Femtosecond Time-Resolved Spectroscopy of Iron(II) Complexes with Long-lived Metal-to-Ligand Triplet State

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Ru-based organometalic complexes are explored for a large range of energy conversion applications, such as in dye-sensitized solar cell (DSSCs)[1], where use is made of the interesting redox properties of the long-lived triplet metal-ligand charge transfer state 3MLCT. Significant research efforts aiming at replacing Ru by abundant metals such as Fe or Cu remained unfruitful so far, since the 3MLCT deactivates within 100fs (e.g. Fe(tpy)2). [2] A possible way to stabilize the 3MLCT temporally is by increasing the ligand field strength in order to avoid the rapid spin cross-over into metal-centered high spin states. Wärnmark and co-workers reported a long-lived, up to 13 ps, MLCT by using δ-donating mesoionic 4,4'-bis(1,2,3-triazol-5-ylidene) (btz) ligands.[3] In the same direction Gros et al. have synthesized and provided novel Iron complexes with modified carbene ligands, Fe(CarbenCOOH)2. Femtosecond Transient Absorption Spectroscopy reveals that the 3MLCT lifetime of Fe(Carben)2 [3] is almost doubled upon addition of a carboxylate group for grafting on TiO2[4]. In addition, the experiments with those iron complexes attached on TiO2 as film will be performed soon.

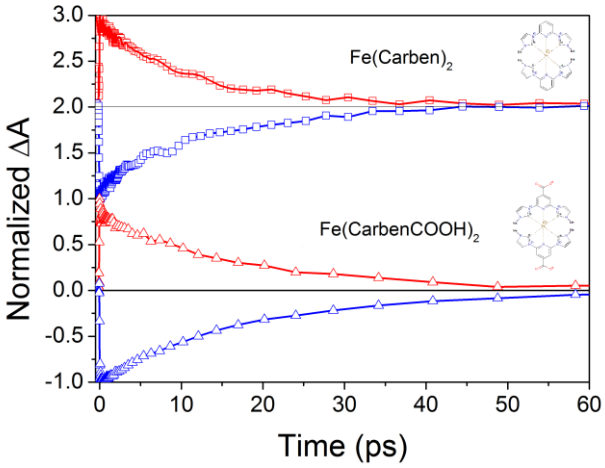

Figure 1. Kinetic traces of excited state absorption (ΔA>0, red) and ground state bleach (ΔA<0, blue) GSB of Iron complexes. Traces are shifted vertically for clarity. 3MLCT lifetimes are 9 ps (Fe(Carben)2), and 16.5 ps (Fe(CarbenCOOH)2).

References:

[1] C.-Y. Chen, M. Wang, J.-Y. Li, N. Pootrakulchote, L. Alibabaei, C.-H. Ngoc-le, J.-D. Decoppet, J.-H. Tsai, C. Gratzel, C.-G. Wu, S.M. Zakeeruddin, M. Gratzel, *ACS Nano* 2009, **3**, 3103.

[2] C. Consani, M. Prémont-Schwarz, A. ElNahhas, Ch. Bressler, F. van Mourik, A. Cannizzo, M. Chergui, *Angew. Chem., Int. Ed*., 2009, **48**, 7184-7187

[3] Y. Liu, K.-S. Kjar, L.-A. Fredin, P. Chabera, T. Harlang, S.-E. Canton, S. Lidin,, J. Zhang, R. Lomoth, K.-E. Bergquist, P. Persson, K. Wärnmark, and V. Sundström *Chem. Eur. J.* 2015, **21**, 3628 – 3639.

[4] T. Duchanois, T. Etienne, C. Cebrián, Li Liu, A. Monari, M. Beley, X. Assfeld, S. Haacke, P. Gros Eur. J. Inorg. Chem. 2015,**14**,2469-2477