

# **Thermal and Photo Stability of Tungsten Polyoxometalate-surfactant Hybrid Compounds**

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## **Certificate of original authorship**

I, Aaron Victor Colusso declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution. This research is supported by a UTS Doctoral Scholarship from the Graduate Research School and by an Australian Government Research Training Program Scholarship.

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## Acknowledgements

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## **Thesis Overview**

Each chapter of this Thesis contains an individual topic investigated and described in detail. Chapters 3 to 6 contain theory specific to the topic being discussed within it, followed by experimental results, analysis and conclusions. In this way, each chapter is able stand alone as an individual piece of work. A list of my publications related to the work covered in this thesis follows this statement, which is then followed by a statement regarding the contribution of the authors listed in them. A complete List of Abbreviations and Symbols used in this work is also provided, along with a Table of Contents and a List of Figures and Tables for ease of navigation. An Abstract of my completed work is given before the chapters are listed in sequence, from 1 through to 7. Chapter 1 gives a brief, general introduction on the topic of polyoxometalates. Chapter 2 contains the methods and materials employed to complete my PhD. Chapters 3 to 6 contain the specific topics of my project, which will be generically introduced in Chapter 1. Chapter 7 contains general conclusions of this work, as well as some ideas for possible future work. All references used to study and support the content of my PhD are presented in the Bibliography at the end of this thesis.

## List of Publications

### 1<sup>st</sup> Publication

Colusso, A. Cortie, M. Dowd, A. McDonagh, A., Thermal stability of mesoscopic compounds of cetyltrimethylammonium and Keggin metatungstates. *Dalton Trans.* **2017**, 46, 11053–11062.<sup>1</sup>

### 2<sup>nd</sup> Publication

Colusso, A. McDonagh, A. Gentle, A. Cortie, M., Photomechanical photochromism in a cetyltrimethylammonium isopolytungstate. *RSC Adv.* **2018**, 8, 18776-18783.<sup>2</sup>

### 3<sup>rd</sup> Publication

Colusso, A. McDonagh, A. Gentle, A. Cortie, M., X-ray induced reduction of a surfactant/polyoxotungstate hybrid compound, **2018**, DOI: 10.1002/sia.6516.<sup>3</sup>

In all of my publications, my principal supervisor M. Cortie and co-supervisor A. McDonagh aided me with the sequence of sections and arguments in the paper and overall construction. Help in the interpretation of data was also given, with M. Cortie helping me mainly with problems regarding x-ray diffraction and materials science, and A. McDonagh with problems regarding chemistry. Direction regarding the best way to visualize data in appropriate figures was also given by both supervisors.

Contributors to my first publication other than myself and my supervisors include A. Dowd who collected the transmission electron micrographs displayed within.

Contributors to my second publication other than myself include my supervisors and A. Gentle who aided with the design and set-up of the photochromic hysteresis study.

There are no additional contributors, apart from my supervisors, to my third publication.

# Table of Contents

<b>Thermal and Photo Stability of Tungsten Polyoxometalate-surfactant Hybrid Compounds</b> .....	i
<b>Certificate of original authorship</b> .....	ii
<b>Acknowledgements</b> .....	iii
<b>Thesis Overview</b> .....	iv
<b>List of Publications</b> .....	v
<b>1<sup>st</sup> Publication</b> .....	v
<b>2<sup>nd</sup> Publication</b> .....	v
<b>Table of Contents</b> .....	vi
<b>List of Abbreviations and Symbols</b> .....	x
<b>List of Abbreviations</b> .....	x
<b>List of Symbols</b> .....	xi
<b>List of Figures</b> .....	xiii
<b>List of Tables</b> .....	xix
<b>Abstract</b> .....	xxi
<b>Chapter 1. Introduction</b> .....	1
<b>1.1 Structure and nomenclature of common transition-metal oxo-anion clusters</b> .....	1
<b>1.2 A brief review of polyoxometalate properties and current and possible applications</b> .....	8
<b>1.3 Surfactant-polyoxometalate hybrid compounds</b> .....	10
<b>1.4 Thermal Stability of surfactant-polyoxometalate structures</b> .....	13
<b>1.5 Introduction to photochromism</b> .....	14
<b>1.6 Photochromic quality and the photochromic cycle</b> .....	16
<b>1.7 <i>In situ</i> photo-reduction of TMO-hybrids during X-ray-based measurements</b> .....	17
<b>1.8 Chapter overviews</b> .....	18
<b>Chapter 2. Methods and Materials</b> .....	20
<b>2.1 Chemical synthesis</b> .....	20
<b>2.1.1 Synthesis of CTA-W<sub>12</sub></b> .....	20
<b>2.1.2 Synthesis of CTA-WO<sub>3</sub></b> .....	22
<b>2.1.3 Soxhlet extraction</b> .....	23
<b>2.2 Characterization techniques</b> .....	24
<b>2.2.1 Powder X-ray diffraction</b> .....	24
<b>2.2.2 UV-visible spectroscopy</b> .....	27

