New Pathways for Red Light Driven Photoredox Catalysis

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Within the last decade the field of photoredox catalysis using multi-photonic mechanisms has grown rapidly and a variety of new systems have been investigated.[1–3] In contrast to well established methods that rely on one photoactive compound which absorbs two (or more) photons per catalytic turnover of substrate, combinations of two photoactive catalysts are underexplored.[4–6]

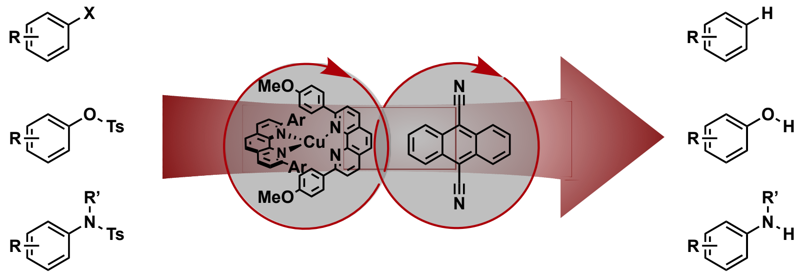

Figure 1: Schematic summary of the investigated catalytic system together with the investigated transformations.

Our approach adapts the concept of using two separate chromophores that is well-known from the Z-scheme of natural photosynthesis. The combination of two photoactive catalysts can perform challenging reductive transformations including dehalogenations of aryl halides as well as detosylations of protected phenols, amines and anilines (Figure 1). By the choice of a copper-based photosensitizer in combination with 9,10-dicyanoanthracene (DCA), red light instead of (typically used) blue or green irradiation sources can be used to achieve successful product formation.

Spectroscopic investigations of the reaction mechanism by time-resolved laser spectroscopy illustrate that a photoinduced electron transfer as well as a sensitization-initiated electron transfer pathway occur in solution. These findings indicate that both pathways can be relevant for the formation of the radical anion of DCA as key intermediate of the catalytic cycle.

The substrate scope - with over 40 substrates investigated - together with the mechanistic insights seem to offer new perspectives for red-light driven photoredox catalysis.

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