IRIDIUM(III)-CATALYZED SIX-ELECTRON PHOTOOXIDATION OF NITROGEN, SULFUR, AND SELENIUM COMPOUNDS

Ulrich Schatzschneider

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg,
97074 Würzburg, Germany

In the context of our studies of [3+2+1] iridium(III) complexes as biological probes, we have discovered that small monodentate ligands coordinated to the metal center *via* an N-, S-, or Se-atom undergo a very efficient six-electron photooxidation under blue light in the presence of molecular dioxygen [1]. Interestingly, in the case of the chalcogen ligands, this is accompanied by a significant increase in luminescence at about 550 nm, while the parent complexes are non-emissive, an effect which was observed both in solution and when the title compound was adsorbed on filter paper (Fig. 1).

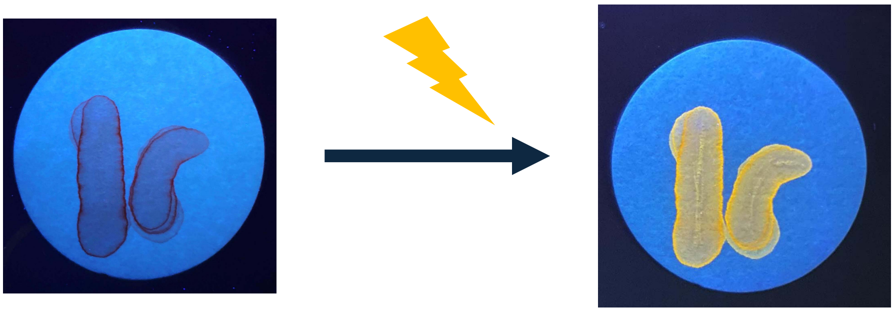

Fig. 1: Response of a [3+2+1] iridium(III) complex adsorbed on filter paper to blue light exposure. The non-emissive parent compound (left) undergoes photooxidation in air to a yellow emissive species (right).

In the present contribution, we will provide spectroscopic, structural, and theoretical insight into the reaction mechanism, intermediates and products, and show by ^{1}H NMR spectroscopy that the system undergoes several cycles without decomposition (Fig. 2).

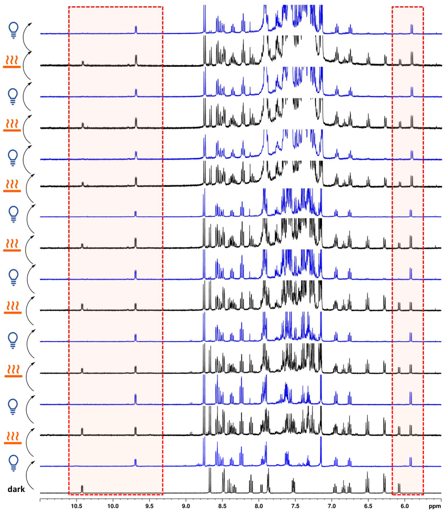

Fig. 2: ^{1}H NMR spectra recorded for the [3+2+1] iridium(III) photocatalyst under repeated cycles of illumination with blue light followed by re-generation upon heating in the dark.

---

[1] V. Müller, D. Moreth, K. Kowalski, A. Kowalczyk, M. Gapinska, R.J. Kutta, P. Nürnberger, U. Schatzschneider, *Chem. Eur. J.* **2024**, *30*, e202401603, doi:10.1002/chem.202401603