

RUTHENIUM

Coordination compounds containing ruthenium, particularly Ru(II) polypyridine complexes, are the group of transition metal complexes which have been studied most intensively from a photochemical point of view. It is an exceptional combination of chemical stability, redox properties, luminescence emission, excited-state lifetime and excited-state reactivity which led many researchers to pursue these types of compounds. Ruthenium polypyridine complexes are good at absorbing visible light; they have relatively intense and long-lived luminescence, and can undergo reversible redox processes in both the ground and excited states. The prototype compound $[\text{Ru}(\text{bpy})_3]^{2+}$ has certainly been studied at length and widely used in research laboratories during the last 30 years. Ru(II) polypyridine complexes have contributed a great deal to the development of all branches of photochemistry and photophysics, electrochemistry, electro-generated chemiluminescence, and electron and energy transfer. They are also favoured for the preparation and investigation of supramolecular assemblies as light-harvesting antennae or luminescent sensors, etc. 20 years ago GRATZEL et al. published a photovoltaic device with a ruthenium dye as sensitizer for mesoporous TiO_2 . with conversion efficiencies around 7 %. Since then the number of investigated dyes and devices increased nearly exponentially. It is therefore only natural that there are several exhaustive reviews dealing with Ru(II) polypyridine.

STRUCTURE AND BONDING

The bipyridine ligands are usually colourless compounds which have σ -donor orbitals localized on the nitrogen atoms and the π -orbitals are more or less delocalized on the aromatic rings. The metal centre Ru^{2+} is a d^6 system displaying an octahedral coordination sphere binding three bpy ligands. The structure of the prototype compound $[\text{Ru}(\text{bpy})_3]^{2+}$ is shown in Figure 1-4.

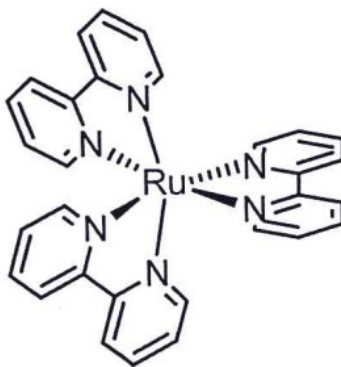


Figure 1-4 Structure of $[\text{Ru}(\text{bpy})_3]^{2+}$.

ABSORPTION SPECTRUM AND EXCITED STATES

Figure 1-5 displays the absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the proposed assignments. Most intense are the high energy bands which are ligand centred (LC) at 185 nm (not shown in the figure) and 285 nm.

They result from spin-allowed LC $\pi \rightarrow \pi^*$ transitions. The two remaining less intense bands at 240 and 450 nm originate from spin-allowed metal-to-ligand charge transfer (MLCT) $d \rightarrow \pi^*$ transitions. The shoulders at 322 and 344 nm are speculated to be metal-centred (MC) transitions.

