

SOLVENT-TUNING OF A Fe^{II} EXCITED STATE TOWARD UNDERSTANDING LIGAND DESIGN

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Cyanide-containing d^6 transition metal complexes are known to exhibit strong solvatochromism of their MLCT band, but also a solvent-lifetime dependence. These effects are understood to be modulated by second-shell donor-acceptor interactions at the cyanide nitrogen, the strength of which are dictated by solvent acceptor number, a measure of relative Lewis acidity. These modulations can be understood as altering the σ -donor π -acceptor character of the cyanide ligands. A recently reported long-lived Fe^{II} complex, $\text{Fe}(\text{HMTD})(\text{CN})_2$, exhibits a biphasic solvent-lifetime relationship, with a rising and falling edge as acceptor number increases, making it difficult to pin down the nature of the relationship. In this work, a variant of the $\text{Fe}(\text{HMTD})(\text{CN})_2$, $\text{Fe}(\text{TIM})(\text{CN})_2$ (TIM=2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and its bound lewis acid counterpart, $\text{Fe}(\text{TIM})(\text{CNBPh}_3)_2$, are investigated. $\text{Fe}(\text{TIM})(\text{CN})_2$ exhibits a largely monophasic solvent-lifetime relationship, with lifetime falling nearly exponentially as solvent acceptor number rises. This relationship is probed more closely by UV-Vis transient absorption experiments, and DFT calculations, to elucidate the effects of modulating σ -donor π -acceptor character of ligands bound to Fe^{II} chromophores.