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Theoretical Study of The Photophysics of Two Tetrapyrrolic Photosensitizers

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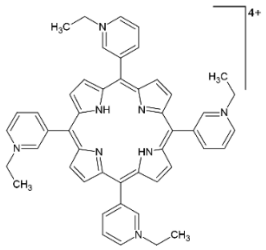
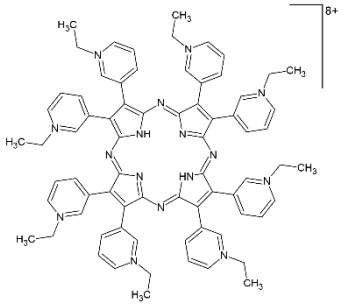
Tetrapyrrolic macrocycles are known in the literature as promising photosensitizers for Photodynamic Therapy[1,2]. Two promising compounds of this class were recently studied for their capability to generate singlet oxygen ($^1O_2$) and results showed that the porphyrin, $H_2T(3EPy)P^{4+}$ had appreciable quantum yield for $^1O_2$ generation (ϕ_Δ) both in water and acetonitrile. The second compound, a porphyrazine $H_2(3EPy)_8Pz^{8+}$ had appreciable ϕ_Δ only in acetonitrile, while, in water, $^1O_2$ generation could not be detected[1]. To explain this, DFT calculations were performed on these two compounds to determine their photophysical mechanisms of intersystem crossing (ISC). Ground and excited electronic states' geometries were obtained at the B3LYP/def2-SVP level of theory and energies, spin-orbit coupling and transition dipoles were calculated at the ωB97X-D3/def2-TZVP level with CPCM model simulating water and acetonitrile solvation. Fluorescence rates (k_f) were calculated using Einstein's Coefficient and ISC rates (k_{ISC}) through Fermi's Golden rule and Marcus' Theory[3]. Results show a very large underestimation of ISC rates, probably caused by the low spin-orbit coupling between states at the equilibrium geometries. This is attributed to the fact that tetrapyrrolic macrocycles tend to have high vibronic coupling and need this to be included in the model to achieve a good representation of ISC rates[2,4]. Calculations of ISC rates including vibronic coupling are currently being carried out to explain the difference between porphyrins and porphyrazines as photosensitizers.

Table 1. Fluorescence (k_f) and ISC (k_{ISC}) rates for $H_2T(3EPy)P^{4+}$ and $H_2(3EPy)_8Pz^{8+}$ in water and acetonitrile.



$H_2T(3EPy)P^{4+}$



$H_2(3EPy)_8Pz^{8+}$

	$H_2T(3EPy)P^{4+}$		$H_2(3EPy)_8Pz^{8+}$	
	Acetonitrile	Water	Acetonitrile	Water
k_f (s^{-1})	$2{,}3 \times 10^5$	$2{,}4 \times 10^5$	$1{,}1 \times 10^8$	$1{,}0 \times 10^8$
k_{ISC} (s^{-1})	$6{,}0 \times 10^0$	$5{,}5 \times 10^0$	$1{,}2 \times 10^{-10}$	$6{,}3 \times 10^{-11}$

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