A Friday Synthesis Symposium Presentation:
Harnessing Photophysical Processes to Improve Photoredox Catalysis

Speaker: Ben Ravetz (Rovis Group)

When: Friday, March 15, 2019 at 4:00 PM

Where: Havemeyer 209

Abstract: Recent advances in photoredox catalysis have made it possible to execute a multitude of challenging synthetic transformations, polymerizations, and surface modifications. In all cases, these transformations require ultraviolet or visible light stimuli. The use of visible light irradiation has intrinsic challenges; the penetration of visible light is very low through most reaction media, leading to problems in large scale reactions, and reactants can compete with the photocatalysts for incident light absorption, limiting scope. Near infrared (NIR) radiation can overcome many of these fundamental problems. NIR light is known to have a much higher penetration depth through a variety of media, notably biological tissue. We demonstrate a variety of photoredox transformations under infrared radiation by utilizing the photophysical process of triplet fusion (TF) upconversion. This approach allows us to execute catalysis through several barriers that are impenetrable by visible light, expanding the landscape of photocatalysis to a variety of new materials and environments. In addition to harnessing the photophysics of TF upconversion, I will discuss the photoactivation of catalytic intermediates in first-row transition metal catalysis. We have found that cobalt acetylides, formed in situ, are photoactive complexes that undergo ligand-to-metal charge transfer (LMCT) using visible light. The net transformation uses air-stable Co(II) complexes as precatalysts and induces Co(I) chemistry. The acetylide is an electron reservoir forming the Co(I) but accepting the electron back at the end of the catalytic cycle. The electronic nature of the acetylide leads to either on–off behavior or simply initiates catalysis, depending on electronics.