

Computational investigation of vibronic effects on reverse intersystem crossing in CMA1 complexes

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Copper complexes featuring a carbene-metal-amide (CMA1) motif are characterized by linking carbene and amide ligands via a Cu(I) atom, forming a two-coordinate CMA motif. The photodynamics of CMA1 complexes predominantly rely on the properties of the carbene and amide ligands, with a minor contribution from the central coinage metal. Due to the well-separated frontier molecular orbitals, CMA1 complexes typically exhibit small energy gaps between their singlet and triplet states, facilitating access to the TADF channel.

Moreover, compared to purely organic TADF molecules, the inclusion of a coinage metal center in CMA complexes enhances spin-orbit coupling between singlet and triplet states, thus accelerating intersystem crossing and reverse intersystem crossing processes. Consequently, CMA1 complexes generally exhibit sub-microsecond-scale TADF lifetimes, which are significantly shorter than those of purely organic TADF materials.

A critical factor to consider in estimating rates for reverse intersystem crossing is the influence of molecular vibrations. Indeed, experimental evidence has shown that suppressing vibrational modes can greatly impact intersystem crossing processes, highlighting the necessity of accounting for vibronic effects in the phenomenon's description,

Therefore, we propose here a new investigation of CMA1 system based on the nuclear ensemble method¹. We will show that accordingly to surface hopping dynamic², the reverse intersystem crossing process is strongly favored for a perpendicular orientation of the ligands. Indeed, this conformation alleviated a ³MLCT_{Cu→MAC} state, channeling population from the triplet to the singlet manifold. These electronic transitions are concurrent with an elongation of the Cu-N and Cu-C bonds, alongside a reduction of the N-Cu-C bonding angle. From a coplanar geometry, the electronic population remains in the lowest-lying triplet state.

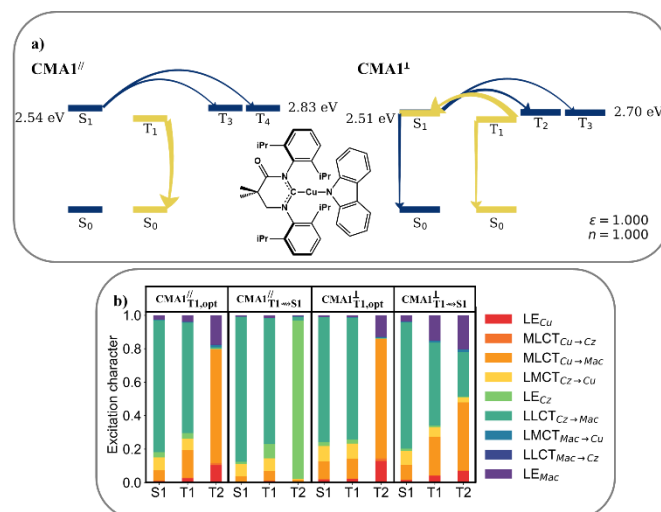


Figure 1a) Energy diagram of both configurations of CMA1. b) Electronic contribution associated to each transition

Keywords: TADF, Nuclear Ensemble Method, Photophysic properties

¹ L.E. de Sousa, P. de Silva, J.Phys. Chem. A 127 (2023) 8200–8208

² J.P.Zobel, A.M. Wernbacher, L. González, Angew. Chem. Int. Ed. 62 (2023) e202217620