Optimising Titanium-Oxo Cluster Based Materials for Sustainable Photocatalysis

A. Chikara,[1,2] *S. Brown*[1], *B Wang*[2], *F. Tielens*[2], *F. De Proft*[2], *S. D. Pike*[1]

[1]Department of Chemistry, University of Warwick, Coventry, UK
[2] General Chemistry, Vrije Universiteit Brussels, Belgium

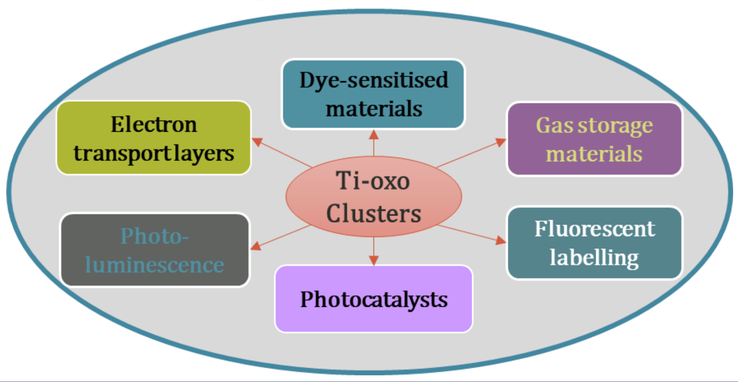
: ashwani.ashwani@warwick.ac.uk

𝕏: @_ashwanichikara

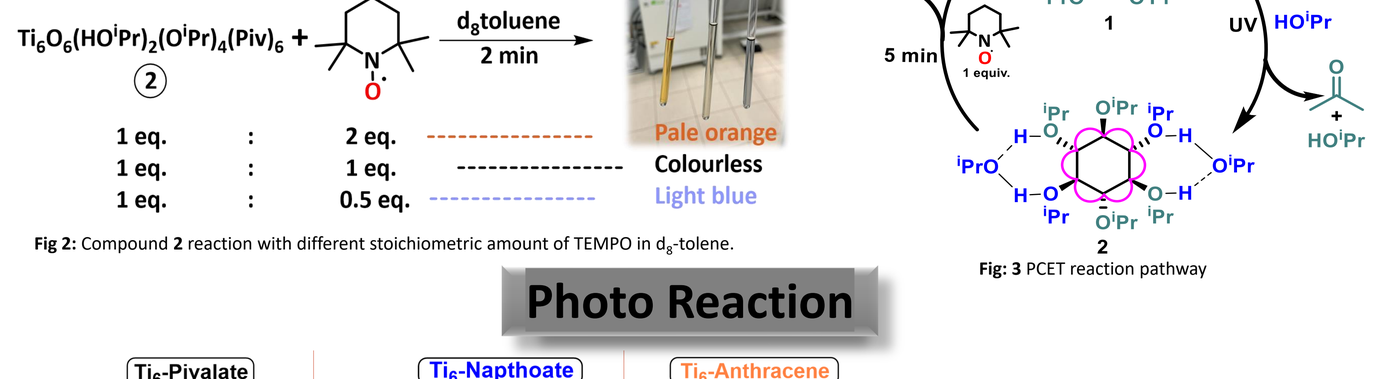
Introduction

What are the Ti-oxo clusters?

- Molecular analogues of titanium dioxide.
- Serve as a link between molecular and materials chemistry.
- TiO_2 is an important semiconductor material with uses in Photocatalytic degradation, self-cleaning windows, water oxidation, and hydrogen production.



