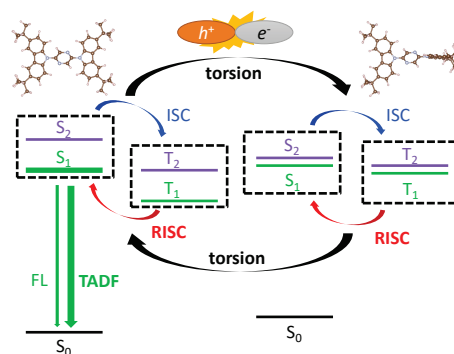


ENHANCING THERMALLY ACTIVATED DELAYED FLUORESCENCE THROUGH STRUCTURAL AND ENERGETIC FLEXIBILITY: THEORETICAL STUDIES

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Thermally activated delayed fluorescence (TADF) is one of the most promising routes to enhance the luminescent efficiency of an organic light-emitting diode (OLED) device by converting a non-emissive triplet exciton (T_1) back to an emissive singlet configuration (S_1) through reverse intersystem crossing (RISC) before it fluoresces back to the ground state (S_0). However, the TADF rate is generally restricted if only the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are involved. This is due to the conflict between a fast RISC rate between S_1 and T_1 (which requires a small HOMO–LUMO overlap), and a large transition dipole moment (μ_T) between S_1 and S_0 (which requires a large HOMO–LUMO overlap).^a In the present study, we proposed two solutions to enhance the overall fluorescent rate: an inclusion of higher-lying singlet and triplet states ($S_{n \geq 2}$ and $T_{n \geq 2}$) in ISC–RISC routes to avoid the trade-off, and a fluxional molecular conformation to sample a broad range of HOMO–LUMO overlap. We provided a proof-of-concept for our solutions based on computational modeling of sample di-tert-butyl carbazole derivatives with the pyrazine or dipyrazine substituents (DTCz-Pz or DTCz-Pz), using a combination of density functional theory (DFT) and molecular dynamics (MD). Our study will provide a computational and quantitative strategy for the design of new TADF emitters with maximum luminescent efficiency.



^aA. Endo et al., *Appl. Phys. Lett.* **2011**, 98, 083302.