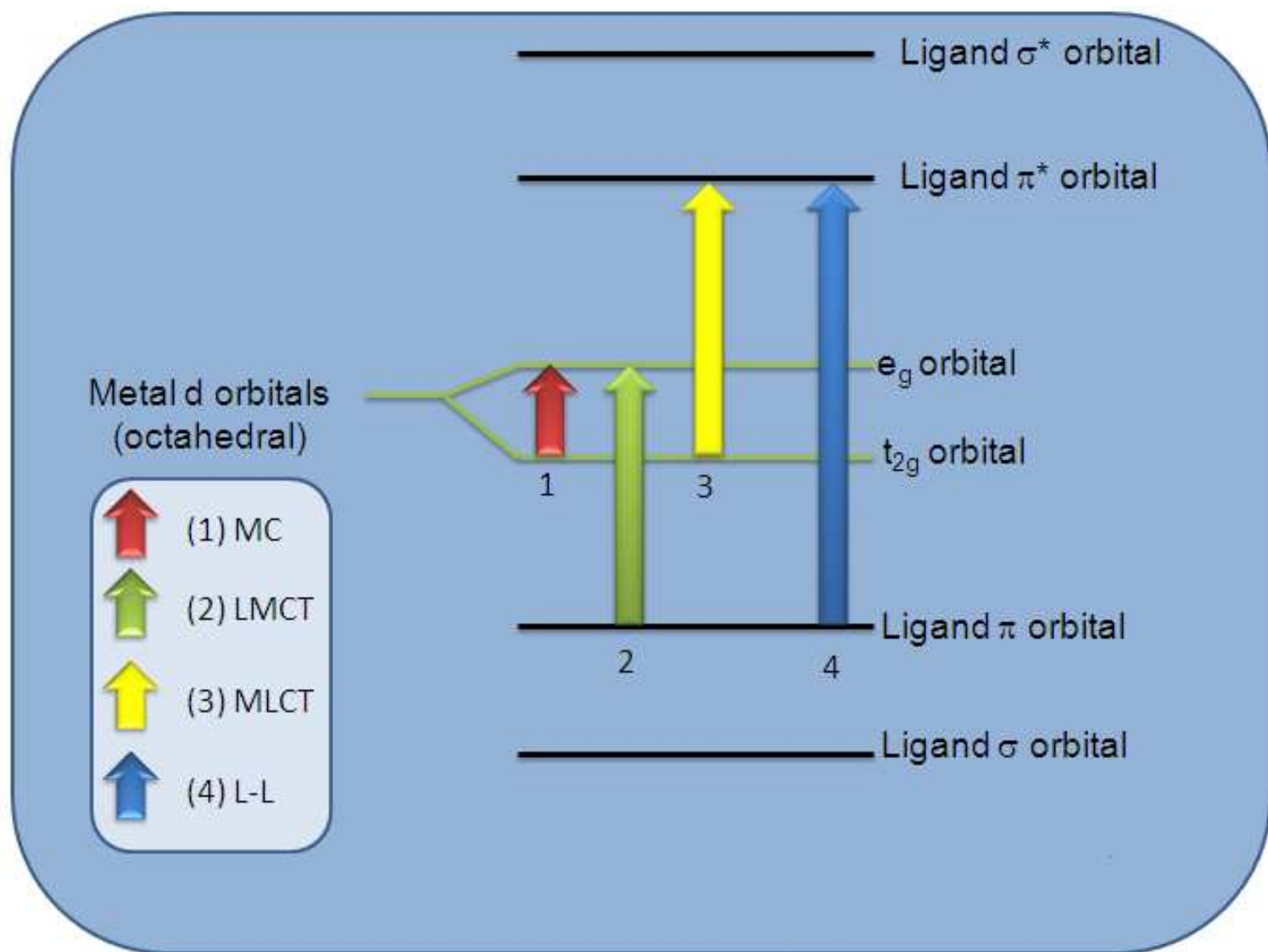
A large ligand-field splitting parameter is required for the observation of long lifetimes in this class of excited states. The presence of low-lying, ligand-field states can rapidly deactivate MLCT excited states and decrease excited-state lifetimes.

