Poster

Photoinitiated Single-Crystal to Single-Crystal Redox Transformations of Titanium-Oxo Clusters

Stephen E. Brown[1] **Mark R. Warren**[2] **Dominik Kubicki**[3] **Ann Fitzpatrick**[4] **Sebastian D. Pike**[1]

[1]Department of Chemistry, University of Warwick; [2]Diamond Light Source, Harwell Science & Innovation Campus, [3]School of Chemistry, University of Birmingham [4]RAL Space, Harwell Science & Innovation Campus.

Stephen.E.Brown@warwick.ac.uk

Titanium-oxo clusters are molecular analogues for bulk and nanomaterial titanium dioxide. They consist of an inner core of titanium oxide, which is supported by coordinated organic ligands. In the solution phase UV light causes clusters with formula $[TiO(O^{i}Pr)L]_n$ ($L = O_2C^{t}Bu$, $n = 6$; $L = O_2PPh_2$, $n = 4$) to undergo a photochemical transformation.[1, 2] In this process, two Ti(IV) sites become reduced to Ti(III) and an isopropoxide ligand becomes oxidised to acetone, with the resulting photoreduced cluster adopting a deep blue colour. Intriguingly, solution experiments imply a two-electron mechanism occurs without the production of free radicals. However, the resulting photoreduced Ti-oxo clusters undergo ligand rearrangement in solution and, therefore, it is challenging to directly characterise the initial product of photoreaction. This inspired us to study this photoreaction in the crystalline phase.

Crystals of **1**, $[TiO(O^{i}Pr)(O_2PPh_2)]_4{\cdot}py$, and **2**, $[TiO(O^{i}Pr)(O_2CCH_2{}^{t}Bu)]_6$, are observed to undergo a colour change under UV irradiation whilst retaining crystallinity. Using a laser at the Diamond Light Source (PORTO, 305 nm) and EH2 on the i-19 beamline it was possible to irradiate crystals *in situ* and to collect diffraction patterns suitable for structural determination at increasing irradiation times. This allowed the photochemical single-crystal to single-crystal transformation to be tracked over increasing extent of photoreaction.

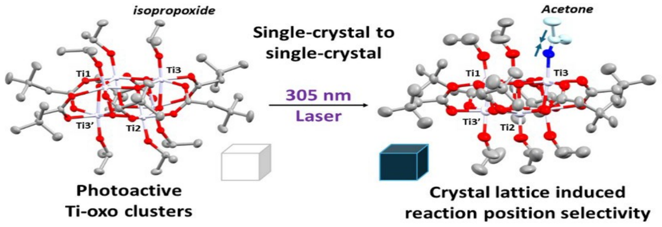

Figure 1. Single-crystal x-ray diffraction structures of **2** before and after irradiating with UV laser light. The acetone produced during the photoredox transformation is highlighted with blue atoms in the photoproduct.

In the crystal phase isopropoxide is photooxidised to acetone which remains coordinated to the Ti-oxo cluster due to the confined environment of the crystal lattice. Changes in the average structure observed by SCXRD, confirm the formation of acetone on the Ti-oxo cluster as well as the photoreduction of titanium. This gives direct evidence for a concerted two electron photoreaction locally on the Ti-oxo cluster, which is confirmed by EPR and solid-state NMR spectroscopy experiments. Remarkably, compound **2** shows selective reactivity at one crystallographically independent $Ti–O^{i}Pr$ site, even though all sites are chemically identical. The crystalline environment desymmetrises the molecule and enables this selective reactivity. This work highlights the possibility of studying photoreactivity in the crystal state, as well as, the ability of the crystal state to direct selective reactivity.

[1] T. Krämer, F. Tuna and S. D. Pike, *Chemical Science*, **2019**, 10, 6886.

[2] S. E. Brown, I. Mantaloufa, R. T. Andrews, T. J. Barnes, M. R. Lees, F. De Proft, A. V. Cunha and S. D. Pike, *Chemical Science*, **2023**, 14, 675.

I am grateful to the EPSRC for a studentship through a Doctoral Training Partnership (DTP) grant and for access to synchrotron facilities at Diamond Light Source made possible by support of proposals CY29891 and CY26668.