The Spin-vibronic ISC Mechanism in TADF-based OLED Emitters

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DFT/MRCI, a density functional theory-based multireference configuration interaction method, [1, 2, 3] and the associated property programs SPOCK [4, 5], DELTA [6] and VIBES [7, 8] have proven well suited for evaluating internal conversion (IC), intersystem-crossing (ISC) and phosphorescence rate constants of organic light-emitting diode (OLED) dyes. In this field, the focus has shifted from the phosphorescent metal-to-ligand charge-transfer states of well-established Ir^{III} and Pt^{II} emitters to charge-transfer (CT) states of coinage-metal coordination complexes and metal-free donor–acceptor systems based on thermally activated delayed fluorescence (TADF). In the latter compounds, spin–orbit coupling (SOC) between the S_1 and T_1 states typically is very small, but ISC can be promoted by spin-vibronic interactions with a neaby locally excited state. [9, 10] Efficient TADF-based OLED emitters where vibronic effects are found to markedly accelerate the forward and reverse ISC processes are 4,5-di(9H-carbazol-9-yl)-phthalonitrile (2CzPN) and the triptycene bridged acridine–triazine donor–acceptor molecule TpAT-tFFO. [11, 12]

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