2.2.3 Scanning electron microscopy.....	28
2.2.4 Transmission electron microscopy .....	29
2.2.5 X-ray photoelectron spectroscopy .....	29
2.2.6 Infrared and Fourier transform infrared spectroscopy .....	30
2.2.7 Raman spectroscopy .....	32
2.2.8 Thermogravimetric analysis and differential thermal analysis.....	33
2.2.9 Nuclear magnetic resonance spectroscopy.....	34
2.2.10 Microanalysis/combustion analysis .....	35
2.2.11 CTA-W <sub>12</sub> photochromism investigation.....	35
2.2.12 Hysteresis study.....	36
2.2.13 Gas chromatography-mass spectrometry .....	37
<b>Chapter 3. Synthesis of CTA-W<sub>12</sub>.....</b>	<b>39</b>
3.1 Background Theory .....	39
3.1.1 Aqueous tungstate equilibria .....	39
3.1.2 Tungstate-quaternary ammonium equilibria and Keggin cluster formation.....	41
3.1.3 Surfactant-polyoxometalate chemistry .....	43
3.1.4 Surfactant-polyoxometalate packing.....	44
3.1.5 The SEP lamellar phase and the 1:4 ratio .....	48
3.1.6 Solvent effects .....	53
3.2 Synthesis of CTA-W <sub>12</sub> .....	55
3.2.1 Characterization of CTA-W <sub>12</sub> .....	55
3.2.2 Synthesis and characterization of layered tungsten hydroxides .....	59
3.2.3 Synthesis of other tungstate-CTA compounds .....	66
3.2.4 CTA-tungstate products from high pH solutions.....	77
3.3 Tungstate-CTA <sup>+</sup> solution dynamics.....	78
3.3.1 Tungstate-CTA equilibria .....	78
3.3.2 Conversion of CTA-WO <sub>3</sub> to CTA-W <sub>12</sub> .....	79
3.4 Structural characterization of CTA-W <sub>12</sub> .....	82
3.4.1 P-XRD, SEM and TEM of CTA-W <sub>12</sub> .....	83
3.4.2 Hyper-digitation of CTA-W <sub>12</sub> .....	86
3.5 Conclusions: surfactant-mediated aqueous synthesis of Keggin polytungstates.....	87
<b>Chapter 4. Thermal Stability and Decomposition of Surfactant-Polyoxometalate Frameworks</b>	
.....	89

4.1 Background Theory .....	89
4.1.1 Calcination of surfactant-metal-oxide precursors .....	89
4.1.2 Thermal stability of organic spacers including alkyl-ammonium surfactants .....	92
4.1.3 Keggin fragmentation .....	95
4.1.4 Crystallographic phases of $WO_x$ .....	99
4.1.5 Hexagonal tungsten oxides .....	103
4.2 Thermal decomposition of CTA-Br .....	106
4.3 Thermal decomposition of CTA- $W_{12}$ .....	109
4.3.1 Dehydration and expansion – phases I - III.....	109
4.3.2 Lamellar decomposition – phase IV .....	113
4.3.3 Keggin fragmentation and adoption of HCP structure – phase V.....	115
4.3.4 Bulk-oxide formation .....	119
4.3.5 Effect of environment on CTA- $W_{12}$ thermal decomposition.....	121
4.4 Thermal Decomposition of CTA- $WO_3$ .....	123
4.4.1 Lamellar phases of CTA- $WO_3$ , phases I – III.....	124
4.4.2 Lamellar decomposition and bulk-oxide formation.....	127
4.4.3 Effect of environment .....	128
4.4.4 Comparison to CTA- $W_{12}$ thermal decomposition.....	129
4.5 Phase V (CTA- $W_{12}$ thermal decomposition intermediate).....	132
4.5.1 Soxhlet extraction.....	134
4.5.2 Analysis of fractions.....	136
4.5.3 Characterization of fractions .....	145
4.6 Conclusion: Formation of $WO_x$ from the thermal decomposition of CTA- $W_{12}$ .....	147
Chapter 5. Photochromism of Quaternary Alkyl-Ammonium Polyoxometalate Hybrids .....	150
5.1 Background Theory .....	150
5.1.1 Structure of the Keggin anion.....	150
5.1.2 Band-gap structure of the Keggin anion.....	152
5.1.3 Electronic structure of the Keggin anion .....	154
5.1.4 Photochromism of POM materials .....	156
5.1.5 Photocatalysis of POMs .....	159
5.1.6 Photochromism of quaternary-ammonium POM hybrids.....	162
5.2 Photochromism of CTA- $W_{12}$ .....	165
5.2.1 Colouration of CTA- $W_{12}$ in alcohols .....	165
5.2.2 Colouration of CTA- $W_{12}$ in air .....	167



