

Abstract

In this work we revisit and re-evaluate the photophysical behavior of prototypical $[\text{Zn}(\text{SC}_6\text{H}_4\text{-4-R})_2(\text{phen})]$ as the most in-depth studied type of Zn(II)-based triplet state emitters. Previous reports suggest population of ligand-to-ligand charge transfer (LLCT) states via phenanthroline localized $\pi\pi^*$ states, with an energy barrier between the $^3\pi\pi^*$ and the $^1/3\text{LLCT}$ states requiring thermal activation. Besides very weak prompt fluorescence, the dominant radiative mechanism was attributed to phosphorescence. Our photophysical studies, including temperature-dependent quantum yield determination and time-resolved luminescence measurements, reveal a high radiative rate constant $k_r = 3.5 \times 10^5 \text{ s}^{-1}$ at room temperature and suggest thermally activated luminescence as the major emission path. High-level DFT/MRCI calculations confirm this assignment and provide deeper insight into the excited-state kinetics, including rate constants for the (reverse) intersystem crossing processes. Thus, our study demonstrates that further optimization of the photophysical properties of this type of Zn(II) triplet exciton emitter bears great potential for future application in devices.