Charge Accumulation through Potential Inversion in a Molecular Heptad

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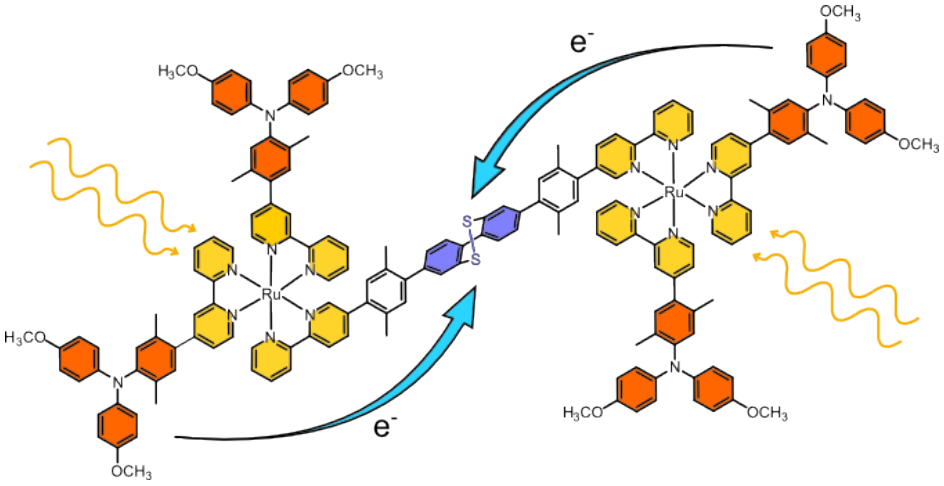
Charge accumulation lies at the basis of many important processes in nature. For example, photosynthesis relies on the temporary storage of redox equivalents on plastoquinone and the oxygen-evolving complex.[1] In context of the need for sustainable energy sources, where artificial photosynthesis is a promising approach, it is highly important to understand the fundamental underlying processes of electron accumulation.



In this project, a central dibenzo [1,2] dithiin was incorporated between two $Ru(bpy)_3^{2+}$ photosensitizers with triarylamine subunits as electron donors on the bipyridine ligands. Upon excitation of both photosensitizers, two electrons are transferred from the triarylamine-donors to the central electron-accepting unit.[2] The advantage of the sulfur-bridged acceptor is its unusual potential inversion in the two-electron reduction, where the second reduction is observed at a significantly less negative potential than the first one.[3]
However, to drive the water splitting reaction, it is necessary to accumulate four electrons on an acceptor unit.[3] Therefore, electron acceptors with two disulfide bridges are currently investigated.

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[2] J. Nomrowski, O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 5343–5346.
[3] G. B. Hall, R. Kottani, G. A. N. Felton, T. Yamamoto, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc.* **2014**, *136*, 4012–4018.