



Selective Synthesis via Light and Electricity

Abstract: We are investigating how organic radical ions—typically thought of as fleeting intermediates—can be tamed and exploited as a new family of organocatalysts and small molecule reagents. We identified selective generation of such species as a key hurdle stymying exploration these electronically-destabilized systems. To address this problem, we have leveraged electrochemistry to develop new synthetic transformations driven by organic radical ions. Electrochemistry offers not only an environmentally benign approach to promote redox events but also substantially simplifies the study of these unusual systems by enabling the exclusion of byproducts from oxidation or reductive generation of the key radical ion promoters.

This seminar will describe two new platforms for synthetic reaction development based on electrogenerated persistent organic radical ions. In the first system, we describe the development of a new family of radical anion photoredox catalysts over a volt more reducing than conventional photocatalyst systems. These potent catalysts have enabled abundant but classes of arene substrates to now act as general aryl radical precursors for diverse radical coupling reactions. In the second system, we will discuss a new approach to oxidatively functionalize alkenes via a metastable dielectrophilic intermediate derived from reaction with thianthrene radical cation. This strategy has enabled new synthetic methods to construct high value aliphatic amine products by coupling amines and feedstock hydrocarbons.

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