

Exploiting the Disulfide/Dithiol Switch for Artificial Photosynthesis and Photoredox Catalysis

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Light-driven proton-coupled electron transfer (PCET) processes are receiving great attention because they are key to innovative approaches for solar-to-fuel transformations, such as photocatalytic H₂ formation. In this context we have equipped bipyridine-ligated photoactive transition-metal complexes with peripheral disulfide/dithiol redox switches (**1-3**; Figure 1), and we have studied their PCET thermochemistry, excited-state dynamics and photoinduced reactivity.^[2]

This presentation will focus on a new rhenium photosensitizer **4** decorated with a disulfide moiety,^[3] which is capable of storing two electrons and one proton in a light reaction and release these in the form of H-atom transfer (HAT) or hydride transfer in a dark reaction. **4** can also serve as a combined photoredox- and HAT catalyst. The disulfide/dithiol-couple offers interesting perspectives in molecular artificial photosynthetic systems, as 2e⁻ transformations can benefit from potential inversion.

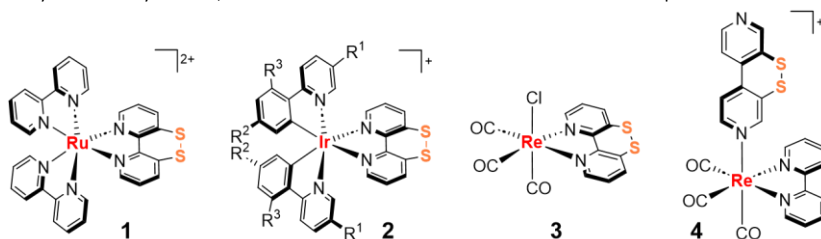


Figure 1: Photoactive complexes with peripheral disulfide/dithiol redox switches.

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[2] (a) S.-A. Hua *et al.*, Inorg. Chem., 2020, **59**, 4972, DOI: 10.1021/acs.inorgchem.

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[3] J. Franz *et al.*, J. Am. Chem. Soc., 2024, **146**, 11272, DOI: 10.1021/jacs.4c00548