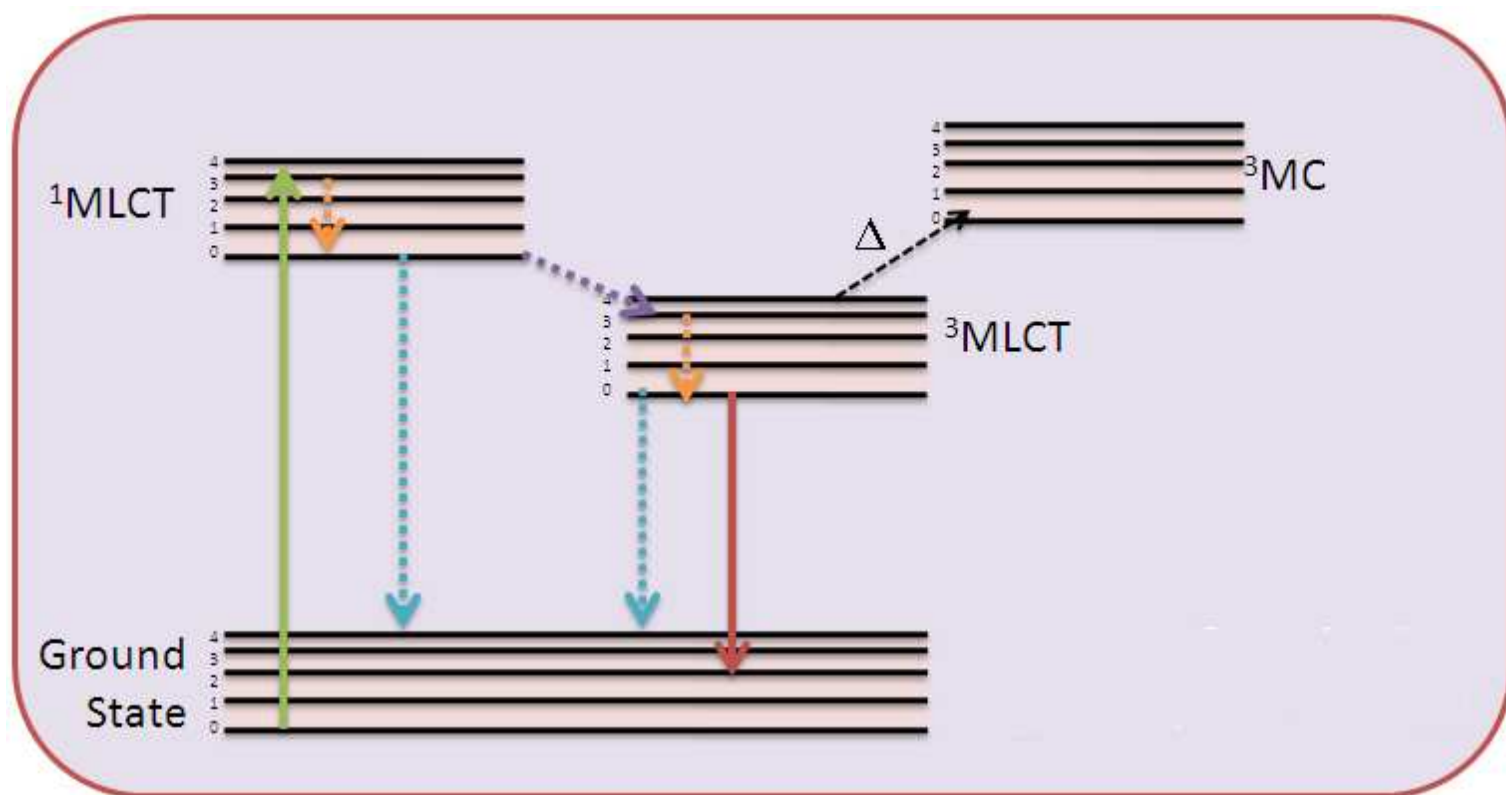
Electronic Properties of d_{π}^6 Coordination Compounds

The metal-to-ligand charge transfer (MLCT) excited states of d_{π}^6 coordination compounds have emerged as the most efficient for both solar cells and Organic Light-Emitting Diodes.

