Molecular design parameters for extended ³MLCT lifetimes in Fe(II)-NHC complexes

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The development of renewable energy sources is one of the biggest challenges in the 21th century. Within this context, researchers are spending great efforts to evolve and develop new materials for solar cells. Commercial dye-sensitized solar cells are based on Ru(II) transition metal complexes as a photo-sensitizers. But, ruthenium is rare and expensive, hence iron, abundant and cheap, is a good candidate to replace it. It has recently been shown that photo-induced spin crossover can be avoided in Fe(II) complexes featuring N-heterocyclic carbene (NHC) ligands, and excited state lifetimes up to 26 ps were reported^[1], making these complexes promising photo-sensitizers in DSSCs or photo-catalytic applications.

In this work, the effect of structural parameters and variations of the proto-typical octahedric Fe(II)-NHC complexes are investigated by femtosecond transient absorption spectroscopy at room temperature in order to understand which factors contribute to increase ³MLCT lifetime. The parent framework C1^[2] (Fig.1) is modified in different ways: i) an anchoring group is attached into the pyridine rings to graft complex on the surface of TiO₂ (C2, C4^[2]), ii)the imidazoly group is replaced with a benzimidazolydene in order to increase the electron donating character (C3,C4^[2]) and finally, iii) to improve the σ -character of the NHC and the geometry structural rigidity, different N-substitutions are linked to the carbene ring (C5 to C9^[4]).

Theoretical analysis^[2] (DFT and TD-DFT) compared to the experimental data show that two properties are important for a prolonged ³MLCT lifetime:



- electronic coupling of the excite state (³MLCT) and ground state orbitals (affected by
- the delocalization of ${}^{3}MLCT$ orbital away from Fe center)
- structural rigidity, *i.e.* hindering of the structural relaxation needed for ${}^{3}MLCT S_{0}$ decay [5]

In addition, distortion from the octahedric symmetry (*e.g.* C5 to C9, Fig.1) may affect ³MLCT lifetime, however a detailed understanding needs to be developed.

In conclusion, to maximize ³MLCT lifetime a more conjugate framework as C3 has to be used. Carboxylic groups, needed for grafting onto TiO₂, increase the ³MLCT delocalization. In addition, higher structural rigidity of the complexes increases ³MLCT lifetime.

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References:

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