5.2.3 XPS of CTA-W <sub>12</sub> .....	170
<b>5.3 Reversibility of CTA-W<sub>12</sub> photochromism .....</b>	<b>172</b>
5.3.1 Hysteresis study of CTA-W <sub>12</sub> photochromism .....	173
5.3.2 Chemical changes to CTA-W <sub>12</sub> during photochromism .....	174
5.3.3 Long-lived W <sup>5+/4+</sup> sites.....	180
5.3.4 Products of CTA-W <sub>12</sub> photochromism.....	182
<b>5.4 Structural changes during CTA-W<sub>12</sub> photochromism.....</b>	<b>185</b>
5.4.1 CTA-W <sub>12</sub> photo-decomposition.....	185
5.4.2 Lattice expansion and contraction during photochromism .....	188
<b>5.5 Conclusion: Photochromism of quaternary-ammonium polytungstate hybrids.....</b>	<b>191</b>
<b>Chapter 6. Photochromic Reduction During XPS Measurements .....</b>	<b>193</b>
6.1 Background theory .....	193
6.1.1 X-ray/Matter interactions .....	193
6.1.2 Measurement induced x-ray damage .....	195
6.1.3 Photoreduction during x-ray measurements .....	198
6.1.4 X-ray photoreduction of organic-inorganic hybrids.....	200
6.2 XPS-induced reduction of CTA-W <sub>12</sub> .....	202
6.2.1 W4f core-level spectra during XPS induced reduction.....	203
6.2.2 Kinetics of XPS induced reduction.....	206
6.2.3 Binding Energy of W oxidation-states during XPS induced reduction.....	207
6.3.1 Probable causes of XPS induced Reduction .....	209
6.4.1 Conclusions: XPS measurements of metal-oxide based inorganic-organic hybrids ...	210
<b>Chapter 7. Conclusions and prospective future work .....</b>	<b>212</b>
7.1. Conclusions.....	212
7.2. Future Work.....	216
<b>References.....</b>	<b>217</b>

# List of Abbreviations and Symbols

## List of Abbreviations

ATR	Attenuated total reflectance
CD	Conduction-band
CIF	Crystallographic Information File
CT	Charge-transfer
CTA <sup>+</sup>	Cetyltrimethylammonium cation, C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>
CTA-W <sub>12</sub>	Studied surfactant-polyoxometalate material, (C <sub>19</sub> H <sub>42</sub> N) <sub>7</sub> Cl.[H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> ].2H <sub>2</sub> O
CTA-WO <sub>3</sub>	Studied surfactant-tungsten oxide material, (CTA).6[WO <sub>3</sub> ].7H <sub>2</sub> O
DODA <sup>+</sup>	Dimethyldioctadecylammonium cation, (C <sub>18</sub> H <sub>37</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
DNA	Deoxyribonucleic acid
DTA	Differential thermal analysis
DTG	Differential thermogravimetric
EDX	Energy-dispersive X-ray
EtOH	Ethanol
FT-IR	Fourier-transform infrared
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
HATB	Hexagonal ammonium tungsten bronze
HTB	Hexagonal tungsten bronze
HCP	Hexagonal-close-packed
HOMO	Highest occupied molecular orbital
ICDD	International Centre for Diffraction Data
IR	Infrared
IVCT	Inter-valence charge-transfer
JCPDF	Joint Committee on Powder Diffraction File
L→M	Ligand-to-metal
LMCT	Ligand-to-metal charge-transfer
LUMO	Lowest unoccupied molecular orbital
MeOH	Methanol
MS	Mass spectrometry
MCM	Mobil Composition of Matter

NIR	Near-infrared
NMR	Nuclear magnetic resonance
O→M	Oxygen-to-metal
P-XRD	Powder X-ray diffraction
PhD	Doctorate of philosophy
POM	Polyoxometalate
RBF	Round-bottom flask
RT	Room temperature
SAXS	Small angle x-ray scattering
SE	Secondary electron
SEC	Surfactant encapsulated cluster
SEM	Scanning Electron Microscope
SEP	Surfactant encapsulated polyoxometalate
Surfactant	Surface acting agent
TBA <sup>+</sup>	Tetrabutylammonium cation, N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>+</sup>
TGA	Thermogravimetric analysis
TMA <sup>+</sup>	Tetramethylammonium cation, N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>
TrMA <sup>+</sup>	Trimethylammonium cation, HN(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>
UHV	Ultra-high Vacuum
UV	Ultraviolet
UV-vis	Ultraviolet-visible
VB	Valence-band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

### **List of Symbols**

<i>a</i>	Scaling factor
<i>A</i> <sub>0</sub>	Effective surfactant head-group cross-sectional area
<i>b</i>	Scaling factor
<i>c</i>	Rate of photo-colouration or bleaching
CTA <sub><i>m</i></sub>	Fraction of micellized CTA <sup>+</sup> surfactants
ΔAbs.	Change in absorbance
ΔR	Change in reflectance