The focus will be on the redox potentials and absorption and emission spectra of $M(L)_6^{2+}$ compounds ($M = \text{Fe(II)}, \text{Ru(II)}, \text{and Os(II)}$), as well as Ir(III) complexes, where L includes various ligands.

Light absorption transitions in octahedral complexes: metal centered (MC); ligand-to-metal charge transfer (LMCT); metal-to-ligand charge transfer (MLCT); and ligand-ligand (L-L)

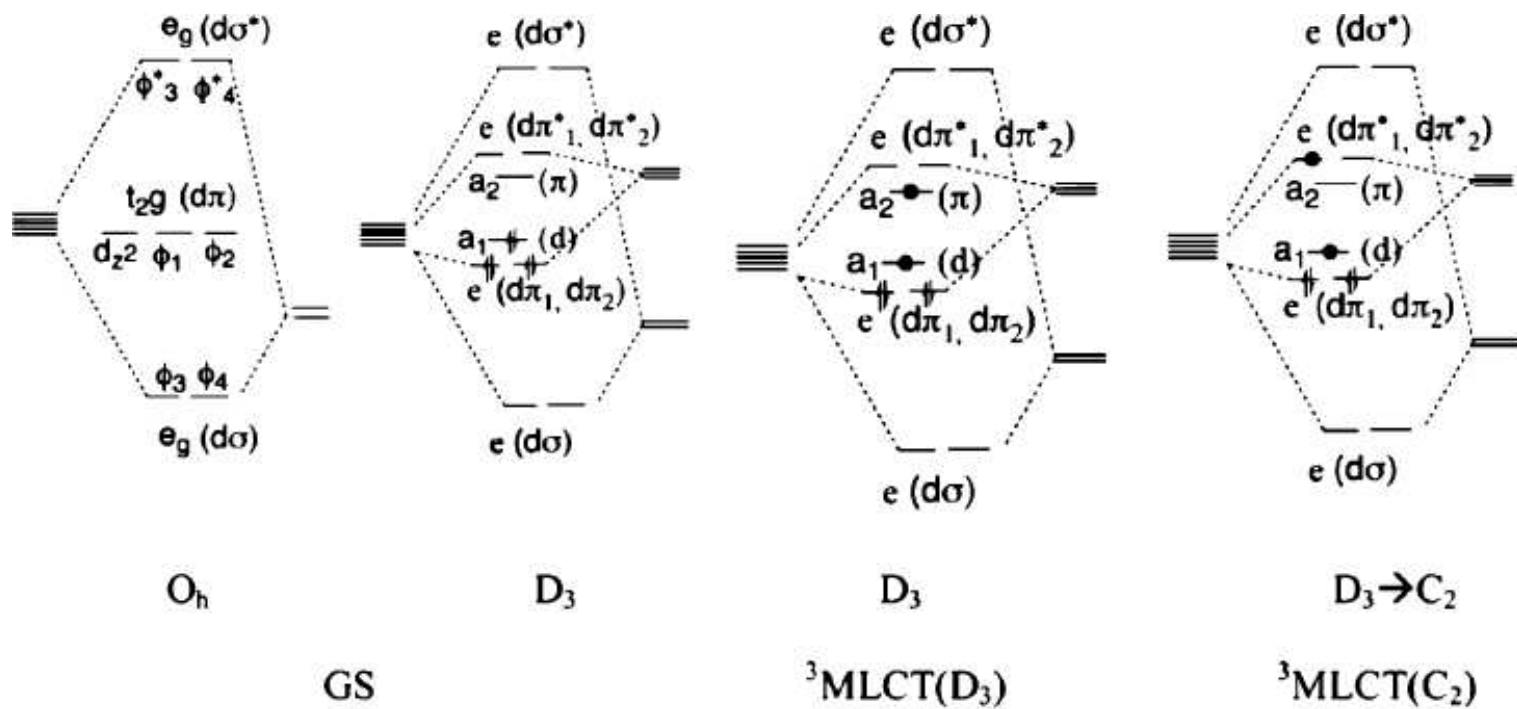




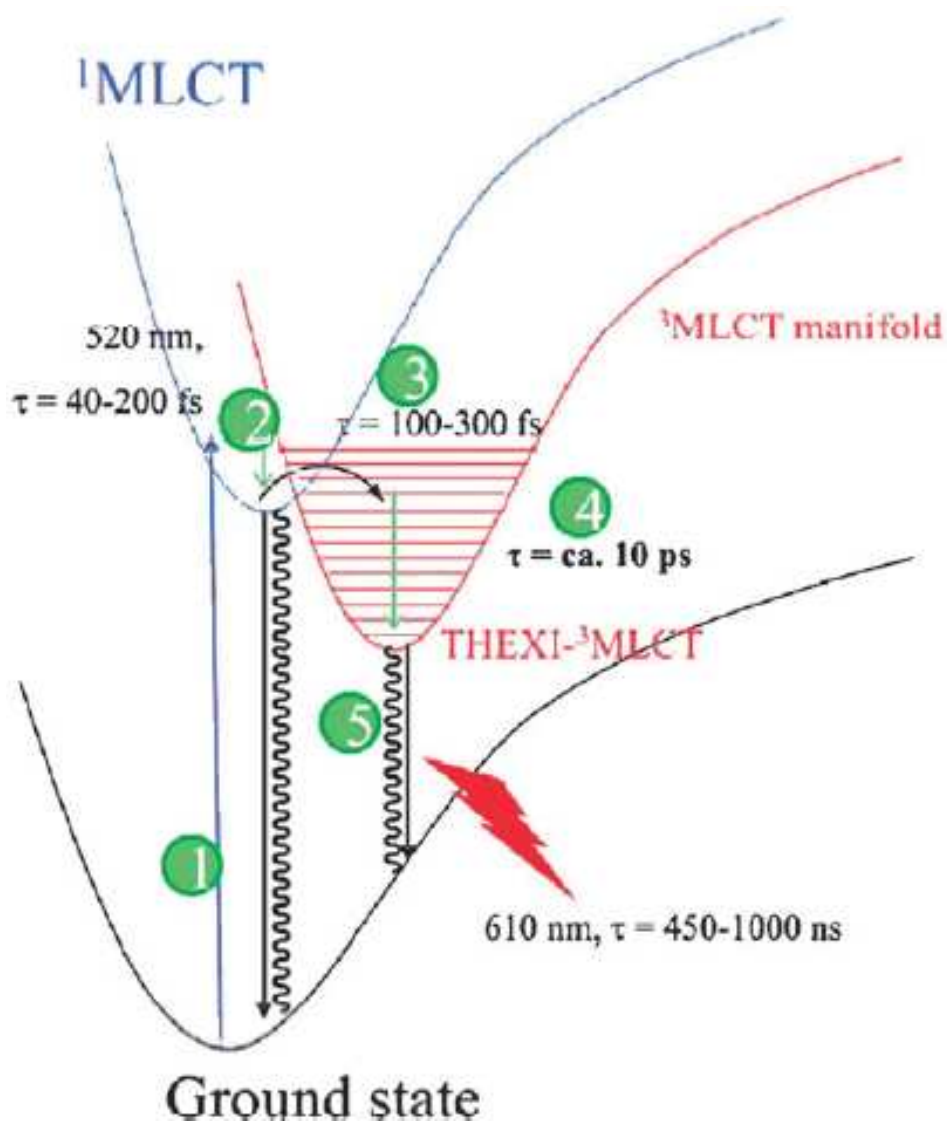
Jablonski diagram for a $\text{Ru}(\text{bpy})_3^{2+}$ complex. Solid lines indicate a radiative process while dashed lines indicate a non-radiative process.

