Intersystem crossing rates of tetapyrrole molecules: a theoretical study

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The oxygen singlet generation by molecules that are used in applications of photodynamic therapy (PDT) requires the absorption of light in the therapeutic window (600 - 800 nm), and a subsequent singlet to triplet transition between excited states, a process known as intersystem crossing (ISC). Recent theoretical developments have allowed to calculate the ISC rates for molecules of moderate to large sizes [1]. This enables the study of candidate molecules for PDT applications to be performed by computer simulations. The aim of this study is to evaluate the spectroscopy properties and the spin-orbit coupling (SOC) rates of tetapyrrole-like molecules. Tetapyrrole-like molecules are seen to be potent photosensitizers [2]. They have long triplet lifetimes and high absorption as well as oxygen singlet quantum yields. These facts turn tetapyrroles important candidates for clinical PDT. This study is focused on the influence of different aromatic ligands on the porphyrin and corrol molecules. Density functional theory and its time-dependent extension (DFT, TDDFT) have been herein employed to elucidate the structural and electronic properties of the studied tetapyrrole molecules. The spin-orbit coupling matrix elements between the singlet and triplet excited states are calculated by a noninterative method using the full Breit-Pauli operator, \( \langle \Psi^I | \hat{H}^{SO}_{BP} | \Psi^{II} \rangle = \frac{\gamma^2}{2} \left\{ H^{SO}_{el} - H^{SO}_{2el} \right\} \).