$\Delta T$	Change in transmittance
$e^-$	Electron
$E_g$	Energy difference across a molecular orbital band-gap
$E_\gamma$	Photon energy
$g$	Surfactant packing parameter
$\gamma$	Photon
$h^+$	Electron hole
$I$	Collected light-spectrum intensity
$I_0$	Light-spectrum intensity of a known standard material
$k_{aq}$	Rate of reaction outside a surfactant micelle in an aqueous solution
$k_m$	Rate of reaction within a surfactant micelle in an aqueous solution
$K_{OH}^{Cl}$	rate of exchange between $Cl^-$ and $OH^-$ anions across a micelle interface
$K_{OH}^X$	Rate of exchange between halide and $OH^-$ anions across a micelle interface
$l$	Curvature elastic energy
$n$	Oxidation state
$n$	Surfactant packing number
$[OH_{aq}^-]$	Concentration of $OH^-$ anions in aqueous solution
$[OH_m^-]$	Concentration of $OH^-$ anions within a surfactant micelle
$p$	Probability of x-ray interaction with an atom
$t$	Time in seconds
$t_{1/2}$	Time taken to photo-colour or bleach to half the full extent
$V$	Surfactant alkyl-tail volume
$[X_{aq}^-]$	Concentration of halide anions in aqueous solution
$[X_m^-]$	Concentration of halide anions in a surfactant micelle
$y$	Diffuse reflectance or transmittance
$Z$	Atomic number

## List of Figures

**Figure 1.1.1.** Depiction of the Lindqvist polyoxometalate.

**Figure 1.1.2.** Depiction of a mixed-addenda Lindqvist polyoxometalate.

**Figure 1.1.3.** Depiction of the Dawson polyoxometalate.

**Figure 1.1.4.** Depiction of a lacunary polyoxometalate based on the combination of Lindqvist polyoxometalate derivatives.

**Figure 1.1.5.** Example of the many ways that polyoxometalates can be further functionalized by the attachment of organic groups.

**Figure 1.1.6.** Depiction of the ‘recipe-based’ method to synthesize ionic polyoxometalate-hybrid compounds.

**Figure 1.1.7.** Depiction of the Keggin anion.

**Figure 1.1.8.** Illustration of the predictability of surfactant-polyoxometalate self-assembly via manipulable parameters such as cation-anion charge-balancing.

**Figure 2.1.1.** Depiction of a Soxhlet apparatus.

**Figure 2.2.1.** Experimental set-up for CTA- $W_{12}$  hysteresis study.

**Figure 3.1.1.** Tungstate equilibrium scheme devised by J. Hastings and O. Howarth.

**Figure 3.1.2.** Processes methyl-ammonium concentration-dependent precipitation of tungsten octahedra from aqueous solutions.

**Figure 3.1.3.** Curvature elastic energy versus surfactant-tail volume of different length surfactants.

**Figure 3.1.4.** Keggin anions within the hydrophilic layer of  $(CTA)_4[SiW_{12}O_{40}]$ . (a) Keggin anions form a pseudo hexagonal pattern within the layer, separated by the mutually pseudo-hexagonally arranged dimers of cations quaternary-ammonium head-groups. (b) View of the same layer parallel to the  $b$ -axis. (c) Simplified diagram of the pseudo-hexagonally arranged species.

**Figure 3.1.5.** View of  $(CTA)_5(CH_3CN)_4[H_xSiMo_{12}O_{40}]$  down the  $a$ -axis highlighting the interdigitation, tilting and individuality of the hydrophobic alkyl-chains.

**Figure 3.1.6.** (a) Lamellar width as a function of the POM anionic charge. (b) Additional surfactants beyond a 1:4 POM:alkyl-chain ratio increases lamellar width due to surfactant binding to bottom surface of POMs.

**Figure 3.1.7.** Solvent-dependent reversible transformations of  $(\text{DODA})_3[\text{PW}_{12}\text{O}_{40}]$  structures in butanol/chloroform mixtures.

**Figure 3.2.1.** Raman spectrum of CTA- $\text{W}_{12}$ .

**Figure 3.2.2.** ATR FT-IR spectra of CTA- $\text{W}_{12}$ .

**Figure 3.2.3.** P-XRD pattern of CTA- $\text{W}_{12}$ .

**Figure 3.2.4.** Powder XRD pattern of CTA- $\text{WO}_3$ .

**Figure 3.2.5.** Raman spectrum of CTA- $\text{WO}_3$ .

**Figure 3.2.6.** FT-IR Spectrum of CTA- $\text{WO}_3$  in a KBr pellet.

**Figure 3.2.7.** SEM image of CTA- $\text{WO}_3$ .

**Figure 3.2.8.** P-XRD pattern of the product of  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ .

**Figure 3.2.9.** Raman spectrum of  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ .

**Figure 3.2.10.** FT-IR spectrum of  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  collected in a KBr pellet.

**Figure 3.2.11.** P-XRD patterns of products of CTA- $\text{WO}_3$  colloidal suspensions raised to pH 4 and pH 7.

**Figure 3.2.12.** Raman spectra of samples as described in Figure 3.2.11.

**Figure 3.2.13.** ATR FT-IR of samples as described in Figure 3.2.11.

**Figure 3.2.14.** P-XRD pattern of  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  suspension alkalized to pH 4 followed by addition of CTA-Br.

