

# Photophysical Properties of Ruthenium(II) Polypyridyl DNA Intercalators: Effects of the Molecular Surroundings Investigated by Theory

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Environment effects on the structural and photophysical properties of  $[\text{Ru}(\text{L})_2(\text{dppz})]^{2+}$  complexes (L = bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, tap = 1,4,5,8-tetraazaphenanthrene; dppz = dipyrido[3,3-a:2',3'-c]phenazine;) used as DNA intercalators are studied by means of DFT, TD-DFT and QM/MM calculations.<sup>1</sup> The electronic characteristics of the low-lying triplet excited states in water, acetonitrile and DNA are investigated in order to decipher the influence of the environment on the luminescent behaviour of this class of molecules. The lowest <sup>3</sup>IL state calculated around 800 nm for the three complexes and localized on the dppz ligand is not very sensitive to the environment and is available for electron transfer from a guanine nucleobase. Whereas the lowest <sup>3</sup>MLCT states remain localized on the ancillary ligand (tap) in  $[\text{Ru}(\text{tap})_2(\text{dppz})]^{2+}$  whatever the environment is, their character is drastically modified in the other complexes  $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$  when going from acetonitrile ( $\text{MLCT}_{\text{dppz/phen}}$  or  $\text{MLCT}_{\text{dppz/bpy}}$ ), to water ( $\text{MLCT}_{\text{dppz}}$ ) and DNA ( $\text{MLCT}_{\text{phen}}$  and  $\text{MLCT}_{\text{bpy}}$ ). The change of character of the low-lying <sup>3</sup>MLCT states accompanying the nuclear relaxation in the excited state controls the emissive properties of the complexes in water, acetonitrile and DNA. For the first time the light switch effect has been rationalized on the basis of environment-induced control of the electronic density distributed in the lowest triplet excited states.

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