

Factors Impacting Cage-Escape Yields in Iron(III) Photoredox Catalysis

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In natural and artificial photosynthesis, light absorption and catalysis are separate processes linked together by exergonic electron transfer. There is a plethora of organic transformations that can be sensitized to visible light, but the corresponding reaction mechanisms are not always straightforward. Here, we will present recent advances in the field of mechanistic photoredox catalysis by means of steady-state and time-resolved spectroscopies. A special emphasis will be placed on cage-escape yields, i.e. the efficiency with which the radicals formed after excited-state electron transfer separate and escape the solvent cage. To do that, we have used a series of rare earth and earth abundant photosensitizers that were engaged in either oxidative or reductive excited-state electron transfer processes.^[1-5] Cage-escape could be modulated and in some cases were shown to increase when the driving force for photo-induced electron transfer increased. Results show that an increase in cage-escape yields from 10% to 60% led to an increase in reaction yields from 30% to over 90%. Current efforts are focused on providing a deeper understanding of these fundamental cage-escape processes.

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