**Figure 3.2.15.** Raman spectra of sample as described in Figure 3.2.14.

**Figure 3.2.16.** ATR FT-IR spectrum of sample as described in Figure 3.2.14.

**Figure 3.2.17.** P-XRD of a CTA- $\text{W}_{12}$  suspension alkalized to pH 8, followed by acidification to pH 4 and pH 7.

**Figure 3.2.18.** Raman spectra of the samples as described in Figure 3.2.17.

**Figure 3.2.19.** ATR FT-IR of the samples as described in Figure 3.2.17.

**Figure 3.2.20.** (a) XRD patterns of CTA-Para and  $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$  (b) Raman spectra of CTA-Para and  $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$ .

**Figure 3.3.1.** (a) TGA and DTA of CTA- $\text{WO}_3$  (b) TGA and DTA of B4 (c) TGA and DTA of B7 (d) Organic ( $\text{CTA}^+$ ) fraction of sample versus synthesis pH

**Figure 3.4.1.** (a) Lamellar structure of CTA- $\text{W}_{12}$  depicting the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  clusters separated by the interdigitated surfactant tails of  $\text{CTA}^+$ . (b) 2D pseudo-hexagonal arrangement of the POMs within the hydrophilic layer.

**Figure 3.4.2.** (a) SEM image of CTA-W<sub>12</sub>. (b) and (c) TEM images of CTA-W<sub>12</sub>. (d) Typical 35nm contrast-dependent length section used to calculate interlamellar distance of CTA-W<sub>12</sub>.

**Figure 3.4.3.** Distortion within the 2D pseudo-hexagonal arrangement of anionic POMs across the (001) plane due to the POM:surfactant ratio exceeding 1:4 (a), as compared to the more symmetrical arrangement within a 1:4 SEP (b).

**Figure 4.1.1.** Production of MCM-41 catalytic substrate.

**Figure 4.1.2.** Mesostructure representations of (a) hexagonally arranged silicates (MCM-41), (b) cubically arranged silicates (MCM-48) and (c) meso-lamellar arranged silicates (MCM-50).

**Figure 4.1.3.** Hoffman degradation mechanism of CTA<sup>+</sup>.

**Figure 4.1.4.** Thermodynamics of CTA<sup>+</sup> decomposition.

**Figure 4.1.5.** Model of Keggin anion fragmentation and condensation.

**Figure 4.1.6.** Temperature dependent phases of WO<sub>3</sub>.

**Figure 4.1.7.** (a) WO<sub>6</sub> octahedral network of monoclinic  $\gamma$ -WO<sub>3</sub>, and (b) distorted WO<sub>5</sub>(OH<sub>2</sub>) alternating octahedral network.

**Figure 4.1.8.** (a) Structural representation of WO<sub>3</sub>·2H<sub>2</sub>O, depicting sheets of alternating WO<sub>5</sub>(OH<sub>2</sub>) octahedra and intercalated H<sub>2</sub>O. (b) Hydrogen-bonded network of intercalated H<sub>2</sub>O monolayer. (c) Sheet of WO<sub>5</sub>(OH<sub>2</sub>) octahedra highlighting the alternating positions of the coordinated water.

**Figure 4.1.9.** Crystallographic structure of the h-WO<sub>3</sub> phase.

**Figure 4.1.10.** Complete removal of cations from results in the collapse of the porous hexagonal structure into the condensed m-WO<sub>3</sub> phase.

**Figure 4.2.1.** Molecular structure of the surfactant CTA-Br, indicating all non-equivalent chemical environments of the C and H atoms.

**Figure 4.2.2.** TGA, DTG and DTA of CTA-Br heated in air.

**Figure 4.3.1.** TGA, DTG and DTA of CTA-W<sub>12</sub> in air.

**Figure 4.3.2.** (a) Heat map of CTA-W<sub>12</sub> thermal decomposition consisting of *in situ* synchrotron P-XRD patterns (b) Stacked P-XRD plot of CTA-W<sub>12</sub> thermal decomposition containing the distinct phases.

**Figure 4.3.3.** *Ex-situ* ATR FT-IR spectra of the phases present across CTA-W<sub>12</sub> thermal decomposition.

**Figure 4.3.4.** (002) Peak position as a function of temperature illustrating interlamellar expansion from 30 to 220°C.

**Figure 4.3.5.** Measured and calculated XRD patterns of phase V, compared with a similar HCP array of Au atoms.

**Figure 4.3.6.** *ex-situ* ATR FT-IR spectra of phase V from 270 to 310°C.

**Figure 3.3.7.** Depiction of the multi-step process of Keggin anion decomposition over the course of phase V, involving separation into edge-sharing trimers before condensing into larger edge-sharing isopolytungstates.

**Figure 4.3.8.** (a) Conversion of phase V to VI to VII to VIII during thermal decomposition, and (b) increase in amorphous background with stability ranges of various phases superimposed.

