

Coordination of a PCET ligand to an iridium photocatalyst limits charge recombination and enhances quantum yield

Scientific Achievement

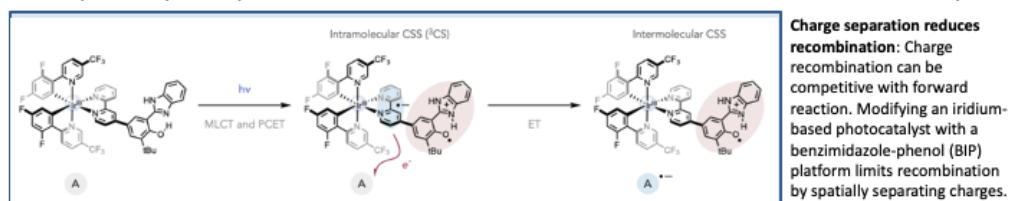
By slowing charge recombination in a photoredox reaction by coordinating a proton-coupled electron transfer ligand to an iridium photocatalyst quantum yields were improved

Significance and Impact

A photosynthesis-inspired approach is used to mitigate a major non-productive pathway.

Research Details

- A charge-separated excited state was seen upon photoexcitation of the PCET-appended photocatalyst. Oxidation of the charge-separated excited state leaves a hole on the PCET ligand rather than on Ir(IV).
- The rate constant for charge recombination following photoinitiated electron transfer to methyl viologen was an order of magnitude less than with the control catalyst.
- The quantum yield of phthalimide ester reduction increased 2-fold with the PCET-coordinated catalyst.



H. Sayre, H. H. Ripberger, E. Odella, A. Zieleniewska, D. A. Heredia, G. Rumbles, G. D. Scholes, T. A. Moore, A. L. Moore, R. R. Knowles, J. Am. Chem. Soc. (2021), DOI: 10.1021/jacs.1c01701.



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Upon photoinitiated electron transfer, charge recombination limits the quantum yield of photoredox reactions for which the rates for the forward reaction and back electron transfer are competitive. Taking inspiration from a proton-coupled electron transfer (PCET) process in Photosystem II, a benzimidazole-phenol (BIP) has been covalently attached to the 2,2'-bipyridyl ligand of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})][\text{PF}_6]$ ($\text{dF}(\text{CF}_3)\text{ppy}$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; bpy = 2,2'-bipyridyl). Excitation of the $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{BIP-bpy})][\text{PF}_6]$ photocatalyst results in intramolecular PCET to form a charge-separated state with oxidized BIP. Subsequent reduction of methyl viologen dication (MV^{2+}), a substrate surrogate, by the reducing moiety of the charge separated species demonstrates that the inclusion of BIP significantly slows the charge recombination rate. The effect of ~ 24 -fold slower charge recombination in a photocatalytic phthalimide ester reduction resulted in a greater than two-fold increase in reaction quantum efficiency.