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Promising complexes in light-directed therapies: Investigation of the photochemical properties of new ruthenium polypyridyl complexes

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Ruthenium (II) polypyridyl complexes have several photochemical and photophysical properties, which allow these complexes to be studied as potential metallodrugs in photodynamic therapy (by generation of $^1O_2$), DNA photocleavage and promising candidates in solar cells as sensitizers.[1,2] It is well established in the literature that compounds of $[Ru(bpy)_2XY]^{n+}$ type are capable of undergoing photodissociation of monodentate ligands.[3] The ^{3}MLCT state, which is accessed by intersystem crossing from a higher energy ^{1}MLCT excited state, can be deactivated through emission, non-radiative decay or through the population of the d-d excited state, thus contributing to ligands dissociation. One of the most popular applications for compounds with these properties is their use in light-based therapy, such as photoactivated chemotherapy (PACT) and photodynamic therapy (PDT).[4] In PACT, the activation of the prodrug occurs when the metallic excited state is occupied, causing photosubstitution of ligand.[4] In PDT, decay occurs from an excited triplet state of energy, which, being similar to $^3O_2$, is able to transfer this energy to form $^1O_2$. [4] This work presents the synthesis, characterization and chemical properties of new coordination complexes of formula $[Ru(bpy)_2(L)_2](PF_6)_2$ where bpy= 2,2'-bipyridine and L = 5-aminoisoquinoline (NH_2-iq)-**(1)** and 5,6,7,8-tetrahydroisoquinoline(thiq)-**(2)**, which are candidates for light-directed therapies. The syntheses were carried out according to adapted procedures described in the literature,[5] and the products were characterized by electronic and emission spectroscopy, FT-IR, NMR and XRD (figure 1a). The complexes show strong absorption in the visible region of the spectra with $\lambda_{máx}$ close to 450 nm and ε=7300 $M^{-1}cm^{-1}$ assigned to MLCT, and phosphorescence emission at $\lambda_{máx}$ = 333 nm for **(1)** and 630 nm for **(2)**. The emission observed at 333 nm is attributed to the free ligand 5-aminoisoquinoline, which is a product of the photosubstitution of the complex **(1)**. It was also observed that the compounds are very photosensitive in solution when subjected to white light, which leads to the photosubstitution of **L** in the coordination sphere of the complex, producing the solvato complexes $[Ru(bpy)_2(L)(ACN)]^{2+}$. For the complex **(2)**, a rate constant (k_{obs}) was calculated for its photosubstitution with a value of 3.64×10^{-4} s^{-1} (figure 1b). The next steps in this work are to carry out experiments to calculate the quantum yields of emission and photosubstitution of the complexes.

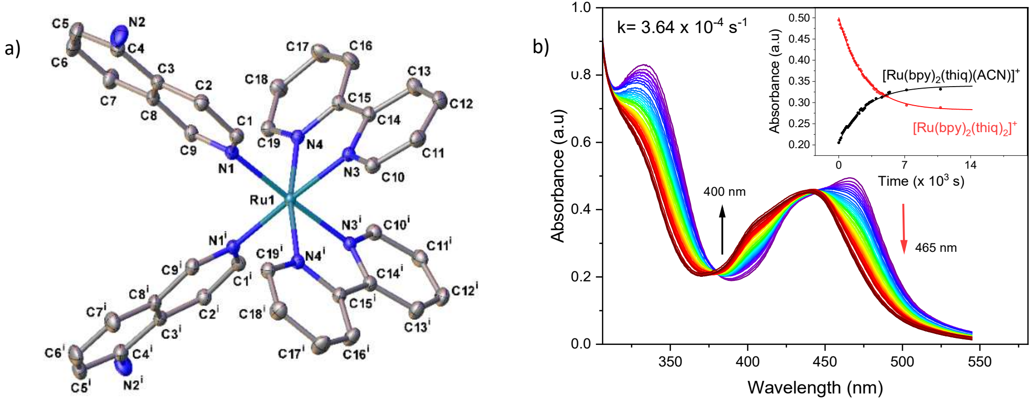

Figure 1. a) X-ray Crystal Struture of **(1)**. b) Electronic absorption spectra in UV-Vis during irradiation with white light of the complex **(2)** in acetonitrile. Inset. Kinetic curves at $\lambda_{máx}$= 400 (●) and 465(●) nm for complex **(2)** in acetonitrile at 25°C.

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References

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