Fs-XES of the NIR-active spin-flip emitters

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The design of photoactive complexes with earth-abundant metal ions is very challenging, yet a very active and rapidly growing field of research. The ultimate aim is to replace expensive noble and rare earth metal ions with earth-abundant and hence sustainable metal ions for applications such as photosensitizing, photoluminescence, electroluminescence or photo(redox) catalysis. [1]

Emission in the near infrared (NIR) spectral region is challenging due to the often, efficient non-radiative multiphonon relaxation via high energy oscillators. The scarcity of luminescent 3d metal complexes arises from the presence of low-energy ligand field excited states (MC, metal centered states), enable efficient non-radiative decay to the ground state. The new chromium(III) complex $[Cr(ddpd)_2]^{3+}$ [2,3] is based on the tridentate ligand (ddpd). The “molecular ruby” features two very sharp NIR emission bands at 775 and 738 nm arising from the metal centered *spin-flip transitions* $^2E \rightarrow {}^4A_2$ and $^2T_1 \rightarrow {}^4A_2$, respectively. It features a high photoluminescence quantum yield of $\Phi = 11\ \%$ and a luminescence lifetime of $\tau = 898\ \mu s$ in water at room temperature. [3] According to Tanabe-Sugano diagram for d^3 octahedral systems, the high ligand field in the complex possibly allows the excited $^4T_2$ state to relax via previously inaccessible $^2T_2$ state. [2]

The deexcitation cascade was studied using femtosecond pump-probe Cr K-edge X-ray emission spectroscopy (fs-XES) on FXE beamline (Fig. 1). The experiment revealed a complex multiplet structure of a transient Cr $K\alpha_1$ emission line ($\Delta\ K\alpha_1$) in Cr(ddpd) and reference Cr(III) compounds, while relatively uneventful evolution of $\Delta K\beta$ signals. The sensitivity of $\Delta K\alpha_1$ was used to extract dynamics and sequence of the excited states. The extraordinary ligand field affects the excited state landscape, affecting the spin-flip luminescence lifetimes. The rigid, octahedral structure of the ddpd ligand has a destabilizing effect on Frank-Condon ^4CT (charge-transfer) states manifold. The preferred subsequent reduction of the axial Jahn-Teller distortion occurs via deexcitation through the $^2T_2$ state leading to the elongation of the luminescence lifetimes in the complex. These findings are in line with theoretical predictions concerning excited states in the molecule and with transient absorption spectroscopic data [4].

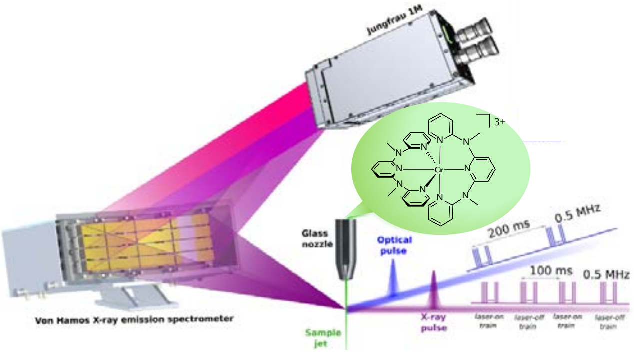

Figure 1. Experimental setup used at FXE beamline and molecular structure of $Cr(ddpd)_2^{3+}$.

While these results represent a step forward in understanding ultrafast phenomena, certain unexpected effects—such as $\Delta K\alpha 1$ evolution—still require a rigorous explanation. The molecule can function both independently and within charge-transfer heterobimetallic assemblies [5]. By identifying key excited states, chemical engineering can leverage its long-lived luminescence for molecular-scale detection of pressure, pH, polarity, changes in electromagnetic fields, or anisotropic forces.

References

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