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A Spin-Flip Excited Cr^{III} Complex in Photoredox Catalysis

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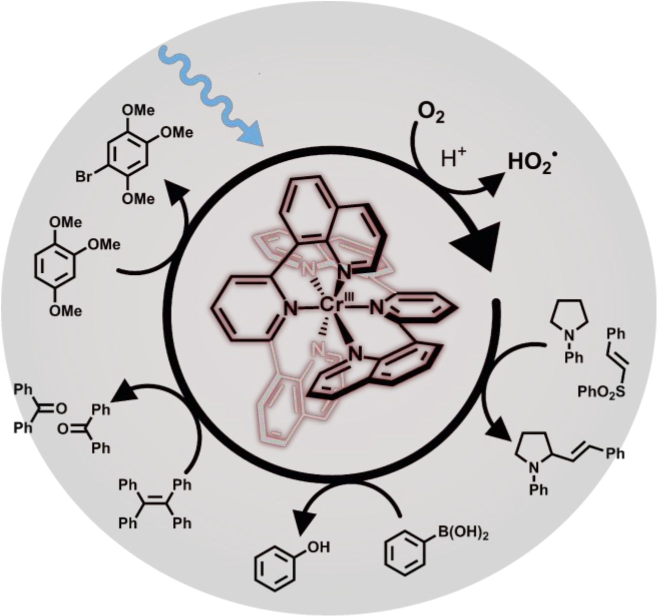
Ru^{II} polypyridines are commonly employed as catalysts in photoredox transformations, whereas Cr^{III} analogues are only little explored in comparison and have been mainly investigated for their luminescence properties.[1] Owing to the spin-flip nature of the lowest electronically excited state of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



$[Cr(dqp)_2]^{3+}$ (dqp=2,6-bis(8′-quinolinyl)pyridine) is part of a novel series of Cr^{III} complexes with tridendate polypyridyl ligands ensuring nearly perfect octahedral and rigid coordination geometries.[2] We found that the driving-force dependence for photoinduced electron transfer from 10 different donors to $[Cr(dqp)_2]^{3+}$ is very similar to that of a Ru^{II} polypyridine reference. We conclude that electron transfer to the spin-flip excited state of $[Cr(dqp)_2]^{3+}$ is facilitated to the same extent as in the case of MLCT-excited Ru^{II} complexes. Consequently, $[Cr(dqp)_2]^{3+}$ 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.