**Figure 4.3.9.** TGA, DTG and DTA of CTA-W<sub>12</sub> in N<sub>2</sub>.

**Figure 4.3.10.** P-XRD of the product produced from (a) TGA in air (Figure 3.3.1) and (b) TGA in N<sub>2</sub> (Figure 3.3.9).

**Figure 4.4.1.** (a) Heat map of CTA-WO<sub>3</sub> thermal decomposition consisting of *in situ* synchrotron P-XRD patterns (b) Stacked P-XRD plot of CTA-WO<sub>3</sub> thermal decomposition containing the distinct phases.

**Figure 4.4.2.** TGA, DTG and DTA of CTA-WO<sub>3</sub> in air.

**Figure 4.4.3.** TGA, DTG and DTA of CTA-WO<sub>3</sub> in N<sub>2</sub>.

**Figure 4.4.4.** Comparison of DTG curves of CTA-W<sub>12</sub> and CTA-WO<sub>3</sub> in air.

**Figure 4.5.1.** SEM image of phase V.

**Figure 4.5.2.** FT-IR spectra of phase V (310°C) as-prepared, after Soxhlet extraction and the soluble fraction that was removed in CHCl<sub>3</sub>.

**Figure 4.5.3.** Labelled <sup>1</sup>H-NMR of (a) CTA-W<sub>12</sub> as prepared and (b) CHCl<sub>3</sub> soluble fraction of phase V in CDCl<sub>3</sub>.

**Figure 4.5.4.** TGA and DTA of the CHCl<sub>3</sub> insoluble (a) and soluble (b) fractions of phase V, (c) comparative DTA of insoluble and soluble fractions, and (d) comparative DTG of insoluble and soluble fractions.

**Figure 4.5.5.** (a) TGA and DTA of the CHCl<sub>3</sub> insoluble fraction, (b) TGA and DTG of CHCl<sub>3</sub> insoluble fraction, (c) TGA and DTA of the CHCl<sub>3</sub> soluble fraction, (d) TGA and DTG of CHCl<sub>3</sub> soluble fraction, (e) DTA of the insoluble and soluble fractions and (f) DTG of the



insoluble and soluble fractions. All measurements performed at the slower heating rate of 1°C/min (as compared to 5°C/min).

**Figure 4.5.6.** P-XRD patterns of phase V as prepared, after Soxhlet extraction with CHCl<sub>3</sub>, and the extracted residue from the Soxhlet apparatus.

**Figure 4.5.7.** RAMAN spectra of phase V, phase V after Soxhlet extraction with CHCl<sub>3</sub>, and the extracted residue.

**Figure 4.5.8.** FT-IR spectra of phase V, and its respective CHCl<sub>3</sub> soluble and CHCl<sub>3</sub> insoluble fractions.

**Figure 5.1.1.** Octahedral representations of WO<sub>6</sub><sup>6-</sup> in the bulk state with an idealised *O<sub>h</sub>* symmetry and at the surface with a distorted *C<sub>s</sub>* symmetry.

**Figure 5.1.2.** Structure of the Keggin anion depicting the edge-sharing capping trimers and the corner-sharing equatorial ring that comprise the anion, as well as the types of oxygen bonds that connect the octahedra.

**Figure 5.1.3.** Splitting of the *t<sub>2g</sub>* d-orbitals in Keggin and other polyoxometalates due to the distortion of MO<sub>6</sub> octahedra away from idealised *O<sub>h</sub>* symmetry.

**Figure 5.1.4.** (a) Structure of the Keggin-anion, (b) ionic representation of the Keggin structure, and (c) example of one of the closed -O<sup>2-</sup>-W<sup>6+</sup>-O<sup>2-</sup>- loops formed within the anion's cyclic-geometry.

**Figure 5.1.5.** Formation of the photo-coloured charge-transfer complex from the bleached state in typical alkyl-ammonium-POM photochromic materials.

**Figure 5.1.6.** Diagram of photon-absorption instigated electronic d-d transitions of excited electrons within the distorted W 5d band.

**Figure 5.1.7.** Photo-catalysed C-H bond activation-mediated reactions of organic molecules and the decatungstate anion, [W<sub>10</sub>O<sub>32</sub>]<sup>4-</sup>.

**Figure 5.1.7.** FT-IR spectra of (a) H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub>, (b) pristine (DODA)<sub>3</sub>[PMO<sub>12</sub>O<sub>40</sub>] film, (c) (DODA)<sub>3</sub>[PMO<sub>12</sub>O<sub>40</sub>] after UV irradiation, (d) (DODA)<sub>3</sub>[PMO<sub>12</sub>O<sub>40</sub>] film after heating photo-coloured film in air, and (e) after further UV irradiation of the bleached film.

**Figure 5.2.1.** UV-vis spectra of CTA-W<sub>12</sub> in MeOH as-prepared and after UV irradiation.

**Insert:** Quartz cuvette containing the described photo-reduced CTA-W<sub>12</sub> in MeOH.

**Figure 5.2.2.** (a) CTA-W<sub>12</sub> particles directly after UV irradiation displaying both coloured and as-prepared/bleached states, (b) UV-vis reflectance spectra of CTA-W<sub>12</sub> as prepared and after UV irradiation.

