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Exploring the photocycle of the [Fe(BPAbipyH)]2+ CO2 reduction catalyst using ultrafast X-ray techniques

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A self-induced photosensitive bis(pyridyl)amine-bipyridine-iron(II) framework [Fe(BPAbipyH)]2+ can convert CO2 to CO without the addition of an external photosensitizer. Direct irradiation of FeDPABipyH by visible light leads to CO2 reduction to CO with >95% selectivity and >800 TON in 24 h in a mixed-solvent solution (acetonitrile: ethanol = 1:1)1. This is two times higher than what is achieved in pure acetonitrile. The ns optical transient absorption (OTA) results show that the excited state lifetime is 297ns in the mixed-solvent solution, while a much shorter 16ns lifetime is seen in pure acetonitrile solution, which is consistent with the simple concept that the longer the excited state lifetime, the more CO2 reduction can take place.
To investigate the details of this long-lived process, ultrafast X-ray techniques have been applied to probe the excited state dynamics and identify the reaction intermediates. Time resolved XAS at a time delay of 2ns was collected at 1W2B of the Beijing Synchrotron Radiation facility (BSRF) where 343 nm was used to photoactivate the catalyst. The fitting of the difference spectrum at 2ns is consistent with a spin crossover (SCO) excitation from low-spin (LS) to high-spin (HS), analogous to other Fe(II) complexes2-4. Spin crossover excited states are normally populated after relaxation through charge transfer and ligand field electronic excited states, which can occur on ultrafast timescales (< 1ps)5,6. To probe the ultrafast charge and spin dynamics we also measured XES in pure acetonitrile and RXES in mixed solvent (acetonitrile:ethonal = 1:1) using 400nm excitation at the FXE instrument of the EuXFEL7.8. The XES data shows a strong Kβ transient signal at 100 fs time delay, which is consistent with 5T2 high-spin character. The RXES shows changes at 1s ⟶ 3d and 1s ⟶ligand transitions in the pre-edge. The XAS data, measured at the SACLA XFEL, tracks the excitation process and relaxation of the sample in both pure acetonitrile and mix (acetonitrile:ethanol = 1:1) solvent. From the preliminary data analysis, after ultrafast excitation within 100fs, the excited state has two or three relaxation processes like the a, b, c in the figure. The process before and after a (~300fs) seems like different. Between a(~300fs) and c(~750fs), the excited process become slower. The WAXS measured in ESRF shows different transient state with different solvents at low Q which may reveal the effect of solvent on the relaxation of excited states after 100 ps. These results from the ultrafast X-ray measurements and the insight they provide into the photochemistry provide important insight into the self-sensitized catalystic cycle of FeDPABipyH. This talk will present the experiments'results and our current interpretation.

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