Cu-F Interactions between cationic linear NHC-Cu\textsuperscript{I}-Pyridine Complexes and their Counterions greatly enhance blue Luminescence Efficiency

Annika Liske,\textsuperscript{a} Lars Wallbaum,\textsuperscript{a} Torsten Hölzel,\textsuperscript{a} Jelena Föller,\textsuperscript{b} Markus Gernert,\textsuperscript{c} Benjamin Hupp,\textsuperscript{c} Christian Ganter,\textsuperscript{a} Christel M. Marian\textsuperscript{b,*} and Andreas Steffen\textsuperscript{c,*}

\textsuperscript{a}Institut für Anorganische Chemie, Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany.
\textsuperscript{b}Institut für Theoretische Chemie und Computerchemie, Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany.
\textsuperscript{c}Fakultät für Chemie und Chemische Biologie, Technische Universität Dortmund, Otto-Hahn-Str. 6, 44227 Dortmund, Germany.

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**ABSTRACT:** A series of easily accessible linear Cu\textsuperscript{I} NHC (NHC = N-heterocyclic carbene) complexes, bearing pyridine (py) and its derivatives as chromophore ligands, are barely emissive in the single-crystalline solid state. However, their powders, neat films and dilute doped films of PMMA (1-10%) show very intense blue to blue-green photoluminescence with remarkable quantum yields $\phi$ of up to 87\% and microsecond lifetimes, indicative of triplet states being involved. These luminescence properties are similar to trigonal coordinated Cu\textsuperscript{I} NHC bis(pyridine) complexes, which we have also isolated and characterized with respect to their structures and photophysics. Our spectroscopic and theoretical studies provide detailed insight into the nature of the luminescence enhancing effect of the linear two-coordinated copper(I) compounds, which is based on the formation of Cu-F interactions between the BF\textsubscript{4}\textsuperscript{-} anions and the [Cu(NHC)(2-R-py)]\textsuperscript{+} (R = H, Me, Ph) cations. These interactions are absent in the single crystals, but lead to a distorted ground state structure in the precipitated powders or in PMMA films, giving rise to high $k_e$. In addition, we found that our linear Cu\textsuperscript{I} complexes exhibit mechanochromic luminescence, as grinding the single crystals leads to enhanced emission intensity. In light of recently reported cation-anion contact induced mechanochromic luminescence of two-coordinate copper(I) complexes, this study supports the generality of this new mechanism for the design of mechano-responsive phosphorescent materials.