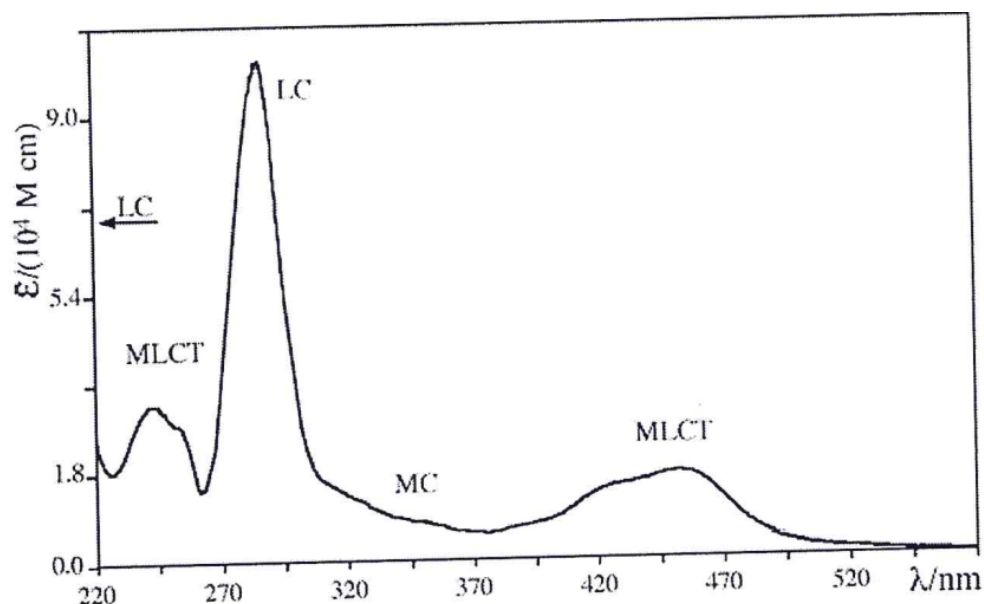
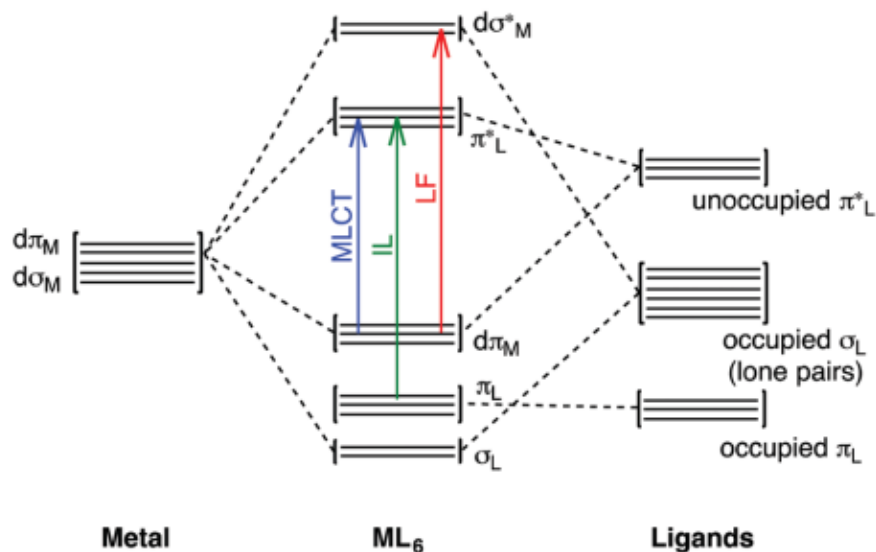


Figure 1-5 Electronic absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in alcoholic solution.²⁷

Scheme 4 shows a simplified molecular orbital diagram to describe the most important transitions in $[\text{Ru}(\text{bpy})_3]^{2+}$. A single-configuration one-electron description of the excited one electron from a π_M metal orbital to π_L^* ligand orbitals which results in MLCT excited states.

MC excited states are possible when an electron is promoted from π_M to σ^*M orbitals.

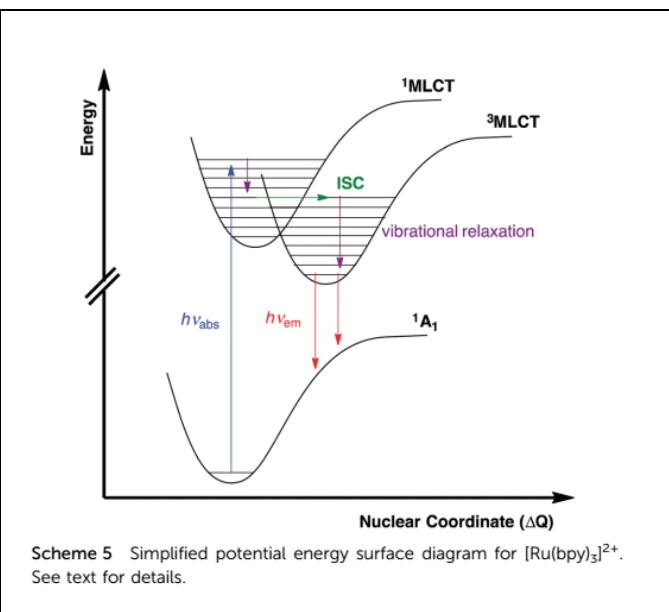
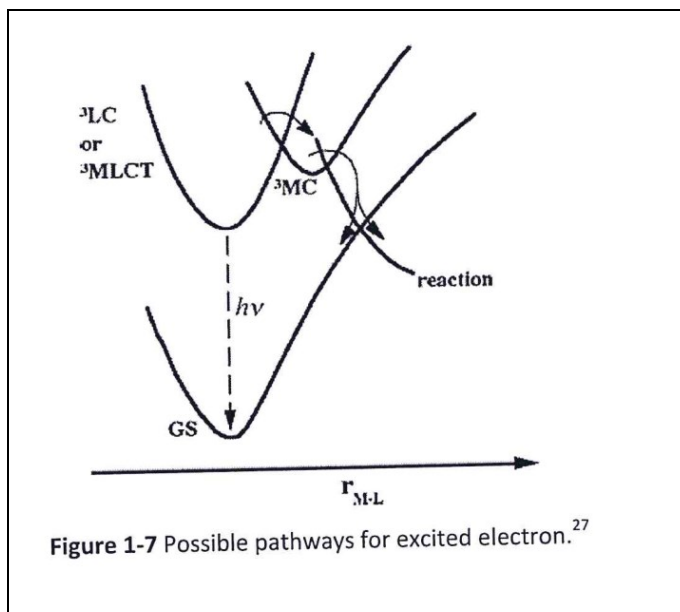
LC excited states can be obtained by promoting an electron from π_L to π_L^* . It is established that all these excited states may have singlet or triplet multiplicity, respectively, although spin-orbit coupling due to the heavy metal centre causes large singlet-triplet mixing, predominantly in MC and MLCT excited states