Computational Details

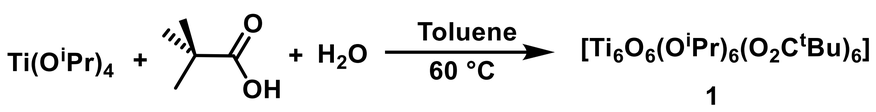


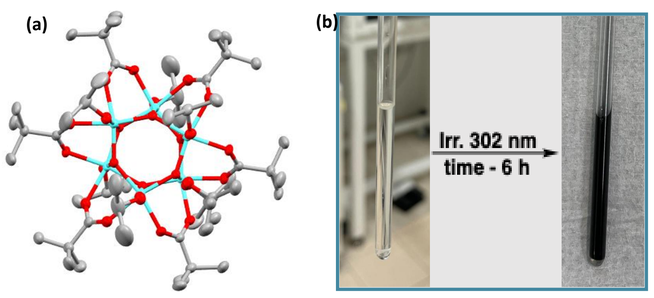
$[Ti_6O_6(O^iPr)_6(O_2C^tBu)_6]$

Objective

To develop sunlight-driven titanium-oxo clusters for efficient photocatalysis, using different ligands and DFT studies to optimize charge transfer for sustainable applications

Synthesis





- NMR shows metal-isopropoxide peaks in starting material
- Loss of metal-isopropoxide peaks and gain of free acetone

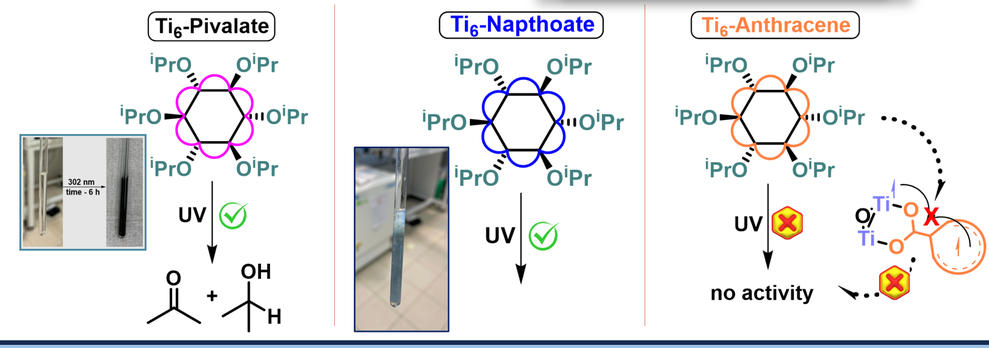
Fig 1: (a) Crystal Structure of **1**. (b) **1** Irradiated under UV for 6 h.

PCET Reaction

Fig 2: Compound **2** reaction with different stoichiometric amount of TEMPO in d_8-tolene.

Fig: 3 PCET reaction pathway

Photo Reaction



- Low solubility of Ti_6nap and Ti_6ac clusters.
- Ti_6ac: It's possible that the hole is localised on the anthracene ligand and doesn't promote oxidation of the alkoxide group.

