

PHOTOPHYSICS OF A RIGID MACROCYCLE Fe^{II} COMPLEX WITH A NANOSECOND LIFETIME MLCT EXCITED STATE

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Replication of the long lifetimes of 4d transition metal complexes in their 3d counterparts is desirable for both cost reduction and environmental concerns. Fe^{II}(rac-HMTI)(CN)₂ is an Fe^{II} complex with a remarkable nanosecond lifetime metal-to-ligand charge transfer (MLCT) state in low polarity solvents. Architecturally, the Fe^{II} center is ligated to axially-oriented strong field cyano ligands, and equatorially to a rigid [14]-tetracene-N₄ macrocycle. This rigidity enforces poor vibrational overlap of excited states, significantly raising the barrier of vibrational relaxation and extending their lifetimes. Fe(HMTI)(CN)₂ is studied by optical transient absorption, and spectroelectrochemical studies reproduce the features of the OTA at potentials consistent with metal oxidation and ligand reduction, confirming the attribution of MLCT character to the transition. DFT, TDDFT and CASSCF computational methods are also used to create a theoretical potential energy manifold, to better describe the deactivation mechanism of the excited state. Further understanding of this molecule's photophysics will allow for more targeted development of longer-lived Fe^{II} complexes.