

ORGANIC SYNTHESIS IN THE EXCITED STATE

Paolo Melchiorre

ICIQ - Institute of Chemical Research of Catalonia, Avinguda Països Catalans, 16
43007 (Tarragona, Spain)
pmelchiorre@iciq.es

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.^[2] 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 the 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 unavailable to ground-state organocatalysis.^[3] Here, the new synthetic possibilities, opened up by the excited-state reactivity of organocatalytic intermediates,^[4] will be discussed.^[5]

[1] V. Balzani, P. Ceroni, A. Juris, in *Photochemistry and Photo-physics*, Wiley-VCH, 2014.

[2] A. Albini, M. Fagnoni, in *Handbook of Synthetic Photochemistry*, Wiley-VCH, 2010.

[3] (a) E. Arceo, I. D. Jurberg, A. Álvarez-Fernández, P. Melchiorre, *Nature Chem.* **2013**, *5*, 750–756. (b) J. J. Murphy, D. Bastida, S. Paria, M. Fagnoni, P. Melchiorre, *Nature* **2016**, *532*, 218–222.

[4] M. Silvi, P. Melchiorre, *Nature* **2018**, *554*, 41–49.

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