

Publication

Pyrene-Decoration of a Chromium(0) Tris(diisocyanide) Enhances Excited State Delocalization: A Strategy to Improve the Photoluminescence of 3d6 Metal Complexes

JournalArticle (Originalarbeit in einer wissenschaftlichen Zeitschrift)

ID 4626129

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There is a long-standing interest in iron(II) complexes that emit from metal-to-ligand charge transfer (MLCT) excited states, analogous to ruthenium(II) polypyridines. The 3d6 electrons of iron(II) are exposed to a relatively weak ligand field, rendering nonradiative relaxation of MLCT states via metal-centered excited states undesirably efficient. For isoelectronic chromium(0), chelating diisocyanide ligands recently provided access to very weak MLCT emission in solution at room temperature. Here, we present a concept that boosts the luminescence quantum yield of a chromium(0) isocyanide complex by nearly 2 orders of magnitude, accompanied by a significant increase of the MLCT lifetime. Pyrene units in the diisocyanide ligand backbone lead to an enlarged π -conjugation system and to a strongly delocalized MLCT state, from which nonradiative relaxation is less dominant despite a sizable redshift of the emission. While the pyrene moiety is electronically coupled to the core of the chromium(0) complex in the excited state, UV-vis absorption and 2D NMR spectroscopy show that this is not the case in the ground state. Luminescence lifetimes and quantum yields for our pyrenyl-decorated chromium(0) complex exhibit an unusual bell-shaped dependence on solvent polarity, indicative of two counteracting effects governing the MLCT deactivation. These two effects are identified as predominant deactivation either through an energetically nearby lying metal-centered state in the most apolar solvents, or alternatively via direct nonradiative relaxation to the ground state following the energy gap law in more polar solvents. This is the first example of a 3d6 MLCT emitter to benefit from an increased π -conjugation network.

Publisher American Chemical Society**ISSN/ISBN** 0002-7863 ; 1520-5126**URL** <https://pubs.acs.org/doi/abs/10.1021/jacs.1c07345>**edoc-URL** <https://edoc.unibas.ch/84908/>**Full Text on edoc** Available;**Digital Object Identifier DOI** 10.1021/jacs.1c07345**PubMed ID** <http://www.ncbi.nlm.nih.gov/pubmed/34516734>**Document type (ISI)** Journal Article