
Mechanistic Analysis and Design of (Novel) Transition-Metal-Complex-Based Photocatalysts for Triplet Energy Transfer Activation

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Chemical research has been steadily driven by the discovery and development of new synthetic methodologies, enabling access to previously uncharted domains of chemical space, or providing efficient, sustainable and cost-effective synthetic routes. To this end, harvesting and utilizing light energy – “energy in its most concentrated form” – represents a highly attractive means to overcome large activation barriers and enable otherwise elusive reactivity patterns. At the same time, the use of visible light demands for an efficient and selective harvesting and distribution of photonic energy, calling for compounds which can absorb, store and specifically transfer photonic energy. In this regard, photocatalysis has played a key role for synthetic chemistry: Most prominently, single-electron transfer processes from a photocatalyst’s excited state can enable access to highly reactive radical intermediates from closed-shell substrates. In this regard, transition metal complexes have been the catalyst system of choice on multiple occasions. In particular, polypyridyl and cyclometalated complexes of Ruthenium(II) and Iridium(III) have been widely applied in this context, owing to their extremely high absorption cross section, and the efficient generation of long-lived metal-to-ligand charge transfer (MLCT) states. Moreover, photostability and the absence of competing atom transfer side reactions have rendered these scaffolds attractive catalysts compared to organic (ketone) sensitizers. However, the fact that none of these catalysts have originally been designed as energy transfer catalysts, has led to undesirable electron transfer side reactivity, and has restricted the applicability to certain domains of substrate triplet energies.

Selectively tuning the properties of these complexes and the corresponding excited states, as well as developing sustainable alternatives to these noble metal complexes, have remained key challenges for achieving reactivity and selectivity control in efficient photon management through triplet-triplet energy transfer. In this context, the design of improved sensitizers and advanced systems requires an in-depth analysis and understanding of the experimentally observed reactivities, trends and correlations.