Scheme 4 Simplified molecular orbital diagram for an octahedral compound with π -acceptor ligands. The three main types of electronic transitions typically observed in metal polypyridyl complexes are indicated by the arrows.

EMISSION PROPERTIES

In d^6 octahedral complexes the MC excited states are strongly displaced compared to the ground-state geometry and metal-ligand vibration coordinates. Therefore MC excited states usually undergo fast radiationless dissipation to the ground state and/or ligand dissociation reactions (Figure 1-7) and no luminescence emission can be observed.



On the other hand, LC and MLCT excited states are usually similar in geometry and bond distances to the ground state. Relaxation can then result in photon emission (Scheme 5). The properties of the excited state in a $[\text{Ru}(\text{bpy})_3]^{2+}$ depend very much on the orbital nature of its lowest excited state. The energy positions of the MLCT and LC excited states depend on the ligand field strength, the redox properties of metal and ligands, and intrinsic properties of the ligands. It is therefore possible to vary the emissive properties by the introduction of functionalized ligands. The design of complexes with desired properties is possible at least to a certain degree.

QUENCHING OF THE $^3\text{MLCT}$ EXCITED STATE:

Energy and Electron Transfer Processes

The possibility of using the long-lived excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ as an energy donor in energy transfer processes is a reason for the early interest in its photochemistry. Hundreds of bimolecular excited-state reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ and of its derivatives have been studied in detail. The most common energy transfers are summarized in the diagram shown in Figure 1-8.

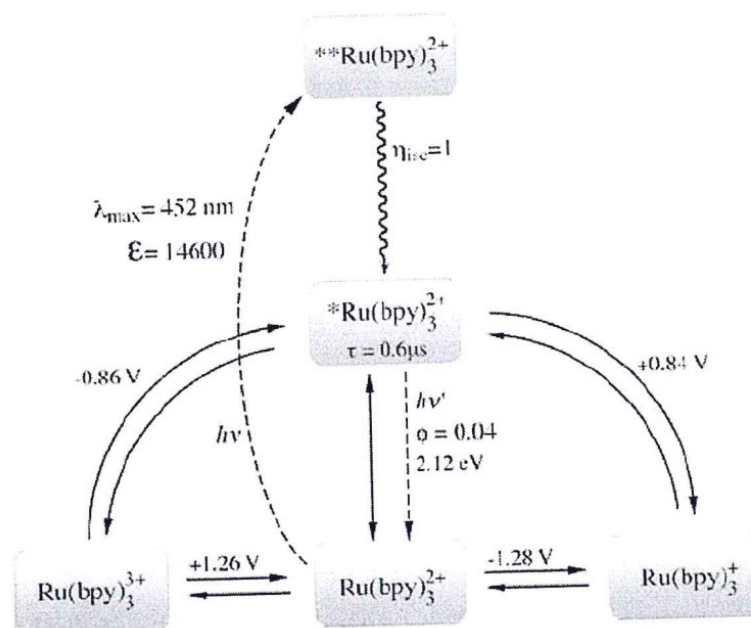


Figure 1-8 Energy and electron transfer processes of $[\text{Ru}(\text{bpy})_3]^{2+}$. $^{**}\text{Ru}(\text{bpy})_3^{2+}$ indicates higher-energy spin-allowed excited states and $^*\text{Ru}(\text{bpy})_3^{2+}$ indicates the lowest spin-forbidden excited state ($^3\text{MLCT}$). Reported potentials are in aqueous solution vs. SCE.²⁷

The lowest $^3\text{MLCT}$ excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ lives long enough to encounter other solute molecules and possesses suitable properties to play the role of energy donor, electron donor, or electron acceptor.

Synthesis

Weigh approximately 0.1g of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ and add to the round bottom flask. Weigh approximately 96.8 mg of 2,2'-bipyridine and add to the round bottom flask. Add 20ml of a 70/30 solution of Ethanol/ water and set up the reflux condenser to the round bottom flask. Place Nitrogen flow at the top of the condenser and heat the solution to boiling. Reflux the solution for 30min (note the color change) and check the reaction by TLC.

