## Mechanisms of excited state deactivation in porphyrin isomers

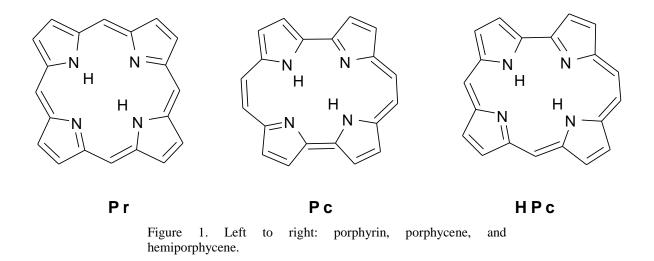
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Recently reported synthesis of parent, unsubstituted hemiporphycene (**HPc**),<sup>[1]</sup> enabled the comparison of its photophysical properties with those of structural isomers: porphyrin (**Pr**) and porphycene (**Pc**) (Figure 1). Different values of the S<sub>0</sub>-S<sub>1</sub> radiative constants can be readily explained by simple models that analyze energy splittings between the occupied and unoccupied frontier  $\pi$  orbitals. Such analysis can also elucidate very different patterns observed in the electronic absorption and magnetic circular dichroism spectra of the three compounds.



Porphycene is a strong fluorescer, but a drastic reduction of the emission intensity occurs in derivatives possessing four alkyl substituents at the meso positions.<sup>[2]</sup> This effect has been explained by theory that postulated the presence of  $S_1$ - $S_0$  conical intersection along the coordinate which includes trans-cis tautomerization and large amplitude distortion from planarity.<sup>[3]</sup> Using this model allowed understanding of the experimentally observed large dependence of the fluorescence intensity on solvent viscosity.

The goal of this work was to check whether the above model, previously applied to the photophysics of porphycene, can be generalized to include hemiporphycene. Because of low symmetry, **HPc** exists in room temperature solutions as a mixture of two trans tautomers that

exhibit different absorption and fluorescence spectra.<sup>[1]</sup> Interestingly, the more stable tautomer exhibits lower fluorescence quantum yield. The experiment also reveals that fluorescence intensity increases with solvent viscosity. Combined with the results of quantum-chemical calculations, the experimental findings are compatible with a model that attributes efficient radiationless  $S_1$  depopulation to the migration of the protons in the inner cavity of the macrocycle.

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## **References:**

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