Light-Activated Oxidation of the Ligand of an Iron(III) Complex

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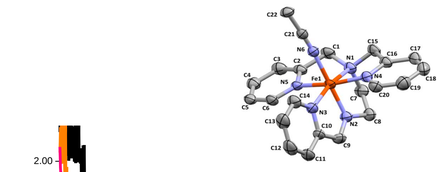
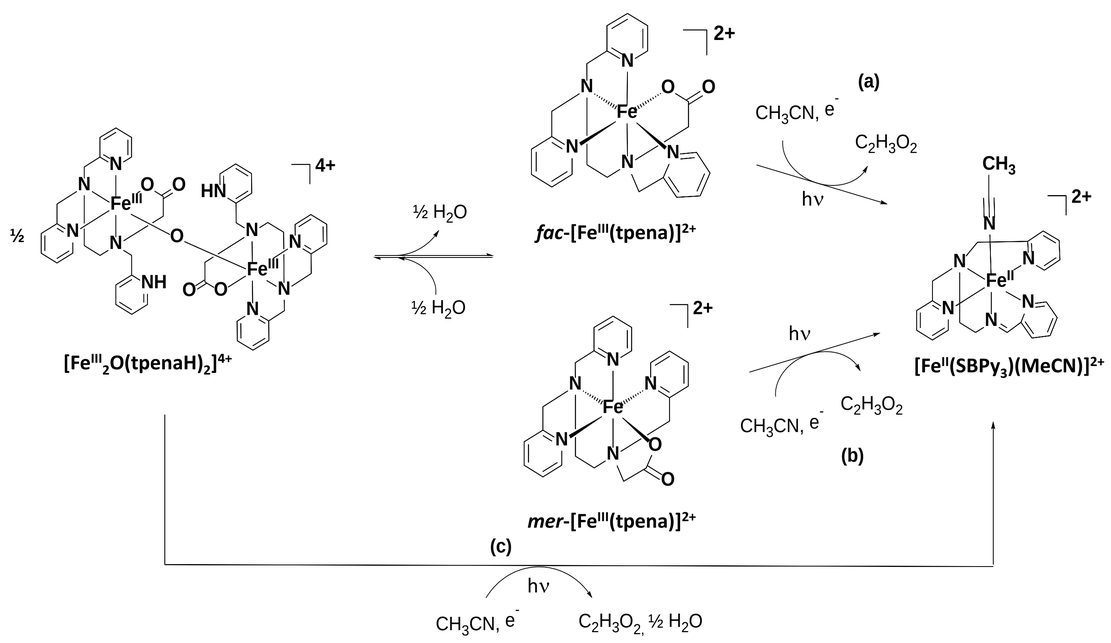
Oxidative C-N Cleavage in a Carboxylato Ligand

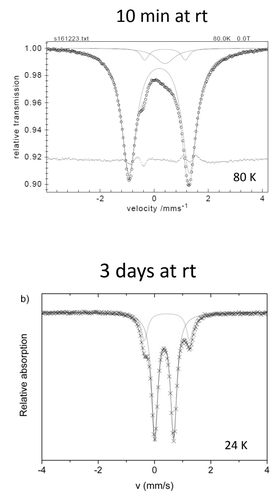


SCXRD structure of the cation $[Fe^{II}(SBPy_3)(MeCN)]^{2+}$

Which pathway (a), (b) or (c)?
And how many steps?
I.e. CH_3OH, CH_2O, CO_2, CH_3COOH are all possible C_1 and C_2 products amounting to the sum of a $C_2H_3O_2$ loss



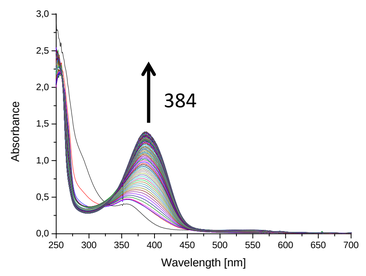
The cations $[Fe_2O(tpenaH)_2]^{4+}$, *fac*-$[Fe(tpena)]^{2+}$ and $[Fe(SBPy_3)(MeCN)]^{2+}$ are all based on SCXRD structures[1-3]

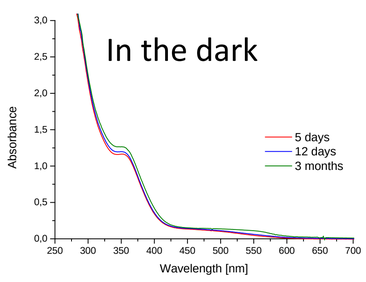


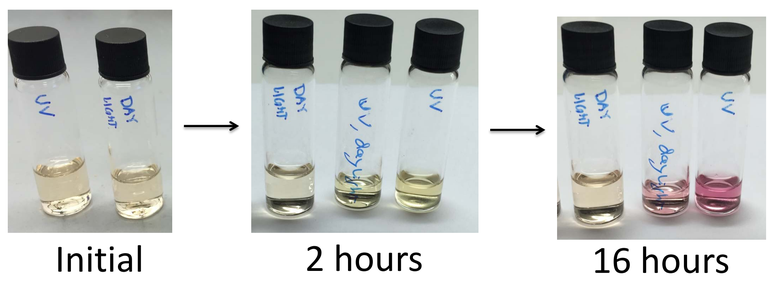
	δ [mms^{-1}]	ΔE_Q [mms^{-1}]	Assignment
$[Fe_2O(tpenaH)_2]^{4+}$	0.46	1.65	high-spin Fe(III)
fac-$[Fe^{III}(tpena)]^{2+}$	0.19	2.23	low-spin Fe(III)
mer-$[Fe^{III}(tpena)]^{2+}$	0.40	-	high-spin Fe(III)
$[Fe(SBPy_3)(MeCN)]^{2+}$	0.34	0.67	low-spin Fe(II)