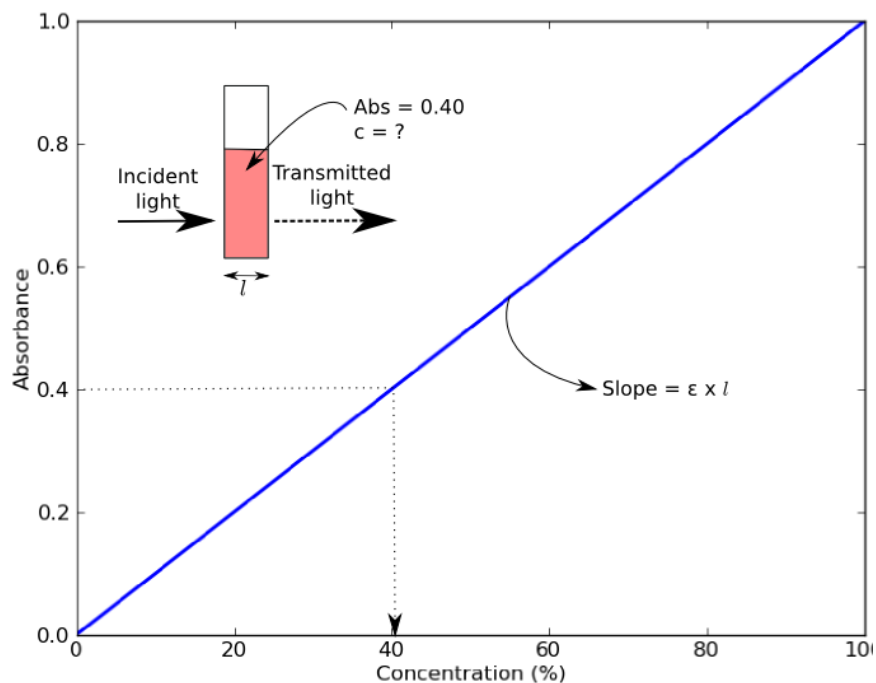
When it is completed ,allow solution to cool and filter the reaction mixture to remove unreacted ligand and impurity (metal oxide) and reduce the volume by rotary evaporation.

Dissolve the complexes synthesized in water and add CH_2Cl_2 . Use funnel extractor to remove the complexes $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ eventually present in the organic phase. The complex $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$

in water is converted to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ by adding saturated water solution of NH_4PF_6 , the insoluble product formed is collect by filtration on glassy frit, rinse with water and then ether.

Molar absorption coefficient

Beer's Law states that molar absorptivity is constant (and the absorbance is proportional to concentration) for a given substance dissolved in a given solute and measured at a given wavelength. For this reason, molar absorptivities are called molar absorption coefficients or molar extinction coefficients. Because transmittance and absorbance are unitless, the units for molar absorptivity must cancel with units of measure in concentration and light path. Therefore, molar absorptivities have units of $\text{M}^{-1}\text{cm}^{-1}$.



