

Ligand-Based Fluorescence from an Tris(diisocyanide) Iron(II) Complex

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Precious 4d⁶ and 5d⁶ transition metal chromophores, for example, Ru^{II}, Os^{II}, Re^I, Ir^{III} complexes are widely used in variety of photochemical applications such as photoredox catalysis, light-emitting devices, photodynamic therapy. Many of these applications are based on long-lived, emissive metal-to-ligand charge transfer (MLCT) excited states. In recent years, the interest to replace these precious photosensitizers by earth-abundant first-row transition metal complexes has been growing.^[1] Major focus is given to find analogues to benchmark 4d⁶ [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) by more abundant, low-toxic and isoelectronic Iron(II) complexes. In contrary to Ru^{II} complexes, the MLCT excited states of Fe^{II} complexes are efficiently deactivated through lower-lying metal-centered (MC) states.^[2] Previously, two examples of emissive Fe^{III} complexes with ligand-to-metal charge transfer (LMCT) excited state were reported,^[3] and very recently, the first MLCT emission from an Fe^{II} complex was reported.^[4]

3d⁶ Cr⁰ and Mn^I complexes with chelating bi- or tridentate isocyanide ligands have emissive MLCT excited states in solution at room temperature.^[5] We were curious to

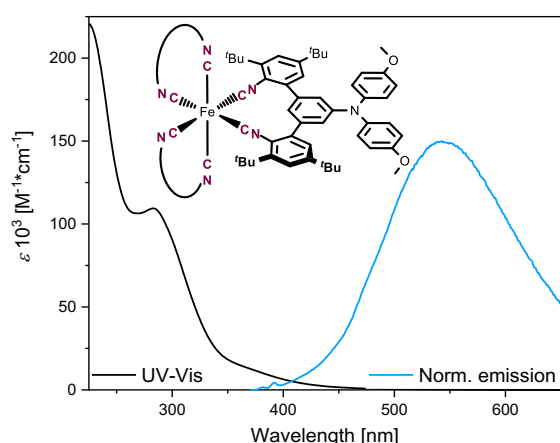


Figure 1. UV-Vis and emission spectra of [Fe(L^{bi-NC})₃](OTf)₂ in dry, deaerated acetonitrile at room temperature.

what extent chelating arylisocyanide ligands are useful for obtaining emissive Fe^{II} complexes. Herein, we report a new bidentate arylisocyanide ligand (L^{bi-NC}) which reacts with iron(II) triflate in tetrahydrofuran (THF) to afford the Fe^{II} complex, [Fe(L^{bi-NC})₃](OTf)₂ (Figure 1). The photophysical properties of L^{bi-NC} and [Fe(L^{bi-NC})₃](OTf)₂ were studied in acetonitrile, dichloromethane and THF. The iron(II) complex emits in solution at room temperature upon excitation at 350 nm. The emission occurs most likely from a ligand-centered excited state.

Literature:

[1] C. Förster, K. Heinze, *Chem. Soc. Rev.*, **2020**, *49*, 1057-1070. [2] Y. Liu, P. Persson, V. Sundstrom, K. Wärnmark, *Acc. Chem. Res.* **2016**, *49*, 1477-1485. [3] K. S. Kjær *et al*, *Science* **2019**, *363*, 249–253. [4] W. Leis, M. A. Arguello Cordero, S. Lochbrunner, H. Schubert, A. Berkefeld, *J. Am. Chem. Soc.* **2022**, *144*, 1169-1173. [5](a) C. Wegeberg, D. Häussinger, O. S. Wenger, *J. Am. Chem. Soc.* **2021**, *143*, 15800-15811; (b) P. Herr, C. Kerzig, C. B. Larsen, D. Häussinger, O. S. Wenger, *Nat. Chem.* **2021**, *13*, 956–962.