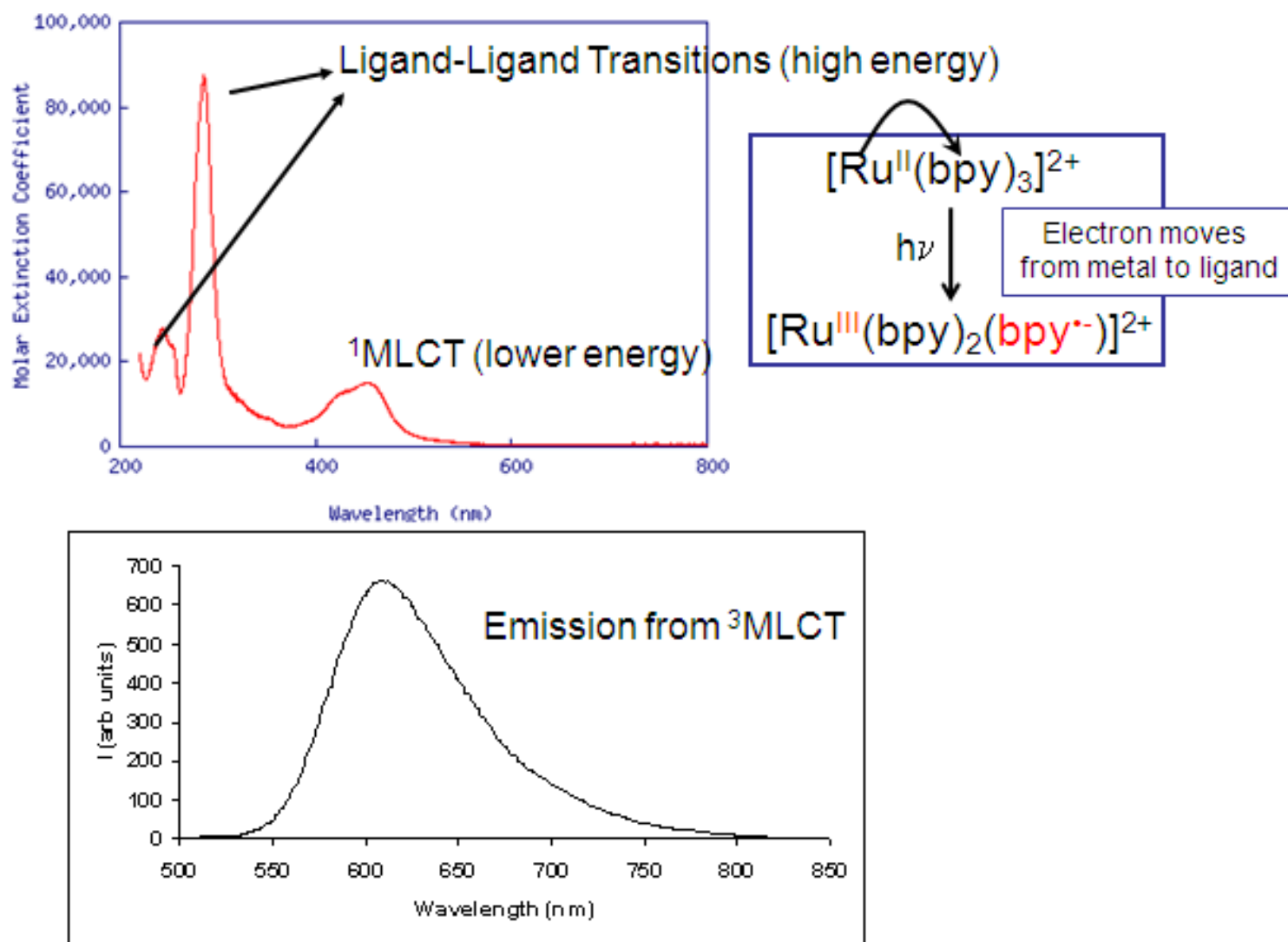
The effects of spin-orbit coupling must be introduced to explain the relative oscillator strengths and absorption spectra of these complexes.

