P3.2 Mechanistic insights and theoretic modeling of the visible-light-mediated oxalate synthesis from CO_2 through a TM-photoredox cascade

Topic and overall goal. This work package is devoted to the establishing a photoredox scheme for the photo-mediated oxalate synthesis from carbon dioxide catalyzed by transition metal biscarboxylate complexes.[1] Photoredox catalysis and visible-light excitation provides access to reactive radical species from abundant native functional groups. By modulating the oxidation state of transition metal complexes or by energy transfer-mediated excitation of catalytic intermediates, photocatalysis can open access to the activation of formally inert molecules, e.g., of CO_2 for the synthesis of oxalates and related products. The following routes will be under investigation: (i) direct reductive elimination through excitation of bismethoxycarbonyl complexes, (ii) synthesis and characterization of bimetallic bismethoxycarbonyl complexes bearing iridium and ruthenium-based photoredox-active nuclei and, (iii) oxalate synthesis from bismethoxycarbonyl complexes using photoredox-active co-catalysts.

Specific Aim. This work will focus on elucidating the plausible mechanistic pathways of the different strategies for the photo-mediated turn-over of bismethoxycarbonyl complexes by experimental and theoretic means. The particular systems will be chosen based on the preliminary work performed in P3.1. The energy profile of the turnover of bismethoxycarbonyl complexes in the ground state and excited state will be evaluated. This work will be done as a symbiosis of theoretical calculations and spectroscopic studies of the ground and the excited state of specially synthesized transition metal complexes. The work package will link preparative and theoretical techniques to identify and verify key parameters for the success of light-mediated, transition metal-catalyzed oxalate synthesis from carbon dioxide.

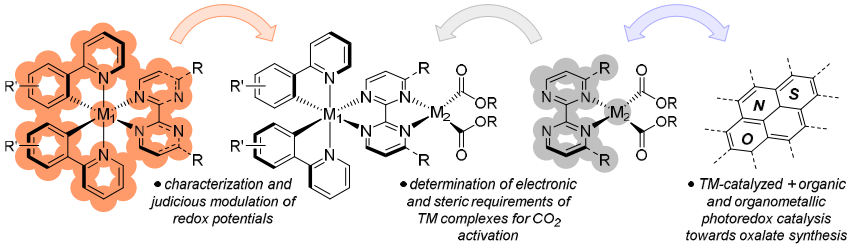

Figure P3.2. Proposed reaction principles for the photo-mediated catalytic turn-over of bismethoxycarbonyl complexes.

Within this project, the Ph.D. student will learn the synthesis of ligands and highly reactive hybrid organic/organometallic compounds, photocatalysis, reaction monitoring by NMR and UV-vis spectroscopy, and receive basic knowledge in modeling of mechanistic steps by quantum chemical calculations.[2]

Connection within the RTG. The work will be supported by the time-resolved IR spectroscopy and the determination of fluorescence lifetimes and quantum yields in collaboration with the Lochbrunner group (TP4), voltammetric measurements (Francke, TP2), as well as the handling of high-pressure facilities (Pospech/Beller). The observed signatures in the experimental spectra will be interpreted by simulations using the approaches developed in P3.4. This P3.2 is closely connected with other projects or TP3 to achieve the synergetic effect for using a multi-instrumental approach.

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1 a) R. Hauptmann, A. Petrosyan, F. Fennel, M. A. Argüello Cordero, A.-E. Surkus, J. Pospech, *Chem. Eur. J.* **2019**, *25*, 4325–4329; b) T. Täufer, M. A. Argüello Cordero, A. Petrosyan, A.-E. Surkus, S. Lochbrunner, J. Pospech, *ChemPhotoChem* **2021**, 5, 999–1003.

2 S. I. Bokarev, O. S. Bokareva, O. Kühn, *Coord. Chem. Rev.* **2015**, *304–305*, 133–145.