Ferrocenes as photoredox catalysts for polymerization under visible to NIR lights

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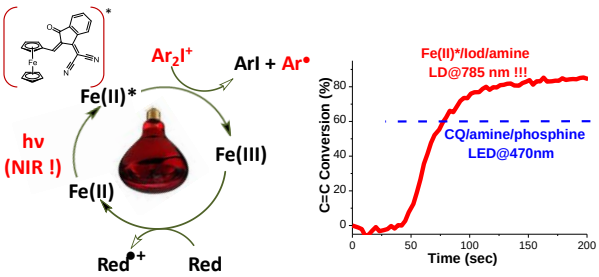
The shift towards higher actinic wavelengths in light induced reactions is a constant challenge in many academic/industrial works. During the last decade, the use of visible light in photoredox catalysis instead of harmful UV irradiations allowed significant advances in i) the selectivity of the photoreaction and ii) in the harmfulness of the actinic setup. Particularly, visible light-emitting diodes (LED) and laser diodes (LD) with their sharp emission spectra allows taylor-made light absorption by photoredox catalysts. Nevertheless, photoredox catalysis – partial and convenient regeneration of the catalyst – remained mostly restricted to actinic lights below 700 nm. Indeed, near infrared (NIR) induced photoredox catalysis remains an old dream which is particularly difficult to achieve as a NIR photon at 900 nm is three times less energetic than a UV one at 300 nm. Out of the challenge, there is a real interest in using NIR wavelengths: it offers several advantages such as an excellent penetration in filled, dispersed or even heterogeneous samples, and a higher selectivity of the photoreaction as the process is less energetic.

In this presentation, an overview of the different photoinitiating systems incorporating ferrocenes as photocatalysts will be presented. Precisely, the mechanisms of photooxidation reaction of Fe(II) in presence of an iodonium salt – leading to a reaction between the excited state of the ferrocenes and the iodonium salt ($Fe(II)^*/Ar^2I^+$) and applied to the highly challenging field of photopolymerization will be detailed. The access to filled and thick samples thanks to NIR photopolymerization will also be discussed.[1]



1 P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V. F. Sidorkin, F. Dumur, D. Duché, D. Gigmes, J.-P. Fouassier, J. Lalevée, *manuscript under submission* (**2019**).