

Light, Organocatalysis & Enzymes: New Radical Opportunities

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The chemical reactivity of molecules in electronically excited states fundamentally differs from that in the ground state. This forms the basis of photochemistry,^[1] which traditionally enables the development of unique chemical transformations not achievable via conventional ground-state pathways.^[2] Consequently, light excitation of organic molecules can unveil unconventional reactivity pathways. In this context, our laboratory has been investigating the capacity of certain organocatalytic intermediates to directly access an electronically excited state upon absorption of visible light, thereby activating novel catalytic functions inaccessible to ground-state organocatalysis.^[3] Additionally, we are exploring the potential of native biocatalytic intermediates, generated within enzyme active sites, to initiate redox chemistry upon light excitation. This enables asymmetric processes beyond the capabilities of small molecule domains.

- (1) Balzani, V.; Ceroni, P.; Juris, A. Eds. in *Photochemistry and Photophysics*, Wiley-VCH, 2014.
- (2) Albini, A.; Fagnoni, M. Eds. in *Handbook of Synthetic Photochemistry*, Wiley-VCH, 2010.
- (3) Silvi, M.; Melchiorre, P. *Nature* **2018**, *554*, 41–49.