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Fe(II)-NHC complexes as sustainable photo-sensitizers: What is the nature of the long-lived excited state(s) ?

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One recent development in the realm of sustainable, green chemistry is to explore the replacement of rare transition metals like Ir, Pt and Pd in metalorganic complexes by more abundant elements like Fe, Cu or Cr. Coordination of Fe(II) with electron-rich carbene bonds can considerably enhance the ligand field splitting energy (LFSE) and ³MLCT lifetimes, up to ≈2 ns, were reported [1]. Indeed, if the LFSE is high enough, a situation akin to the one in noble metals may be created: Metal-centred (MC) states would be higher in energy than the ³MLCT states, thus preventing ultrafast internal conversion.

Our work addresses the ultrafast photophysics of such Fe(II)-NHC (N-heterocyclic carbene) compounds with four carbene bonds [2]. Here, it appears quickly that the ligand field splitting argument applies only to the energy level ordering in the Franck-Condon region. But, the excited state relaxation involves vibrational dynamics, leading to a possible crossing of MLCT's into metal-centered (MC) potential energy surfaces and a progressive change in the nature of the long-lived excited state. Indeed, it was recently shown that the prototypical [Fe(bmip)₂]²⁺ complex, where bmip= 2,6-bis(3-methyl-imidazole-1-ylidene)-pyridine, displays an ultrafast ³MLCT/³MC branching upon relaxation from the optically excited ¹MLCT, which potentially limits the benefit of a purely MLCT-driven excited state photochemistry (e.g. electron transfer) [3].

The double-carboxylated form of [Fe(bmip)₂]²⁺, termed [Fe(bmipc)₂]²⁺, is a decent photosensitizer, with an 18-20 ps excited state lifetime, recently used in solar cell sensitised by Fe(II) complexes and displaying, for the first time, a power conversion efficiency > 1 %. What is the excited state reaction scheme for this complex, and how can ³MLCT and ³MC state be distinguished spectroscopically?

Since both states display similar excited state absorption [5], we used femtosecond fluorescence spectroscopy to evaluate the radiative rate of the long-lived excited state and found for [Fe(bmipc)₂]²⁺ in acetonitrile a radiative rate 500-1000 times smaller than the one of the ¹MLCT fluorescence [6], in agreement with a dominant ³MLCT character, as opposed to ³MC whose transition is spin and symmetry forbidden. In addition, femtosecond impulsive vibrational spectroscopy (pump-IVS) was performed with 15 fs pulses to obtain the excited state Raman spectrum. Two major features observed are: (I) A strong low frequency Raman activity (~110cm⁻¹) decays completely within the first picosecond after initial excitation. (II) A ≈150 cm⁻¹ mode can be reinduced by the push pulse during the 18 ps exc. state lifetime. Normal mode and Raman activity calculations show that these modes are related to global Fe- L breathing modes, in the ³MC and ³MLCT electronic state, respectively [7]. Feature (I) thus clearly demonstrates that excited state ³MLCT/³MC branching occurs also in [Fe(bmipc)₂]²⁺. A detailed analysis of fs TAS and fs-IVS is ongoing in order to determine the branching ratio.

In summary, the present combined experimental and computational study highlights the importance of ultrafast excited state branching in the MLCT/MC manifold for these 4-carbene coordinated Fe(II) complexes with moderate LFSE. The design of novel Fe-based sensitizers needs to take into account, in addition to the LSFE, the dynamic aspects and as much as possible, the excited state energetics along the most prominent reaction coordinates, such as Fe-L bond length changes.

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