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Quantifying Photon-Driven Molecular Electrocatalysis with Cyclic Voltammetry

Dr. Dylan Boucher
Baylor University
Assistant Professor, Chemistry and Biochemistry
Website: https://www.boucher-lab.com/

In the past decade, electrochemical methods in organic synthesis have gone from a niche field to a mainstream methodology capable of unique selectivity. Much of the appeal is that electrochemistry provides a tunable methodology of activating inert substrates. Unique methods like electro-photocatalysis, the co-localization of photons and electrons on a single reaction center, has enabled deeply reducing and oxidizing synthetic reactions. However, directing the selectivity of these highly reactive intermediates remains a challenge due to our poor mechanistic understanding at longer timescales. At present, ultrafast spectroscopy represents the best method for understanding excited state dynamics, yet the difference in timescale (pico- to nanosecond) from synthetic experiments (hours to days) makes a truly quantitative mechanistic relationship difficult. Electroanalytical methods, such as cyclic voltammetry (CV), could provide a much-needed connection between these two timescales to investigate electro-photocatalytic behavior (and at a fraction of the experimental cost). However, a well-defined molecular picture of CV responses under illumination has yet to arise, and the utility of these experiments remain uncertain.

Here, we provide a straightforward and quantitative interpretation of molecular electro-photocatalysis that yields experimentally useful parameters, such as quantum yield and catalytic rates, directly from CV experiments. With a well-behaved experimental model system and mechanistic support from finite element simulations, we provide a detailed picture on physical concerns and the constraints of light-dependent voltammetry. These efforts represent a significant step towards a molecular understanding of photocatalysis at longer timescales and pave the way towards electrocatalytic control of deeply reducing/oxidizing reactions.