

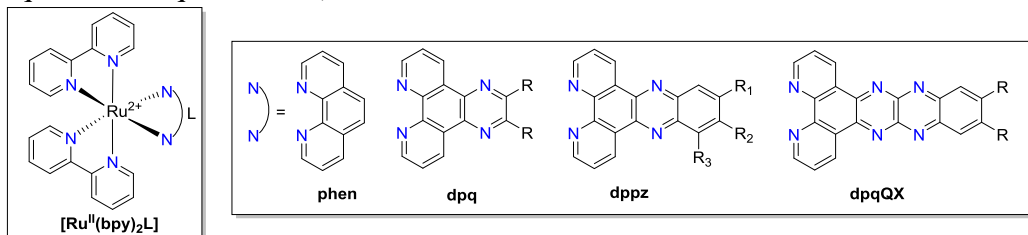
## Investigation of the valence shell of Ru(II) polypyridil complexes by UV vacuum absorption and XEOL

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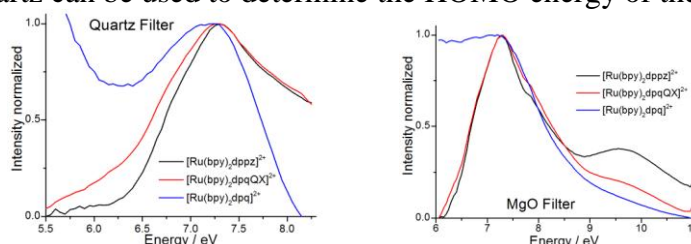
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There are many interests in ruthenium (II) polypyridil complexes due to their chemical stability, rich electrochemistry, high absorption in the UV-visible region dominated by intense ligand-centered  $\pi \rightarrow \pi^*$  bands and metal-to-ligand charge-transfer (MLCT) bands, luminescence characteristics and long lived excited states that make this class of compounds an important target for several applications as dye sensitizer solar cells (DSSC), photocatalysts, bimolecular sensors, artificial photosynthesis and light emitter devices. We are interested in the chemistry of  $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{L}]$  class, where bpy = 2,2'-bipyridine, and L are heterocyclic polyconjugate ligands derivate from 1,10-phenanthroline (see scheme 1), these ligands are divided in three different classes in this work: dpq (dipyridoquinoxaline), dppz (dipyridophenazine) and dpqQX (dipyridoquinoxalinoquinoxaline).<sup>1</sup>



**Scheme 1.** General structure of the studied compounds.

The preliminary results correlated well with our previous photophysical and electrochemical results. The Figure shows the absorption spectra of the 3 main compounds studied. The spectra collected with the quartz can be used to determine the HOMO energy of these compounds.



**Figure 1.** TEY spectra at the valence region of some selected compounds.

DFT calculation were performed at PBE0/def2-TZVP/COSMO level and correlated with the collected TEY spectra. The XEOL spectra were obtained for all compounds and it was observed that the most intense emission occur in the compounds that have large quantum yield in solution. In summary TEY and XEOL are very important techniques to study the electronic structure of ruthenium polypyridil compounds at the valence shell.

[1] F. S. Miranda, et. al., Tetrahedron 64, 5410 (2008).

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