

Luminescent Properties of Copper(I) (2,9-halo-1,10-phenanthroline) Complexes

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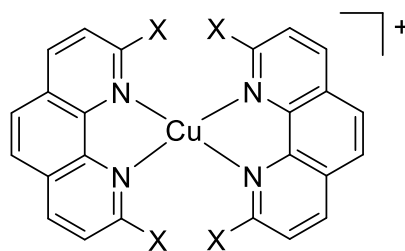
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Ruthenium polypyridine complexes, epitomized by famous $[\text{Ru}(\text{bpy})_3]^{2+}$, feature well-known outstanding properties such as a strong absorption in the visible (MLCT) and long-lived excited states. As such, they overwhelmingly dominate the world of coordination compounds photochemistry despite their toxicity and expensiveness.

Copper(I)-diimine complexes $[\text{Cu}(\text{L})_2]^+$ are very intriguing alternatives to ruthenium compounds. First of all they display very similar absorption features to $[\text{Ru}(\text{bpy})_3]^{2+}$ (broad absorption band at ca. 460 nm, MLCT character). Second, appending onto the diimine L bulky groups G in α of the chelating nitrogen atoms (yielding ligands L^{G}) allows to endow corresponding copper(I) complexes $[\text{Cu}(\text{L}^{\text{G}})_2]^+$ with luminescence and rather long-lived excited state features because the deleterious photo-induced flattening of the coordination cage from tetrahedral to square planar geometry is prevented.¹ Historically, $[\text{Cu}(\text{L}^{\text{Me}})_2]^+$ was the first copper(I) complex illustrating the potency of this family of luminophores;² more efficient ones have been isolated since by increasing the size of G³ and it is commonly accepted now that the bigger G, the longer-lived the excited state.

In this contribution, we present a new class of photoluminescent copper(I) complexes $[\text{Cu}(\text{L}^{\text{X}})_2]^+$, where L^{X} is the 2,9-bishalo-1,10-phenanthroline (X = Cl, Br and I). These complexes feature unexpected intense and broad luminescence peak when excited in the MLCT (ca. 460-480 nm). Excited states structure optimization, by means of time-dependent density functional theory (TD-DFT), indicates that the initial molecular symmetry is broken leading to several minima on the S_1 and T_1 excited states potential energy surfaces being a source of unexpected luminescent properties.



References

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