Light-Induced Intermediate

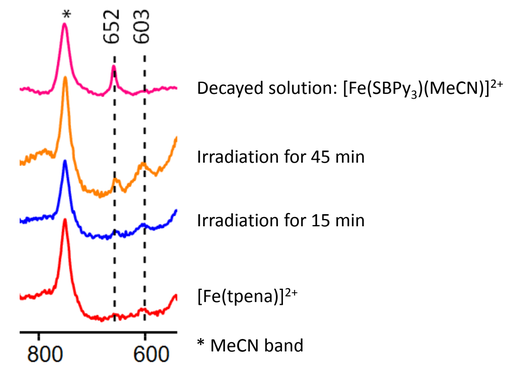
In a UV- or visible laser beam





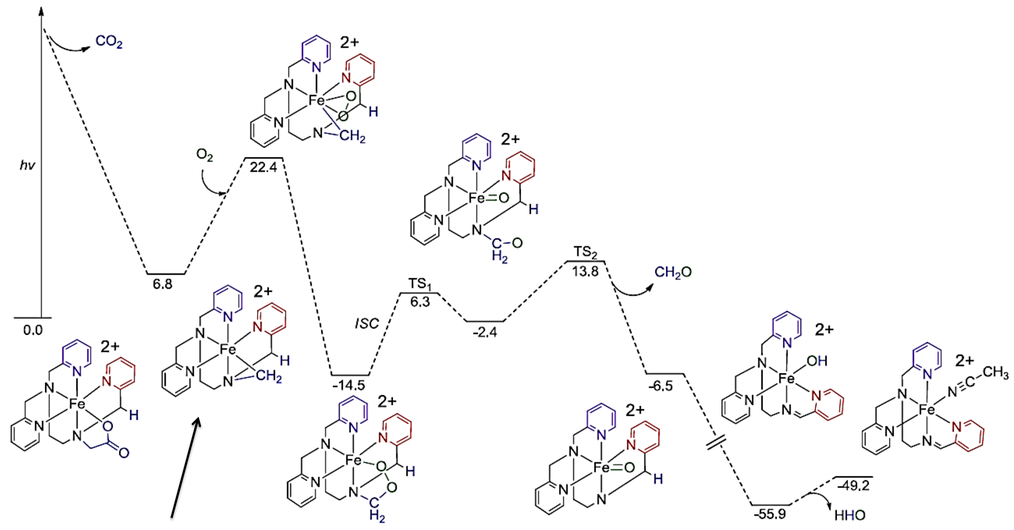


An transient yellow species with λ_{max} = 384 nm is formed, when solutions of $[Fe(tpena)]^{2+}$ are irradiated. The 555 nm band due to $[Fe(SBPy_3)(MeCN)]^{2+}$ appears subsequently.



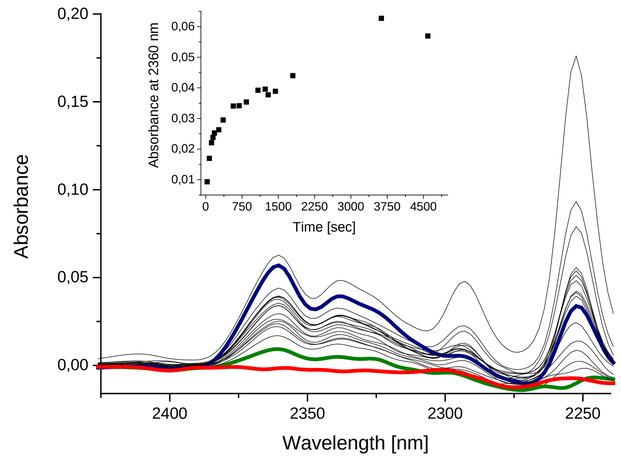
Transient yellow species: 603 cm^{-1}
$[Fe(SBPy_3)(MeCN)]^{2+}$: 652 cm^{-1}

Proposed Reaction Mechanism



Could this be the transient yellow species?

Detection of the Organic Products



Head-space IR spectroscopy was used to confirm the release of CO_2 (2360 nm and 2338 nm) and the Hantzsche reaction was used to detect the formation of formaldehyde. Simultaneous detection and quantification of the CO_2 and CH_2O evolution indicated a 1:1 ratio release of CO_2 and CH_2O verifying the proposed mechanism and eliminating CH_3OH and CH_3COOH as by-products.

(1) *Angew. Chem. Int. Ed.* **2012**, *51*, 6767-6770 (2) *Chem., Eur. J.* **2016**, *22*, 3810-3820 (3) *In preparation*
tpena: *N,N,N'*-tris(2-pyridylmethyl)ethylendiamine-*N'*-acetate, $SBPy_3$: *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine

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