Computational Results

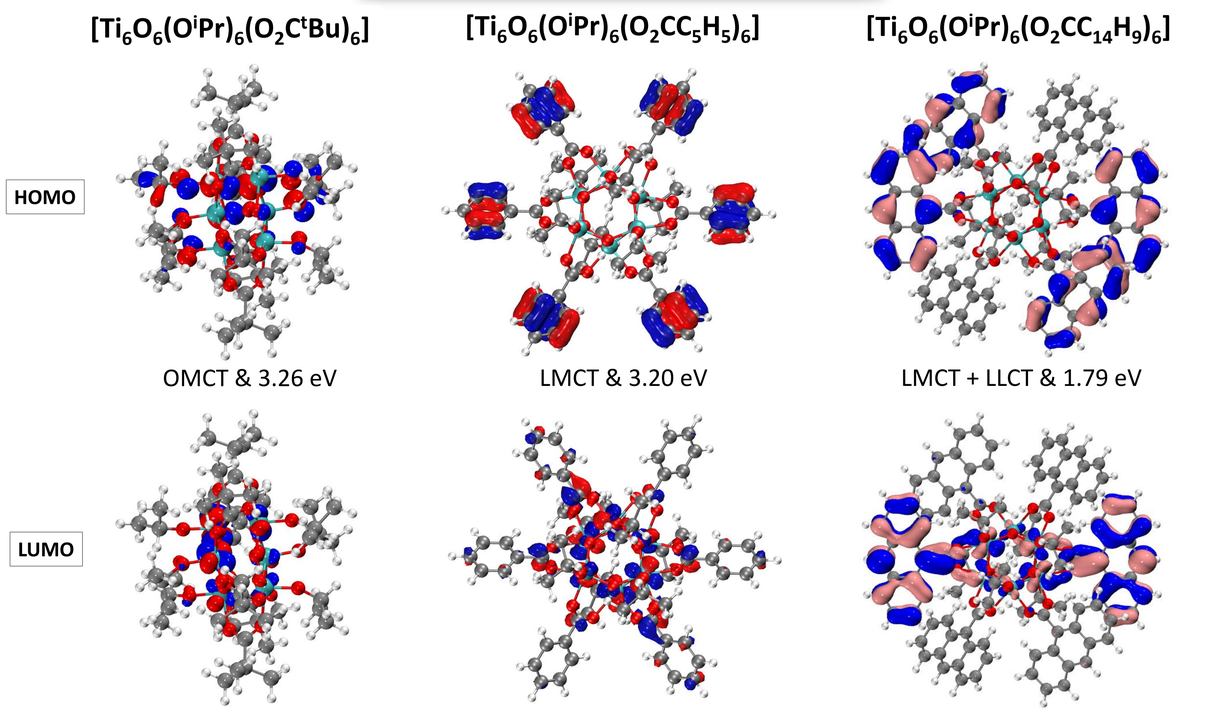


Fig 4: Calculated frontier molecular orbitals (HOMO/LUMO of the Ti_6-oxo clusters with increasing ligand π-conjugation, showing a transition from OMCT, LMCT to mix character, together with a comparison of HOMO-LUMO gaps computed using DFT functionals.

a)

Functionals	Homo-Lumo gap (eV)			
	Ti_6ac	Ti_6nap	Ti_6ben	Ti_6piv
r2SCAN	2.05	2.78	3.62	3.66
B3LYP	3.05	3.83	4.98	5.17
PBE0	3.41	4.22	5.43	5.67
CAM-B3LYP	5.37	6.31	7.65	8.10
wB97X-D3	6.83	7.86	9.29	9.70

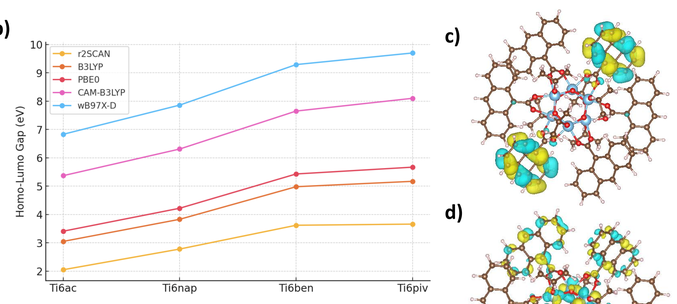


Fig 5: (a) Computational TD-DFT studies including implicit solvent method for Ti-oxo clusters. (b) Graph, (c) & (d) NTOs of $[Ti_6O_6(O^iPr)_6(O_2CC_{14}H_9)_6]$.

B3LYP: 1.79 eV increase in HOMO energy between Ti_6ac and Ti_6piv, is likely due to either strong electron-withdrawing effects of ligand or extended conjugation.