**Figure 4.2.3.** (a) Colouration rate of CTA-W<sub>12</sub> and (b) bleaching rate of coloured CTA-W<sub>12</sub>.

**Figure 5.2.4.** XPS of CTA-W<sub>12</sub> as-prepared (a) and directly after UV irradiation (b).

**Figure 5.3.1.** UV-vis reflectance spectra of CTA-W<sub>12</sub> as-prepared, directly after UV irradiation, bleached and after a subsequent UV irradiation.

**Figure 5.3.2.** Hysteresis study of CTA-W<sub>12</sub> photochromism.

**Figure 5.3.3.** XPS spectra of CTA-W<sub>12</sub> including C1s, O1s and N1s spectra in un-irradiated and UV irradiated samples.

**Figure 5.3.4.** (a) ATR FT-IR spectra of CTA-W<sub>12</sub> as-prepared, and after two, four and six photochromic cycles. (b)  $\nu(\text{C}=\text{O})$ : $\nu(\text{W}-\text{O}_b-\text{W})$  peak-area ratio vs total exposure time.

**Figure 5.3.5.** ATR FT-IR spectra of CTA-W<sub>12</sub> as-prepared and after 18 photochromic cycles.

**Figure 5.3.6.** Intensities of  $\nu_{\text{as}}(-\text{CH}_2)$ ,  $\nu_{\text{ss}}(-\text{CH}_2)$ ,  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{OH})$  FT-IR bands vs number of photochromic cycles.

**Figure 5.3.7.** (a) ATR FT-IR spectra of CTA-Br as-received and after two, four and six UV irradiation. (b)  $\nu(\text{C}=\text{O})$  intensity in CTA-Br and CTA-W<sub>12</sub> vs number of UV irradiation cycles.

**Figure 5.3.8.** Raman spectra of CTA-W<sub>12</sub> as-prepared and after 18 photochromic cycles.

**Figure 5.3.9.** GC-MS spectra of CTA-W<sub>12</sub> after UV irradiation. (a) GC of irradiated CTA-W<sub>12</sub> in CHCl<sub>3</sub> (b) Mass spectrum of 1-hexadecanol (c) Mass spectrum of hexadecylamine (d) GC of un-irradiated CTA-W<sub>12</sub>.

**Figure 5.4.1.** *In-situ* low-angle synchrotron P-XRD patterns of CTA-W<sub>12</sub> at 4min, 40min, 80min, 120min, 160min, 200min and 220 min of UV irradiation time. **Insert:** (001) and (110) peak intensities vs irradiation time.

**Figure 5.4.2.** (001) peak intensity vs X-ray only irradiation, X-ray with intermittent UV irradiation, and continuous UV and X-ray irradiation.

**Figure 5.4.3.** (001) peak intensity for each UV ON-OFF cycle.

**Figure 5.4.4.** Thermal expansion of CTA-W<sub>12</sub> in the [001] direction from 25 to 90°C.

**Figure 5.4.5.** Interlamellar spacing vs X-ray-only irradiation time, X-ray and intermittent UV irradiation, and continuous X-ray and UV irradiation.

**Figure 6.1.1.** Diagram of possible x-ray/matter interactions.

**Figure 6.1.2.** Examples of x-ray induced damage that can be induced by measurement of a sample.

**Figure 6.1.3.** Process of ‘Coulombic explosion’ in ionic compounds.

**Figure 6.1.4.** Diagram of present organic material accelerating oxygen-vacancy generation and x-ray photoreduction of chromium oxides by reaction with photo-oxidized O<sup>+</sup> species.

**Figure 6.2.1.** The first, fifteenth, thirtieth and fiftieth scans of the W4f core-level XPS spectra in CTA-W<sub>12</sub>.

**Figure 6.2.2.** Relative concentration of W<sup>6+</sup>, W<sup>5+</sup> and W<sup>4+</sup> oxidation states as a function of XPS scan time.

**Figure 6.2.3.** Surface plot (a) and coloured heat-map (b) of W4f x-ray photoelectron intensity as a function of XPS scan number.

## List of Tables

**Table 1.1.1.** Notable examples of literature on surfactant-POM hybrids highly-relevant to the subjects covered in this thesis.

**Table 3.1.1.** Value of the surfactant-packing parameter, *g*, within curved and flat mesophases.

**Table 3.2.1.** Comparison between theoretical and experimental C,H&N micro-analysis data of CTA-W<sub>12</sub> based on the empirical formula (CTA)<sub>7</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]Cl.2H<sub>2</sub>O.

**Table 3.2.2.** Comparison between theoretical and experimental TGA data of CTA-W<sub>12</sub> based on the empirical formula (CTA)<sub>7</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]Cl.2H<sub>2</sub>O.

