

Photochemistry, Organocatalysis & Enzymes: New Radical Opportunities

Paolo Melchiorre

p.melchiorre@unibo.it

The chemical reactivity of electronically excited molecules differs fundamentally from that in the ground state. This is the underlying reactivity concept of photochemistry,¹ which has traditionally allowed the development of unique chemical transformations not achievable via conventional ground-state pathways. For example, an excited-state molecule is both a better electron-donor (i.e. a better reductant) and electron-acceptor (i.e. a better oxidant) than in the ground state. This explains why light excitation of organic molecules can unlock unconventional reactivity manifolds.

In this context, our laboratory has been exploring the potential of some organocatalytic intermediates to directly reach an electronically excited state upon visible-light absorption to then switch on novel catalytic functions that are unavailable to ground-state organocatalysis.² A similar photo-activation principle can be applied to enzyme-bound organocatalytic intermediates to trigger non-natural radical processes within an active site. These photochemical approaches allowed us to expand the synthetic possibilities offered by the excited-state reactivity of organocatalytic intermediates and to develop enantioselective radical processes for which there is no general solution with established methods.

References:

- [1] V. Balzani, P. Ceroni, A. Juris, Eds. in *Photochemistry and Photophysics*, Wiley-VCH, 2014.
 - [2] M. Silvi, P. Melchiorre, *Nature* **2018**, *554*, 41–49.
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