

Creating superhot electrons by light

By Amit Biswas



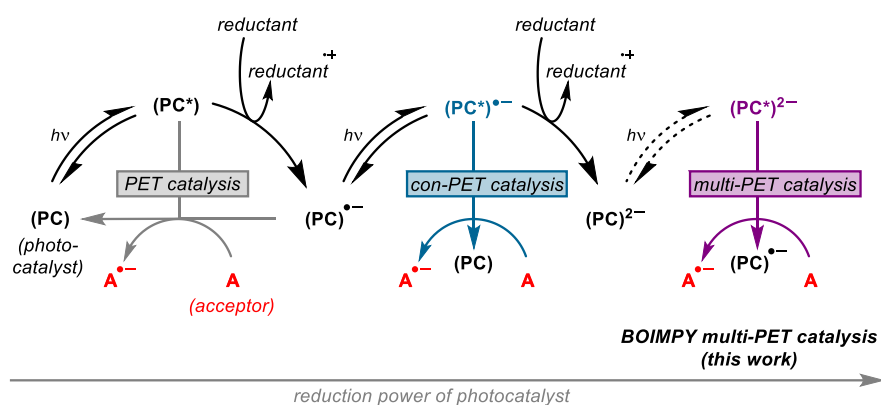
Catalytic reactions driven by light have emerged as a powerful approach in chemical synthesis, a field commonly referred to as photocatalysis. In these processes, the absorption of light (typically through a quantum of light energy, known as a photon) excites an electron to a higher energy state. This "hot" (excited) electron may gain sufficient energy to facilitate various chemical reactions. Single-electron excitation by photon absorption can lead to the formation of highly reactive species called radical anions when an electron donor is present. This, in turn, triggers a process known as photoinduced electron transfer (PET), activating nearby molecules and enabling a range of chemical transformations. By integrating this PET process into a catalytic loop, the efficiency of these reactions can be significantly enhanced.

Building on this concept, researchers later demonstrated that the sequential absorption of two photons instead of one could produce even more hot electrons, enabling consecutive PET (known as con-PET). This process (con-PET), employs two photons to generate highly active catalysts capable of driving challenging reactions. In our study, we extend this paradigm by demonstrating that electrons can become "superhot" through the absorption of three consecutive photons. These superhot electrons are capable of performing exceptionally challenging reactions, such as breaking one of the strongest chemical bonds: the carbon-fluorine (C-F) bond.

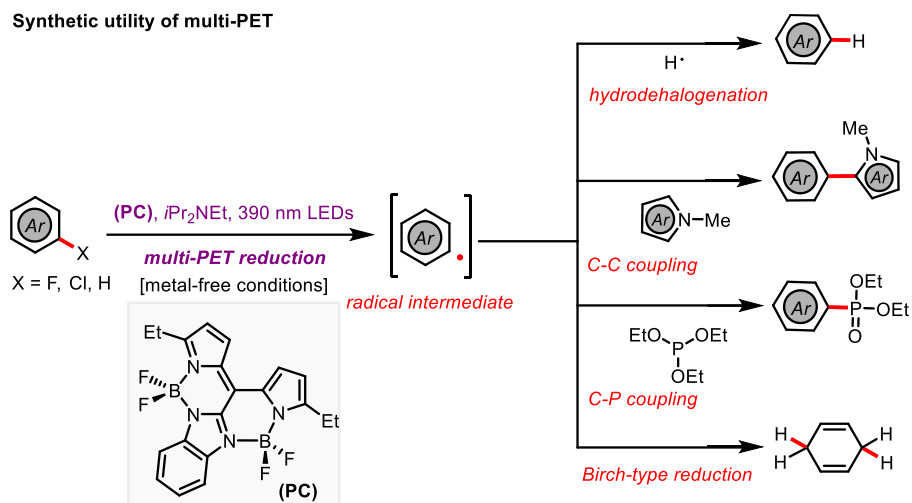
Our research focused on a unique dye molecule reduced by two electrons. By exposing this molecule to three photons of violet light (390 nm), we generated an exceptionally strong reductant—more potent than lithium metal, one of the most powerful known chemical reducers. This metal-free catalyst successfully broke C-F bonds, leading to the formation of radicals that could combine with hydrogen atoms or create new carbon-carbon and carbon-phosphorus bonds.

The implications of this discovery are significant. This process could pave the way for recycling environmentally persistent and toxic "forever chemicals," such as polyfluorinated compounds, which are notoriously difficult to decompose. We are currently exploring such possibilities to address critical environmental challenges.

Catalytic photoredox cycles for reductive transformations



Synthetic utility of multi-PET



Refs: **Amit Biswas**, Simon Kolb, Sebastian Röttger, Arpan Das, Lukas J Patalag, Swagata Sil, Subir Maji, Soumi Chakraborty, Oliver S. Wenger, Anup Bhunia, Daniel B Werz, **Swadhin K Mandal**, *Angew. Chem. Int. Ed.*, **2025**, e202416472,