Ultrafast Spectroscopy

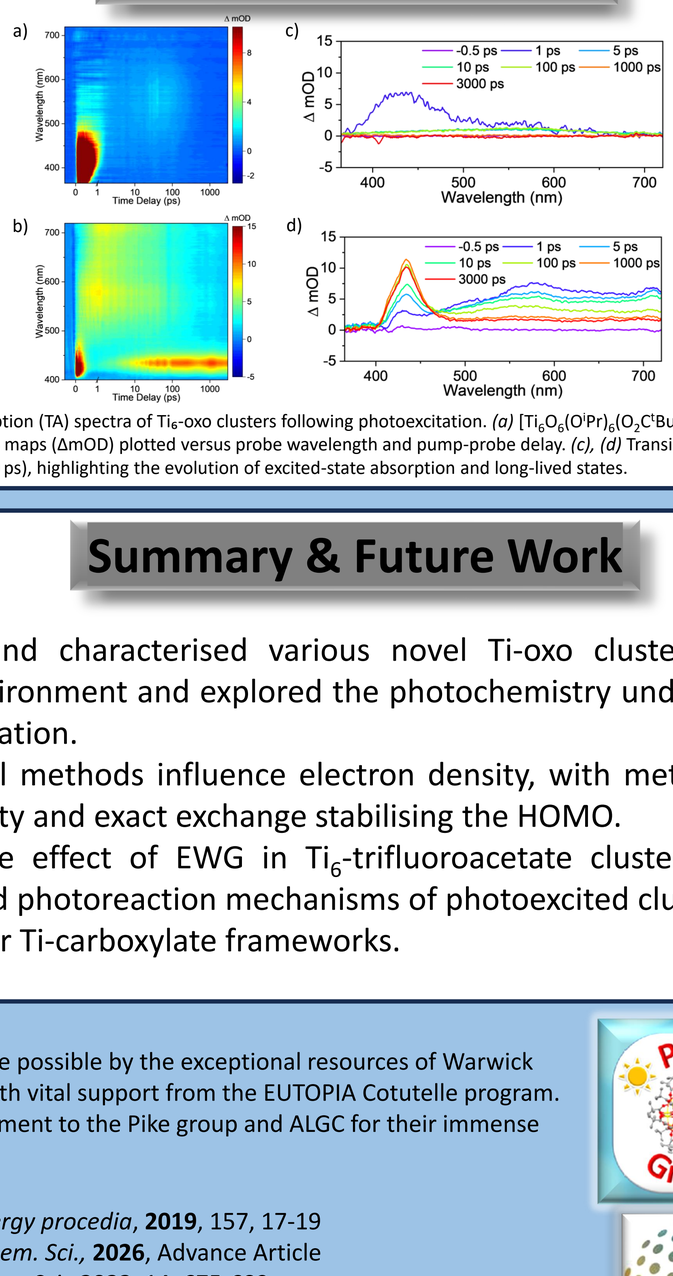


Fig 6: Ultrafast transient absorption (TA) spectra of Ti_6-oxo clusters following photoexcitation. *(a)* $[Ti_6O_6(O^iPr)_6(O_2C^tBu)_6]$, *(b)* $[Ti_6O_6(O^iPr)_6(O_2CC_{14}H_9)_6]$ Two-dimensional false-color TA maps (ΔmOD) plotted versus probe wavelength and pump-probe delay. *(c), (d)* Transient absorption spectra extracted at selected delay times (0.5–3000 ps), highlighting the evolution of excited-state absorption and long-lived states.

Summary & Future Work

- Synthesised and characterised various novel Ti-oxo clusters under different electronic environment and explored the photochemistry under UV (302 nm and 365 nm) irradiation.
- Computational methods influence electron density, with meta-GGA delocalising electron density and exact exchange stabilising the HOMO.
- Investigate the effect of EWG in Ti_6-trifluoroacetate clusters, thermodynamic potentials, and photoreaction mechanisms of photoexcited clusters, using TD-DFT calculations for Ti-carboxylate frameworks.

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References:

1. Haider, A. et al, *Energy procedia*, **2019**, 157, 17-19
2. Chikara, A. et al, *Chem. Sci.,* **2026**, Advance Article
3. Brown, S. et al, *Chem. Sci.,* **2023**, 14, 675-683
4. Kramer, T. et al, *Chem. Sci.,* **2019**, 10, 6886-6898
5. Green, M. A. et al, *Prog. in Photo. Research & Applications*, **2006**, 14, 383-392
6. Lv H. et al, *Dalton Trans.,* **2017**, 46, 12313-12319