**Table 3.2.3.** Measured and theoretical C,H&N micro-analysis of CTA-WO<sub>3</sub> based on the empirical formula (CTA)<sub>6</sub>[WO<sub>3</sub>].7H<sub>2</sub>O.

**Table 3.2.4.** Measured and theoretical volatile organic (CTA<sup>+</sup>), non-volatile (WO<sub>3</sub>) and hydration (H<sub>2</sub>O) content based on the empirical formula (CTA)<sub>6</sub>[WO<sub>3</sub>].7H<sub>2</sub>O as measured by CTA.

**Table 4.1.1.** Bond energies within alkyl-ammonium molecules.

**Table 4.4.1.** Comparison of CTA-W<sub>12</sub> and CTA-WO<sub>3</sub> thermal decomposition events in air.

**Table 4.5.1.** Comparison between volatile (organic and water) and non-volatile ( $\text{WO}_3$ ) content of  $\text{CHCl}_3$  insoluble and  $\text{CHCl}_3$  soluble fractions of phase V as measured by TGA.

**Table 4.5.2.** Comparison between experimental C,H&N micro-analysis and theoretical calculations based on the empirical formula  $(\text{TMA})_{2.5}\text{H}_{3.5}[\text{W}_7\text{O}_{24}]$ .

**Table 6.2.1.** Relative concentration of  $\text{W}^{6+}$ ,  $\text{W}^{5+}$  and  $\text{W}^{4+}$  oxidation states across successive XPS scans.

## Abstract

Inorganic-organic polyoxometalate-hybrid materials have attracted increased interest from researchers in recent years due their favourable photo-redox properties. These compounds have the potential to serve in a wide range of applications including photo-catalysis, gas-sensing and medicine. However, limited thermal and photo-chemical stability of these systems has restricted further development into other applications, such as photochromic technologies.

This thesis focuses on the synthesis and thermal and photochemical stability of the polyoxometalate-hybrid designated CTA-W<sub>12</sub>, formed from the metatungstate anion, [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> and the cationic surfactant cetyltrimethylammonium, (C<sub>16</sub>H<sub>33</sub>)N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> (CTA<sup>+</sup>). Only a narrow window of synthesis conditions actually leads to the production of the studied material because the products produced are very sensitive to pH, temperature, sequence of reactions steps and time. The CTA-W<sub>12</sub> exhibits a lamellar bilayer structure, consisting of 2D sheets of hexagonally arranged polyoxometalate anions separated by interdigitated surfactant alkyl-tails.

The thermal stability of CTA-W<sub>12</sub> was studied using a battery of techniques, including *in situ* synchrotron x-ray diffraction. It was found that the salt went through seven phase and/or chemical transitions from room-temperature to 800°C within the enclosed environment of the quartz capillary. The lamellar structure persisted for the first three transitions and was destroyed by the fifth at 230°C, when the polyoxometalates fragmented and assumed a hexagonally-close-packed (HCP) arrangement. By ~350°C, the fragments reorganized into the bulk tungsten-suboxide W<sub>17</sub>O<sub>47</sub> and by ~550°C all organic material was removed from the sample. At ~600°C the sample underwent a final transition to monoclinic WO<sub>2</sub>. The HCP fifth phase was further studied due to its high crystallinity and was found to be comprised of two types of polyanion fragments, alluding to the complex decomposition kinetics of polyoxometalates and inorganic-organic hybrids.

The photochromism of CTA-W<sub>12</sub> highlighted the photochemical instability of the inorganic-organic polyoxometalate hybrid. Multiple cycles of irradiation followed by recovery were applied to elucidate the behaviour of the material. The first four photochromic cycles coincided with a slight discoloration of the bleached state, detrimentally affecting

photochromic performance slightly. This was ascribed to irreversible oxidation to organic CTA<sup>+</sup> which caused a yellowing of the material, as well the production of long-lived W<sup>5+</sup> sites deep within the material which could not be re-oxidized by atmospheric O<sub>2</sub>. The material maintained reasonable photochromic performance beyond four cycles, which was attributed to the production of more reversible proton-transfer groups, as compared to CH<sub>2/3</sub>, and an equilibrium between the production of long-lived W<sup>5+</sup> sites and the diffusion of O<sub>2</sub> into the material. Lattice expansion and amorphization (which was partially reversed during bleaching) was observed to mutually occur with photo-colouration, as evidenced by XRD. The accumulation of strain in the sample, as indicated by the expansion in lattice parameter along the [001] direction, may represent a new photomechanical phenomenon. The photochemical instability of CTA-W<sub>12</sub> was further revealed during XPS measurements, which caused progressive reduction of tungsten centres with each successive measurement due to the ionizing effect of the X-ray radiation in combination with the high vacuum environment of the instrument.

The project has provided detailed insight into the synthesis, thermal stability and photochemical properties of CTA-W<sub>12</sub>. The mechanism of photochromism, and the reasons for its partial irreversibility, were found. A new photomechanical phenomenon was uncovered and investigated. The new insights provided by the project will facilitate future attempts to develop applications for these and related inorganic-organic hybrid compounds.