FAST ELECTROCATALYTIC PCET VIA REDOX-ACTIVE LIGANDS ENABLES RADICAL CHEMISTRY

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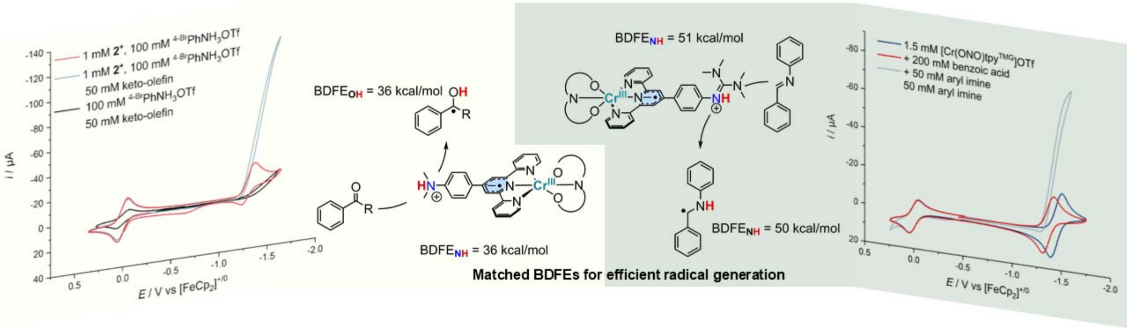
Electrocatalytic proton-coupled electron transfer (ePCET) is an enabling technology for energy-storing reactions and synthetically useful reductions, because it uses electrical energy and protons to form weak X–H bonds that are difficult to access otherwise.[1] ePCET is challenging for forming X–H bonds of <52 kcal/mol because of competition with H_2 release, but this can be limited using molecular mediators with spatially separated redox and acid/base sites.[2] However, very few molecular systems capable of electrocatalysis have been reported. Here, we show that a heteroleptic chromium-terpyridine complex facilitates ePCET to organic substrates at fast rates.



The rapid rate is attributed to the use of a redox-active terpyridine ligand, which can form a stabilized radical anion in the reduced form, while the chromium(III) scaffold is inert. Brønsted-basic substituents on the terpyridine ligand co-localize the proton and electron required for PCET, which leads to advantageous kinetics. By changing the Brønsted-basic substituent, the thermodynamic properties of the mediator can be easily modified and matched to different substrate classes. This design enables the fast, energy-efficient and selective generation of radicals from substrates with C=O, C=N and C=C multiple bonds, and these radicals can be used for subsequent reactivity like cyclizations and additions to electrophiles. Mechanistic studies indicate that the delivery of H^+/e^- to the substrates is concerted, and goes through a transition state that builds up negative charge on the substrates. Thus, the rates follow the driving force for PCET, which allows a predictive approach to the design and optimization of catalytic protocols. Overall, the novel modular mediator system is important for its fast rates, accessibility of mechanistic detail, and easy synthesis.

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[2] Chalkley, M. J.; Garrido-Barros, P.; Peters, J. C. A molecular mediator for reductive concerted proton-electron transfers via electrocatalysis. *Science* **2020**, *369* (6505), 850-854.