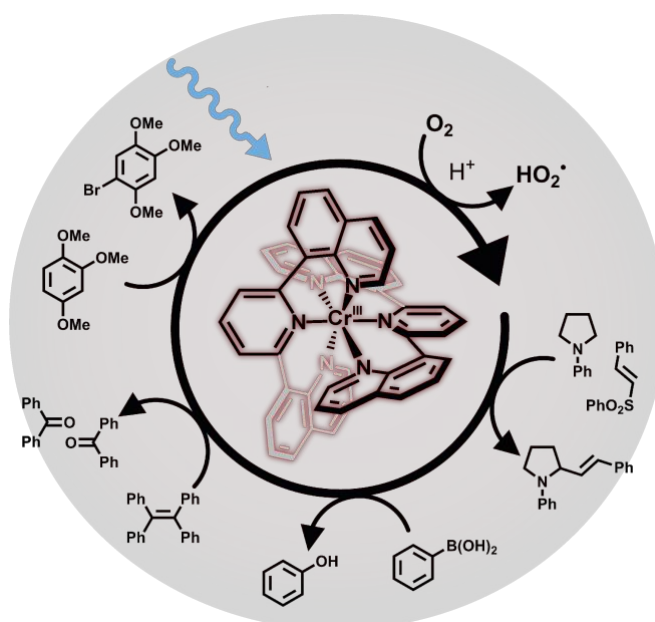


## A Spin-Flip Excited Cr<sup>III</sup> Complex in Photoredox Catalysis

Tobias H. Bürgin, Felix Glaser, Oliver S. Wenger

Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland  
tobias.buergin@unibas.ch

Ru<sup>II</sup> polypyridines are commonly employed as catalysts in photoredox transformations, whereas Cr<sup>III</sup> analogues are only little explored in comparison and have been mainly investigated for their luminescence properties.<sup>[1]</sup> Owing to the spin-flip nature of the lowest electronically excited state of d<sup>3</sup> metal luminophores, which stands in contrast to the metal-to-ligand charge transfer (MLCT) excited state of their d<sup>6</sup> counterparts, it is not self-evident that Cr<sup>III</sup> complexes would have to show similar photoredox activity.



[Cr(dqp)<sub>2</sub>]<sup>3+</sup> (dqp=2,6-bis(8'-quinolinyl)pyridine) is part of a novel series of Cr<sup>III</sup> complexes with tridentate polypyridyl ligands ensuring nearly perfect octahedral and rigid coordination geometries.<sup>[2]</sup> We found that the driving-force dependence for photoinduced electron transfer from 10 different donors to [Cr(dqp)<sub>2</sub>]<sup>3+</sup> is very similar to that of a Ru<sup>II</sup> polypyridine reference. We conclude that electron transfer to the spin-flip excited state of [Cr(dqp)<sub>2</sub>]<sup>3+</sup> is facilitated to the same extent as in the case of MLCT-excited Ru<sup>II</sup> complexes. Consequently, [Cr(dqp)<sub>2</sub>]<sup>3+</sup> was employed as catalyst in photoredox reactions that have not previously been explored for this compound class. This includes aerobic bromination of methoxyaryls, oxygenation of 1,1,2,2-tetraphenylethylene, aerobic hydroxylation of arylboronic acids, and vinylation of *N*-phenyl pyrrolidine.

- [1] W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, doi.org/10.1007/s43630-022-00186-3.
- [2] J. R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244–13252.