

# Singlet-Triplet Coupling in Organic Chromophores

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Inter-system crossing (ISC) plays a central role in photochemistry, photobiology, and photodynamic therapy since many photo-induced chemical reactions proceed on the first excited triplet hypersurface. While a high triplet quantum yield is desirable for photosensitizers, rapid quenching of the  $T_1$  state is preferable for photoprotectors. A prerequisite for the understanding of the underlying mechanisms is the knowledge of the excited states and their interactions. State-of-the-art quantum chemical methods can help to shine light on the cascade of relaxation processes following the primary photo excitation.

The combined density functional and configuration interaction method (DFT/MRCI)<sup>[1]</sup> has proven to yield high-quality electronic excitation spectra. Electronic spin-orbit matrix elements are calculated using the SPOCK<sup>[2-5]</sup> program package while vibrational contributions to ISC rates are determined using the SNF<sup>[5]</sup> and VIBES<sup>[6]</sup> programs.

By means of the above mentioned methods, we have investigated the electronic spectra and spin-orbit coupling of a variety of organic chromophores. In this contribution I would like to present our results on a few model cases: (1) flavone where the ISC mechanism follows the well-known El-Sayed rules,<sup>[7]</sup> (2) porphyrin where vibronic spin-orbit coupling between  $S_1$  and  $T_1$  states is responsible for the high triplet quantum yield,<sup>[8,9]</sup> and (3) flavin where different mechanisms have to be invoked in the gas phase and in solution.<sup>[10,11]</sup>

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