

Photochemical Investigation on the Mechanism of Photoredox Reactions Promoted by Visible Light.

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Light as catalyst is extensively used in chemical synthesis.^{[1][2]} Organic molecules usually absorb ultraviolet light (UV), that is not abundant in the solar radiation (3%) that penetrates the atmosphere. Moreover UV photons are quite high in energy (4.96-3.40 eV), on the order of a C-C bond (bond-dissociation energy at 298 K 3.60-3.69 eV), and can cause decomposition reactions, particularly when relatively weak bonds are present or when the target compounds possess substantial structural complexity.

That's the reason why photosensitizer are widely employed in order to take advantage of visible-light excitation: in any photocatalytic cycle the key step is the absorption of incident light and the formation of the excited state, as a consequence. The excited photocatalyst can act as both a strong oxidant and reductant simultaneously, depending on the oxidative or reductive mechanism of the reaction.

To get better insight on the reactions mechanism, it's really important to monitor the behaviour of the photocatalyst: by absorption spectra it is possible to demonstrate the stability of the photocatalyst during the irradiation (or its degradation) and the selectivity of absorption of the irradiation light; by transient absorption spectroscopy it is possible to investigate short lived excited states or transient intermediates; in the case of luminescent photocatalyst, spectrofluorimetric measurements allow to estimate the quenching constant by different reagents used in the reaction, in order to have more information about the mechanism.

Most commonly photosensitizers employed in organic reactions are based on rare and expensive ruthenium and iridium complexes.^[3] In this contest, the use of iron(II) complexes^[4] and organic chromophores would be in fact quite attractive for photocatalytic reactions, since iron is inexpensive and very abundant and the use of organic chromophores is a metal-free alternative to transition metal complexes.

In order to investigate the possibility to use iron(II) polypyridine complexes in photocatalysis, we have selected, as a standard reaction, the α -alkylation of aldehydes developed by MacMillan,^[5] with the aim of replacing the ruthenium complex. Various Fe(II) complexes were tested in the model reaction: we found out that $[\text{Fe}(\text{bpy})_3]\text{Br}_2$ used in catalytic amount (2.5 mol %) was a compelling and effective photosensitizer for promoting the reaction between 3-phenylpropionaldehyde and dimethyl bromomalonate, in the presence of 20 mol % of the organocatalyst and upon irradiation with visible light. Reaction yields of isolated compounds and enantioselectivities are very good and comparable to the ones obtained with $[\text{Ru}(\text{bpy})_3]^{2+}$.

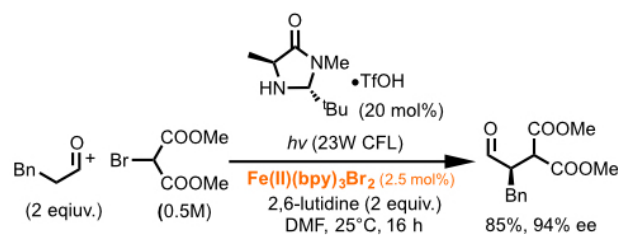


Figure 1: Optimized conditions for the $[Fe(bpy)_3]Br_2$ photocatalyzed reaction.

References:

- [1] D. M. Schultz, T. P. Yoon, *Science*, **2014**, 343, 1239176-1
- [2] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.*, **2016**, 45, 5803-5820
- [3] C. K. Prier, D. A. Rankic, D. W.C. MacMillan, *Chem. Rev.*, **2013**, 113, 5322-5363
- [4] A. Gualandi, M. Marchini, L. Mengozzi, M. Natali, M. Lucarini, P. Ceroni, P. G. Cozzi, *ACS Catal.*, **2015**, 5, 5927-5931
- [5] D. A. Nicewicz, D. W.C. MacMillan, *Science*, **2008**, 322, 77-80