Molecular Orbital Diagram for $\text{Ru}(\text{L})_6^{2+}$ Complexes In Their Ground State



Potential energy surfaces illustrating the relative electronic and vibrational lifetimes for $\text{Ru}(\text{bpy})_3^{2+}$. Both internal conversion thermal relaxation(2) and intersystem crossing(3) occur in the sub-picosecond time scale while the life-time of the *thexi* state(5) is up to a microsecond.





Absorption spectrum (top) and emission spectrum (bottom) for $\text{Ru}(\text{bpy})_3^{2+}$ in water. Ruthenium absorbs at 450 nm (2.8 eV) and emits strongly at ≈ 620 nm (≈ 2.0 eV) in water which is caused by a radiative process from the $^3\text{MLCT}$ state to the ground state.

Exercises

1. Calculate the low-lying triplet and singlet excited states of $M(\text{bpy})_3^{2+}$ ($M = \text{Fe}, \text{Ru}, \text{and Os}$).
Optimize the ground state in the gas phase, and calculate excited states in the gas phase, water, and acetonitrile at the optimized geometry.
2. Characterize the electronic transitions in terms of a molecular orbital diagram.
Discuss which transitions are allowed by symmetry and dipole polarization. How would changes in solvent polarity effect intensities of absorption and emission bands.
Compare your calculated results and experimental results in terms of solvent shifts.
3. Characterize the molecular orbitals that are active in yielding the low-lying excited states with respect to the mixture of MLCT and LC components.

Below is an example of a table that can be constructed in reporting results on excited states.

$\lambda(\text{nm})$		f		$\psi_i \rightarrow \psi_j$	Character of Excitation	Assignment of Excitation
State	Exptl	Calcd	Calcd	TDDFT		
T ₁	489	490		0.58 (125 \rightarrow 126) - 0.29 (125 \rightarrow 128)	(MLCT + L), L'	$d_\sigma + \pi_{\text{ppy}} \rightarrow \pi_{\text{ppy}}^*$
S ₁	448	436	0.0505	0.62 (125 \rightarrow 126) + 0.28 (125 \rightarrow 128)	(MLCT + L), L'	$d_\sigma + \pi_{\text{ppy}} \rightarrow \pi_{\text{ppy}}^*$
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4. Obtain absorption, fluorescence, and phosphorescence band shapes for the salient excited states.
5. The emission lifetimes for $M(\text{bpy})_3^{2+}$ ($M = \text{Fe}, \text{Ru}, \text{and Os}$) are given in the table below:

Complex	Lifetime (ns)
$\text{Fe}(\text{bpy})_3^{2+}$	< 1
$\text{Ru}(\text{bpy})_3^{2+}$	~ 620
$\text{Os}(\text{bpy})_3^{2+}$	~ 20

Examine the radiative and non-radiative properties of these ions in terms of rapid and quantitative internal conversion/intersystem crossing through ligand-field states. Explain the experimental emission and non-emission lifetimes by considering calculated energy gaps in the d-orbital manifold, d_π - L_π^* interaction, and solvent shifts.

Does the trend in d-orbital energies for this series of complexes follow the **Energy Gap Law**? Explain.

Why is the excited-state lifetime of $\text{Os}(\text{bpy})_3^{2+}$ so much shorter than that of $\text{Ru}(\text{bpy})_3^{2+}$, and why is the excited state lifetime of $\text{Fe}(\text{bpy})_3^{2+}$ so short?

6. Examine a structural distortion where M-L bonds are shortened or lengthened to assist in understanding absorption, fluorescence, and phosphorescence of these ions.