

# LUMINESCENT TRIPLET EXCITED STATE IN AN IRON(II) ISOCYANIDE COMPLEX PROVED BY TIME-RESOLVED IR SPECTROSCOPY

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Iron complexes gain increasing attention as the most abundant transition metal element and a congener of well-established photoactive Ru polypyridyl complexes. Although Fe(III) complexes are now recognized as photoactive, Fe(II) complexes remain significantly short-lived. In contrast to the frequently used N-heterocyclic carbene ligands, isocyanides are underexplored as a potential ligand for photoactive Fe(II) complexes, likely due to their negligible visible light absorption and ligand-based fluorescence property.[1] In this contribution, the luminescent visible-light responsive Fe(II) complex with 12 nanosecond lifetime traced by TR-IR will be presented.

Towards achieving long-lived triplet states with Fe(II) complexes, we investigated a photoactive Fe(II) complex with  $\pi$ -extended isocyanides (Fig. 1a).[2] With the newly synthesized  $\pi$ -stabilized ligand, the metal-to-ligand charge transfer (MLCT) absorption is found in the visible light region up to 450 nm (Fig. 1b). Upon photoexcitation at this MLCT band, unexpected blue photoluminescence was observed with an emission maximum at 480 nm. To elucidate the luminescence origin, the time-resolved luminescence, transient UV-vis absorption spectroscopy, and time-resolved IR spectroscopy were carried out in a wide time range from sub-picosecond to nanoseconds. Unfortunately, the transient absorption spectra exhibited a broad and weak signal, which was not informative for assigning the excited state. Thus, we employ time-resolved IR spectroscopy to trace the excited state of the Fe(II) isocyanide (Fig. 1c). Interestingly, the bleach of the Fe(II) complex exhibited long-lived decay (12 ns), and its decay showed good agreement with that of luminescence ( $\tau = 11$  ns) (Fig. 1d). With TR-IR spectra and theoretical calculations, the luminescence is assigned to the phosphorescence from the  $^3\text{LC}$  state in the Fe(II) complex. This finding demonstrates that more higher-energy and longer-lived phosphorescent states of Fe(II) complexes are accessible than previously known Fe(II) complexes. The details of photoexcited state analysis and other new ligands towards long-lived triplet states in first row transition metal complexes will be discussed.

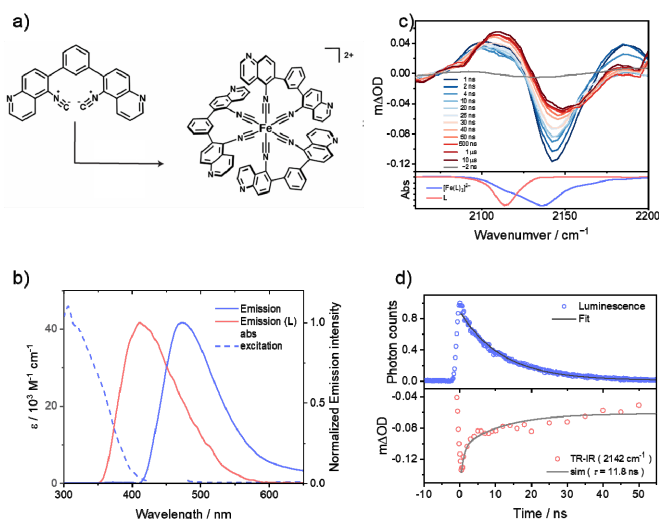


Fig 1. a) Molecular structures of the  $\pi$ -extended isocyanide ligand and its Fe(II) complex, b) absorption, emission and excitation spectra, c) TR-IR spectra, d) decay kinetics of TR-IR and emission

[1] C. Wegeberg *et al.*, *J. Am. Chem. Soc.* **2024**, *146*, 4605 [2] T. Honda, T. Ogawa, *et al.*, to be submitted.