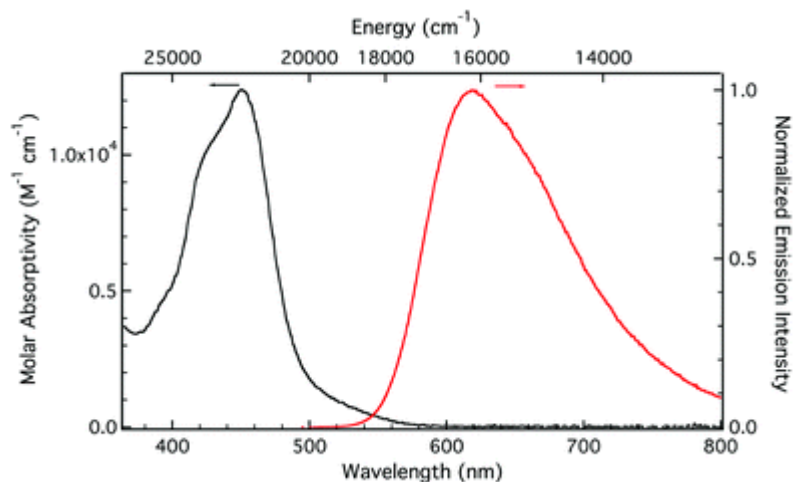
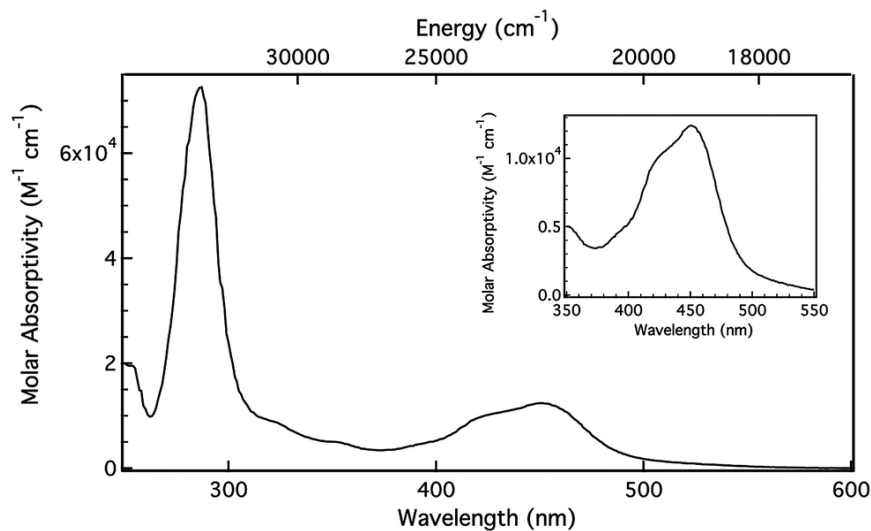
Prepare a stock solution of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in ACN by dissolving approximately 5 mg of complex in 10ml ACN Use the stock solution of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in ACN to prepare 4 different dilute solution , (the more concentrated with value of absorbance max 1 calculated using $15000 \text{ M}^{-1} \text{ cm}^{-1}$ as hypothetical value of extinction coefficient)

. For each solution collect the UV vis spectra in the MLCT range, after alignment of all spectra collect value the absorbance at 450nm. Plot the absorbance in function of concentration of solution and the slope of your absorption spectrum would be your extinction coefficient.

Absorption and emission

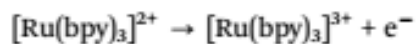
Use the dilute solution to collect a UV Vis spectrum, emission spectrum ($\lambda_{\text{exc}} = 450\text{nm}$) and excitation spectrum of the complexes.

Plot in the same graph the UV Vis spectrum and emission spectrum, after normalization to get the value of energy E^{00} in



Cyclic voltammetry

Cyclic voltammetry is the most common way to measure the ground-state redox potentials of a compound; the cyclic voltammogram for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in acetonitrile solution is shown in Fig.1. The oxidation of the metal center occurs at ~ 1 V (referenced to the ferrocene/ferrocenium couple).



Three reductions are also observed, all of which correspond to one-electron reductions of each of the three ligands in succession.

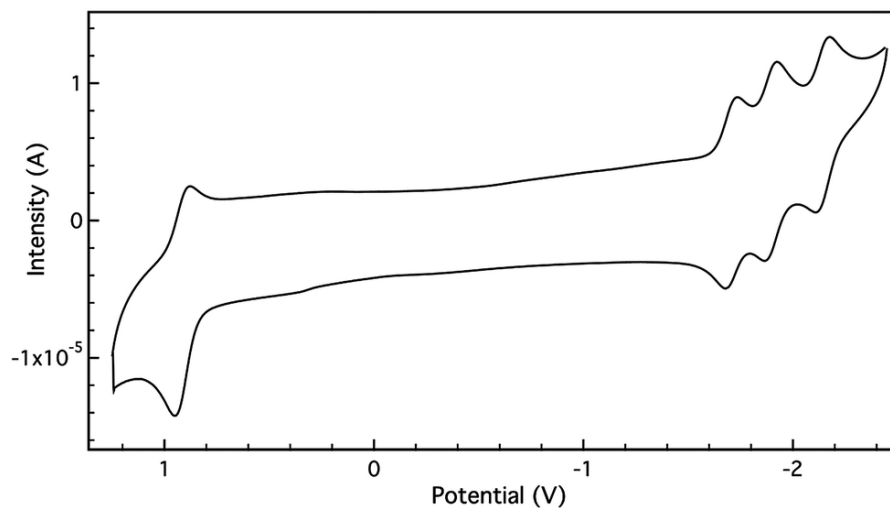
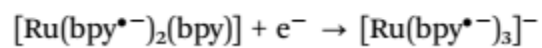
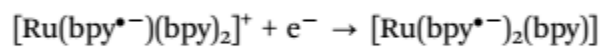
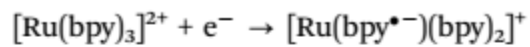


Fig. 1 Cyclic voltammogram of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in CH_3CN , using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. Potentials are referenced to the ferrocene/ferrocenium couple.