Light and Gas Triggered Reactivity of Metal-Oxo Clusters in the Single Crystal Phase

Scientific case for the project: Photoactive metal oxide semiconductors, such as TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3}, are used in antimicrobial surfaces, self-cleaning materials and are in current research to develop renewable ‘solar fuels’ by photocatalytic processes. Therefore, understanding the precise photochemical mechanisms of these materials is important for their development, but is hard to achieve on complex heterogenous surfaces. The Pike group studies atomically precise metal-oxo clusters (0.5-2 nm in size), which are well-defined and tuneable analogues of the widely used semiconductor materials. The Pike group also use these clusters as new nodes for novel photoactive metal-organic-frameworks. The clusters can capture energy from light to form redox reactive states, which can perform both challenging oxidation (e.g. water) and reduction (e.g. CO\textsubscript{2}) reactions. This is of global importance in the development of the sustainable formation of ‘solar fuels’ via artificial photosynthesis.

Recent studies highlight that detailed mechanistic studies can be achieved with these clusters and that reactivity can be uncovered by following reactions in the solid-state, utilising light or gas driven single-crystal to single-crystal (SC-SC\textsuperscript{1,2}) transformations.\textsuperscript{3} We hypothesise that the crystal packing of pseudo-spherical clusters (Fig. 1) allows for some flexibility, with mobility of co-crystallised solvent molecules, allowing for SC-SC transformations without crystal degradation. Ultimately, our objective is to use crystals of these clusters, or novel frameworks built from them, as new tuneable materials for photocatalysis. This project will uncover crucial mechanistic information as well as furthering understanding of the mobility of molecules within the single crystal phase, paving the way towards utilising single-crystal materials for photocatalytic processes.\textsuperscript{4}

SC-SC studies of metal-oxo clusters will establish the direct products of a photoredox reaction captured within the crystal lattice. Furthermore, photoactivated metal-oxo-alkoxide clusters become highly reducing and can react with O\textsubscript{2} or CO\textsubscript{2}. By designing new experimental apparatus to allow both simultaneous or stepwise light irradiation and gas exposure, these multistep reactions can be studied in one controlled experiment. Preliminary studies (including on I19 in 2021) demonstrate photoredox reactivity of Ti-oxo clusters in the crystal phase, and establish initial targets for SC-SC experiments. Remarkably, our initial studies show that photochemical reactions are dependent on co-crystallised solvent molecules, indicating that multi-molecular pathways are occurring within the crystal phase.

I19 instrumentation is essential for conducting experiments on very small crystals to avoid strain-related degradation during the solid-state transformation. Furthermore, the project will study Fe-oxo clusters, utilising synchrotron radiation at DLS to avoid complications with fluorescence on in-house (Cu K-\alpha) instruments. These experiments will capitalise on recent equipment development at I19 (gas cells and flow reactors for studying SC-SC under gas...
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flow), but will introduce a new combined gas + light activation element. The project will involve design and development of apparatus to allow both gas flow and light illumination upon a mounted crystal, extending current capability with a view to allowing for a wide range of different photocatalytic studies on single crystalline materials. An immediate goal will be to acquire UV light sources in the 300-350 nm range which are not currently available on I19, other than by complex arrangement of the femtosecond PORTO laser. New high intensity LEDs have recently come to market (e.g. intelligent LED solutions UVB powerstar) which will allow for a far more straightforward and customisable setup. This collaborative project will enable new cutting edge setups for studying chemistry in the crystalline phase and continue to promote DLS as a world leading centre of excellence for SC-SC transformations.²,⁵

Crystallographic studies at DLS will be complimented by spectroscopic studies of the SC-SC processes at UoW using solid-state EPR, NMR, Raman, IR and UV-vis spectroscopies. The student will also test the photocatalytic potential of crystalline materials as at UoW.


Studentship Deliverables:

- Develop photo-irradiation + gas-flow setup at DLS for light + gas SC-SC transformations.
- Determine the mechanism of photoredox transformations in Ti-oxo clusters & Fe-oxo clusters, and their photoreactivity in the presence of O₂ and CO₂.
- Establish the ground rules for a successful SC-SC transition for cluster molecules.

Research techniques: Single Crystal X-ray crystallography (DLS) (with potential for powder and/or serial crystallography studies), Solid-state EPR/NMR/UV-vis spectroscopies (UoW)


Milestones:

- **Year 1**: Postgraduate Certificate in Analytical Science (from CDT). Acquire and setup new UV light sources and establish working conditions for SC-SC studies at DLS.
- **Year 2**: Collection of SC-SC data, including photoredox reactions of [TiO(OR)(L)]ₙ (L = O₂PPh₂, O₂CCMe₃, n=4-6) and Ti₁₇O₂₀OPr₂₀ under different gas environments (N₂/O₂/CO₂).
- **Year 3**: Solid-state spectroscopic studies, test catalysis, publication of SC-SC projects.
- **Year 4**: Write review article on SC-SC processes in cluster-based materials, finish thesis.

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Year 1 – *CDT taught modules, synthesis, initial DLS experiments, Year 2 – enhancing crystallography skills, developing equipment and studying SC-SC processes. Year 3 – NMR/EPR/UV spectroscopy studies, catalysis. Year 4 – finalising crystallographic studies, review and thesis writing.