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Study of the photophysical properties of DNA binding with [Ru(bpy)$_2$dppz]$^{2+}$ and its derivatives

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Ruthenium polypyridine complexes have unique photophysical and photochemical characteristics that rely on metal-to-ligand charge transfer. Several ligands have been developed to synthesize Ru(II) complexes like [Ru(bpy)$_2$L]$^{2+}$ or [Ru(phen)$_2$L]$^{2+}$ (where bpy = 2,2'-bipyridine, phen = 1,10'-phenanthroline and L = α,α'-diimine ligand). Among the numerous Ru(II) compounds studied in literature, special attention has been given to L = dppz (dipyrido[3,2-a:2',3'-c]phenazine), which is well-known as an intercalative DNA agent. The complexes [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(phen)$_2$dppz]$^{2+}$ are DNA metallointercalators. In aqueous solution, they exhibit an enhancement of luminescence in the presence of DNA, known as the "light switch" phenomenon. This work presents the results of a study on the photophysical properties of the DNA binding of [Ru(bpy)$_2$dppz]$^{2+}$ (**1**) and its derivative [Ru(bpy)$_2$dppzBTDZ]$^{2+}$ (**2**) which has a 2,1,3-thiazole extension (dppzBTDZ = dipyrido[3,2-a:2',3'-c]phenazine-10,11-(2,1,3-thiadiazole)).[1] The steady state emission spectra of compound **2** in acetonitrile, water, and with DNA are presented in Figure 1. A spectral fit was performed using equation 1,[2a] allowing a Franck-Condon analysis (FC) based on the energy gap law.[2b]

$$I(\bar{\nu}) = \sum_{\upsilon_M=0}^{5}\left\{\left(\frac{E_0-\upsilon_M\hbar\omega_M}{E_0}\right)^3\left(\frac{S_M^{\upsilon_M}}{\upsilon_M!}\right)\exp\left[-4\ln(2)\left(\frac{\bar{\nu}-E_0+\upsilon_M\hbar\omega_M}{\Delta\bar{\nu}_{0,½}}\right)^2\right]\right\} \qquad \text{(eq. 1)}$$

The results show that **1** and **2** have similar quantum yield and emission lifetime, with **2** having slightly lower values of quantum yield and lifetime. However, in water, **2** has a longer lifetime of 466 ns compared to 360 ns for **1**. In the presence of DNA, the emission decay was fitted by a biexponential function for both compounds, indicating the presence of two intercalative modes with DNA. The lifetimes values in the presence of DNA for compound **1** are slightly higher than those for 2, $\tau_1 = 154, \tau_2 = 580\ ns$) versus ($\tau_1 = 127, \tau_2 = 512\ ns$), respectively. The solvent reorganization energy in the presence of DNA is more favorable in **1**, while in water is lower in 2. The largest differences in the FC factors calculated in the presence of DNA were found in the Huang-Rhys factor (S_M). Compound **2** had a value that was 10% larger, indicating a high degree of distortion in the excited state. In summary, the preliminary results showed that making small structural changes to the ligands can result in significant changes in the excited state.

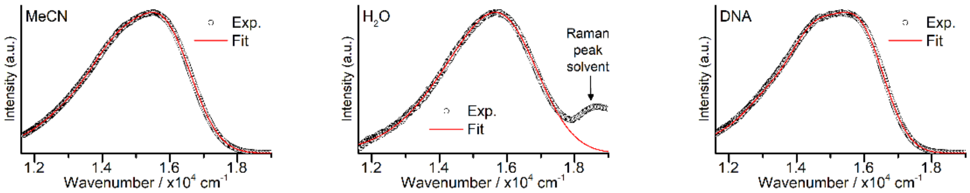

Figure 1. Normalized emission spectra and spectral fits (eq 1) of **2** in different conditions.

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