Extended Excited State Lifetimes in New Iron(II) Complexes with N-heterocyclic Carbene Ligands

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Over last decades, the transition metal complexes (Pt, Ir and Ru) have been received attention featuring long-lived electronic excited states, for applications such as OLEDs and DSSCs.[¹] However, the replacement of these expensive, scarce and toxic metals by earth-abundant metals as Fe or Cu is still extremely changing due to a smaller ligand field splitting. A possible way to stabilize the ³MLCT temporally is by increasing the ligand field strength in order to avoid the ultrafast spin cross-over into metal-centered high spin states observed in Fe-pyridine complexes[²]. Recently, Wärnmark and co-workers reported the use of N-heterocyclic carbenes (NHC) ligands can prolong the ³MLCT lifetime (9 ps).[³] Our group recently improved the ³MLCT lifetime up to a record 16.5 ps from a homoleptic carbene-based complex bearing carboxylic groups.[⁴] Very recently, the Wärnmark group working on the same complex, published an important additive to this work by demonstrating that the injection into TiO₂ semiconductor can occur efficiently from the ³MLCT state.[⁵] We have designed new complexes where iron was coordinated by benzimidazolyldiene-based (Biz) ligands wherein a new record ³MLCT lifetime of 26 ps is reached. Experiments on complexes grafted on TiO₂ and Al₂O₃ substrates are in progress, using a spectroscopic approach that enables to directly discriminate the relative amount of electron-injecting and non-injecting complexes.

Figure 1. Kinetic traces of excited state absorption (ΔA>0, red) and ground state bleach (ΔA<0, blue) GSB of Iron complexes. ³MLCT lifetimes are 9 ps (Fe(Carben)₂), 16.5 ps (Fe(CarbenCOOH)₂), 16.4ps(Fe(Biz)₂) and 26ps (Fe(BizCOOH)₂). Panel (A) and (B) highlight the increased 3MLCT lifetime due to enhanced delocalization due to COOH groups.