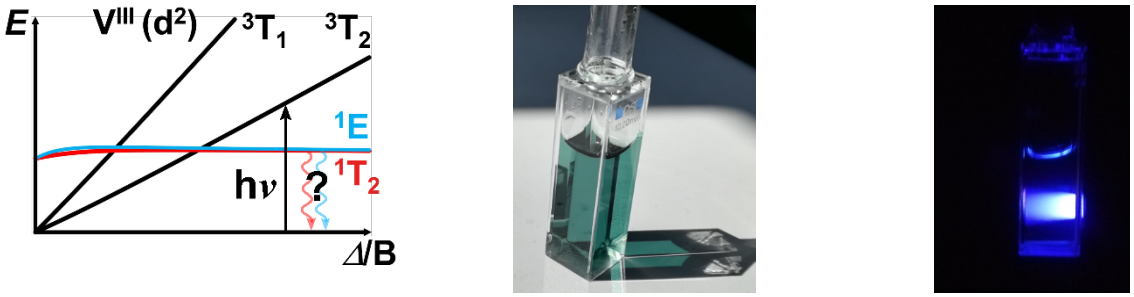
A vanadium(III) complex with dual emission in solution

M. Dorn,[a] J. Kalmbach,[b] P. Boden,[c], A. Päpcke[d], L. Büldt[b], M. Seitz,[b] M. Gerhards,[c] S. Lochbrunner[d] and K. Heinze[a]

[a] Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany, email: katja.heinze@uni-mainz.de
[b] Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany
[c] Institute of Physical and Theoretical Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany
[c] Institute of Physics, University of Rostock, Albert-Einstein-Straße 23, 18059 Rostock, Germany

Enabling luminescence from 3d metal complexes is a difficult task due to their intrinsically low ligand field splittings. Intraconfigurational spin-flip states of $3d^3$ complexes, however, as in $[Cr(ddpd)_2]^{3+}$ have been successfully employed for room temperature NIR luminescence featuring six-membered strong field chelate ligand ddpd (*N,N'*-dimethyl-*N,N'*-dipyridin-2-yl-pyridine-2,6-diamine)[1]. The $3d^2$ ion vanadium(III) has received much less attention, while in theory also offering access to such low-lying spin-flip states. With smaller Racah parameters, conceivable phosphorescence should occur at even longer wavelengths than in $[Cr(ddpd)_2]^{3+}$. Here, we report on the synthesis of a rare vanadium(III) oligopyridine complex and its intriguing luminescence properties[2].



TS diagram (l.), photograph of an oligopyridine vanadium(III) complex in solution (m.) and under irradiation @ 350 nm (r.).

The structure, absorption and luminescence spectra as well as time-resolved spectroscopic analyses (luminescence, fs-transient absorption and ns-step scan IR spectroscopy) combined with high-level quantum chemical calculations and dynamics simulations are reported along with the effect of ligand deuteration[4,5].

Literature:

[1] Ch. Förster, K- Heinze, *Chem. Soc.Rev*. **2020**, *49*, 1057.
[2] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576.
[3] M. Dorn, J. Kalmbach, P. Boden., A. Päpcke, L. Büldt, C. Förster, F. Kuczelinis, L. Carrella, N. Bings, E. Rentschler, S. Lochbrunner, M. Gerhards, M. Seitz, K. Heinze, *J. Am. Chem. Soc.* **2020**, *142*, 7947-7955.
[4] S. Otto, M. Dorn, Ch. Förster, M. Bauer, M. Seitz, K. Heinze, *Coord. Chem. Rev.*, **2018**, *359*, 102–111.
[5] C. Wang, S. Otto, M. Dorn, E. Kreidt, J. Lebon, L. Srsan, P. Di Martino-Fumo, M. Gerhards, U. Resch–Genger, M. Seitz, K. Heinze, *Angew. Chem. Int. Ed.* **2018**, *57*, 1112–1116.