Catalyst discovery for metal-free, photoredox CO$_2$ reduction

Organic photoredox catalysis will be an important part of an energy-efficient, sustainable future as these catalysts can access highly reactive states upon excitation and quenching to carry out reactions that are otherwise thermally inaccessible or energy-intensive. Our group aims to identify sustainable photoredox routes for CO$_2$ utilization. Prior experiments show that a simple organic chromophore, *p*-terphenyl, can reduce and transform CO$_2$ into useful molecules such as amino acids. However, the steps of the photoredox cycle and reasons for low turnover numbers of these catalysts are poorly understood. Our goal is to utilize quantum chemistry methods to delineate mechanisms of key steps in this cycle and leverage these insights to drive discovery of novel chromophores that are both active and yield high turnover numbers. Thus far, we have demonstrated that the electron transfer (ET) step from the *p*-terphenyl radical anion to CO$_2$ is adiabatic, and ET barriers are lowered when electron-donating groups are substituted to p- terminal positions of the catalyst. To probe degradation pathways from the excited state, we are establishing a computational protocol for calculation and characterization of excited-state donor-acceptor charge transfer complexes, or exciplexes. We are also taking our first steps towards driving discovery of new chromophores by implementing a genetic algorithm (GA) whose fitness function factors in both catalyst activity and degradation resistance by means of simple descriptors obtained from routine DFT calculations. The GA yields several candidates that are more viable than experimentally studied terphenyls, highlighting the importance of automated computational tools in accelerating experimental efforts.