

# A Transient Look on Photocatalytic Reactions Involving Preassembly

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With the goal to decipher the underlying reaction mechanism, we discuss the light-induced dynamics observed with time-resolved spectroscopy for several systems where preassembly between a photocatalyst and substrate molecules is decisive. This preassembly may fulfil different roles, on the one hand to circumvent diffusion and hence make short-lived excited states exploitable for photocatalysis, on the other hand to achieve well-defined orientations and facilitate selective reactions.

For an octahedrally coordinated bis(diiminopyridine)cobalt complex whose excitation enables the visible-light-driven arylation of pyrroles with chloro- and bromoarenes, spectroscopic studies elucidate that its excited-state lifetime is only a few picoseconds. Ultrafast quenching and computational studies confirm that an interaction within the short excited-state lifetime occurs, owing to a preassembly of the substrate molecules with the complex [1]. Further photochemical reactions involving xanthine derivatives [2], their photochemical rearrangement, and their potential for photocatalysis as a ligand in Ni-xanthine complexes will be discussed.

Photoreactions in preassembled species can also be employed for deracemization, as is discussed for hydantoins. The substrate binds to a chiral benzophenone-based photocatalyst by two-point hydrogen bonding, i.e., a pre-complexation exists when the catalyst is excited by light. We show that two criteria have to be met for the reaction to work efficiently: First, light absorption triggers a transfer process that works better (or exclusively) for one of the enantiomers. Second, an achiral intermediate has to be formed whose lifetime exceeds that of the complex, so that the subsequent reformation of the chiral substrate is not enantioselective [3].

[1] J. Märzsch *et al.*, *Angew. Chem. Int. Ed.* 2024, **63**, e202405780, 10.1002/anie.202405780

[2] R. E. Rodriguez-Lugo *et al.*, *under review*, 2024.

[3] R.J. Kutta *et al.*, *J. Am. Chem. Soc.* 2023, **145**, 2354, 10.1021/jacs.2c11265

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