Intersystem Crossing Processes in TADF Emitters

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Abstract: *This book chapter gives a brief overview over quantum chemical methods for computing rate constants of radiative and nonradiative molecular excited-state processes and summarizes recent theoretical research on the photophysics of metal-free as well as copper-containing thermally activated delayed fluorescence (TADF) emitters. The methods for computing temperature-dependent intersystem crossing (ISC) and reverse intersystem crossing (rISC) rate constants focus on Fermi golden rule expressions whereas fluorescence and phosphorescence rate constants are determined employing multi-reference spin–orbit configuration interaction approaches. TADF and phosphorescence are competitive in many copper(I) complexes whereas TADF dominates in metal-free donor–acceptor systems. In addition to a small singlet–triplet energy splitting, spin-vibronic interactions are found to play an essential role in the ISC and rISC processes of metal-free TADF emitters.*

Key words: multi-reference configuration interaction, density functional theory, spin–orbit coupling, spin-vibronic coupling, rate constants, phosphorescence, prompt fluorescence, thermally activated delayed fluorescence, hyperfluorescence, intersystem crossing, reverse intersystem crossing, Cu complexes, donor–acceptor systems