Deep-red Emitting Copper(I) Complexes with Minimized Skeletal Vibrations and Configurational Disorder

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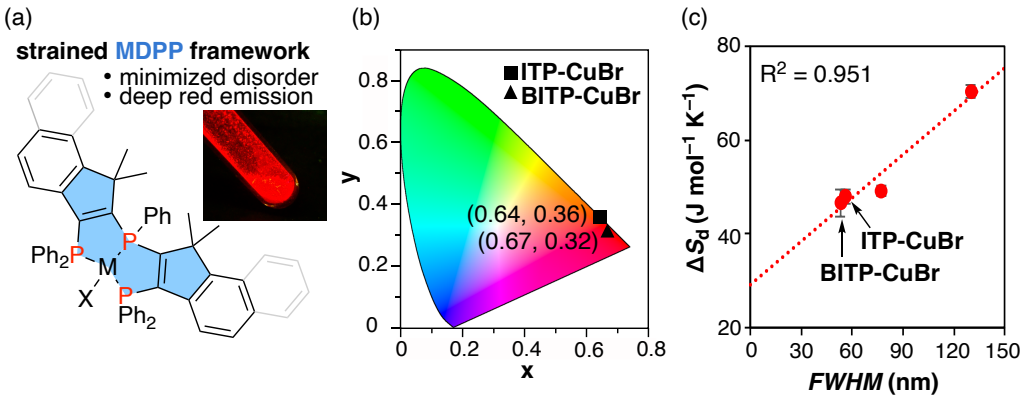
Luminescent copper(I) complexes have garnered significant attention for their potential applications in optoelectronics due to their excellent emission properties.[1] However, their intrinsic structural flexibility often results in broad emission with low color purity, limiting the achievement of deep-red emission[2]. To address this challenge, we incorporated a strained[3] and rigid[4] metalaphosphadicyclopenta[a,f]pentalene (**MDPP**) motif into Cu(I) complexes by utilizing trisphosphine ligands with a 1H-indene-2,3-diyl backbone (**ITP**, **BITP**).[5] Herein, we present the synthesis, structural characterization, and emission properties of **(B)ITP-CuX** and related congeners, which exhibit genuinely deep-red emission with narrow full-width-at-half-maximum (FWHM) values as small as 53 nm. Unlike the broader emissions observed in prior studies, these materials demonstrate color coordinates that are remarkably close to pure red on the CIE diagram. Furthermore, entropy of disorder measurements for the emissive crystals, conducted using a recently developed statistical mechanical method, revealed a quantitative positive correlation between FWHM values and the number of microstates (degrees of freedom) within the crystals. This finding not only validates our design strategy but is also expected to provide a general design principle for achieving sharply emissive metal complexes.



Figures. Brief summary of this project. (a) Design of **MDPP** framework with strained coordination geometry. (b) Deep-red emission from **MDPP**-based Cu(I) complexes. (c) Experimentally determined entropy of disorder (ΔS_d) of Cu(I) complexes.

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