

Reverse Intersystem Crossing in Carbene-Metal-Amide TADF Emitters

J. Patrick Zobel¹

¹*Institute of Theoretical Chemistry, University of Vienna, Vienna, Austria*

OLEDs function by recombining positive and negative charges which generate electronic excited states that relax by emitting light. Efficient emitters function via thermally activated delayed fluorescence (TADF), where the lowest triplet state T_1 in the emitter can undergo reverse intersystem crossing (rISC) to a highly fluorescent singlet state S_1 . TADF is thermally allowed for small T_1 - S_1 energy gaps as realized in donor-acceptor systems when both states are of charge-transfer (CT) character. The CT character however restricts the rISC efficiency through small T_1 - S_1 spin-orbit coupling as well as the S_1 fluorescence rate. This dilemma inspired models involving intermediate states to rationalize the TADF mechanism.[1] A dynamical picture of the rISC, however, so far remained elusive.

We have now simulated[2] the rISC process of a carbene-copper-amide TADF emitter[3] using nonadiabatic dynamics based on vibronic coupling potentials.[4] We find rISC happening not around the global T_1 minimum, where the two ligands assume a co-planar coordination geometry, but around a higher-lying local T_1 minimum of perpendicular geometry. Efficient rISC is enabled by a higher-lying triplet metal-to-ligand charge transfer state. After rISC, the complex returns to a co-planar coordination geometry in the lowest-lying singlet state S_1 with efficient emission. The electronic cascade and the rotation of the metal-ligand bond shows the importance of the metal in TADF processes in carbene-copper-amides.

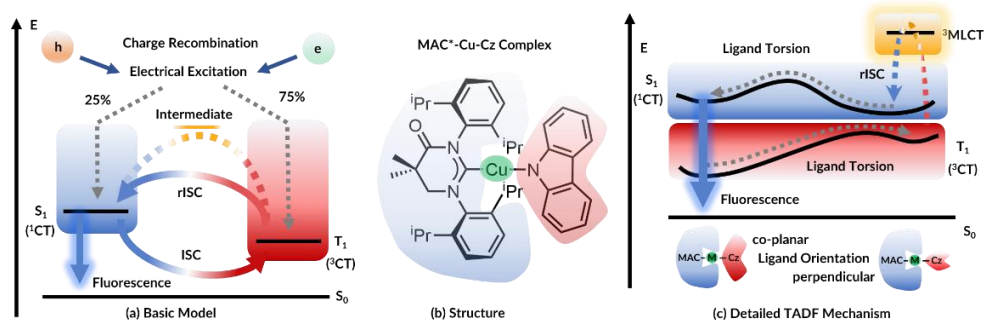


Figure: Basic/detailed TADF mechanism in the OLED emitter MAC-Cu-Cz.

- [1] Etherington, Gibson, Higginbotham, Penfold, Monkman, *Nat. Commun.* **7**, 13680 (2016)
- [2] Zobel, Wernbacher, González, *Angew. Chem. Int. Ed.* e202217620 (2023)
- [3] Shi, Jung, Coburn, Tadde, Sylvinson, Djurovich, Forrest, Thompson, *JACS* **141**, 3576 (2019)
- [4] Zobel, Heindl, Plasser, Mai, González, *Acc. Chem. Res.* **54**, 3760 (2021)