

# Synthesis and characterisation of a lanthanide-capped dodecavanadate cage

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## Experimental

All materials were purchased from *Sigma Aldrich* and all solvents were purchased from *Fisher Scientific* and used without further purification. The precursors  $(\text{TBA})_4[\text{V}_{10}\text{O}_{26}]$  and  $(\text{TBA})_4[\text{V}_{12}\text{O}_{32}(\text{CH}_3\text{CN})]$  were synthesised according to slightly modified versions of procedures previously reported in the literature.<sup>1</sup>

**Synthesis of  $(\text{TBA})_2[\text{Gd}(\text{V}_{12}\text{O}_{32}(\text{Cl}))(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2]$  (**1**):**  $(\text{TBA})_4[\text{V}_{12}\text{O}_{32}(\text{CH}_3\text{CN})]$  (213mg, 0.1mmol) was dissolved with stirring in 5ml acetonitrile and to the brown solution was added  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  (74mg, 0.2mmol). The resultant mixture was stirred vigorously for 24 hours before filtration to remove any undissolved  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ . The dark amber filtrate was collected in a 25ml conical flask which was sealed with pierced parafilm to allow for slow evaporation and after standing for ca. 1 week at 4°C, orange block crystals of **1** could be collected. Yield = 76mg (40% based on V). Elemental analysis for  $\text{C}_{36}\text{H}_{82}\text{ClGdN}_4\text{O}_{34}\text{V}_{12}$  (calculated values in brackets): C: 20.16 (22.52), H: 4.26 (4.31), N: 1.53 (2.92). The discrepancy in the experimental values can be accounted for by the loss of the 2  $\text{CH}_3\text{CN}$  ligands under air-drying. Characteristic IR bands (in  $\text{cm}^{-1}$ ): 3625(w), 3275(w,b), 2964(m), 2938(m), 2874(m), 1646(m), 1589(m), 1465(s), 1379(s), 999(vs), 803(s), 771(s), 628(vs), 603(vs).

**Synthesis of  $(\text{TBA})_2[\text{Tb}(\text{V}_{12}\text{O}_{32}(\text{Cl}))(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2]$  (**2**):** Compound **2** could be prepared using exactly the same method as described for **1** but replacing  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (75mg, 0.2mmol). Yield = 72mg (38% based on V). Elemental analysis for  $\text{C}_{36}\text{H}_{82}\text{ClN}_4\text{O}_{34}\text{TbV}_{12}$  (calculated values in brackets): C: 20.56 (22.50), H: 4.23 (4.30), N: 1.55 (2.92). The discrepancy in the experimental values can be accounted for by the loss of the 2  $\text{CH}_3\text{CN}$  ligands under air-drying. Characteristic IR bands (in  $\text{cm}^{-1}$ ): 3626(w), 3275(w,b), 2966(m), 2939(m), 2874(m), 1645(m), 1589(m), 1466(s), 1379(m), 999(vs), 803(s), 771(s), 629(vs), 601(vs).

**Synthesis of  $(\text{TBA})_2[\text{Dy}(\text{V}_{12}\text{O}_{32}(\text{Cl}))(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2]$  (**3**):** Compound **3** could be prepared using exactly the same method as described for **1** but replacing  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (75mg, 0.2mmol). Yield = 81mg (42% based on V). Elemental analysis for  $\text{C}_{36}\text{H}_{82}\text{ClDyN}_4\text{O}_{34}\text{V}_{12}$  (calculated values in brackets): C: 20.37 (22.44), H: 4.23 (4.29), N: 1.60 (2.91). The discrepancy in the experimental values can be accounted for by the loss of the 2  $\text{CH}_3\text{CN}$  ligands under air-drying. Characteristic IR bands (in  $\text{cm}^{-1}$ ): 3624(w), 3275(w,b), 2965(m), 2938(m), 2874(m), 1645(m), 1590(m), 1466(s), 1379(m), 999(vs), 803(s), 771(s), 629(vs), 600(vs).

**Synthesis of (TBA)<sub>2</sub>[Ho(V<sub>12</sub>O<sub>32</sub>(Cl))(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (4):** Compound **4** could be prepared using exactly the same method as described for **1** but replacing GdCl<sub>3</sub>·6H<sub>2</sub>O with HoCl<sub>3</sub>·6H<sub>2</sub>O (76mg, 0.2mmol). Yield = 90mg (47% based on V). Elemental analysis for C<sub>36</sub>H<sub>82</sub>ClHoN<sub>4</sub>O<sub>34</sub>V<sub>12</sub> (calculated values in brackets): C: 20.36 (22.43), H: 4.21 (4.29), N: 1.59 (2.91). The discrepancy in the experimental values can be accounted for by the loss of the 2 CH<sub>3</sub>CN ligands under air-drying. Characteristic IR bands (in cm<sup>-1</sup>): 3622(w), 3275(w,b), 2965(m), 2940(m), 2874(m), 1645(m), 1591(m), 1466(s), 1379(m), 999(vs), 805(s), 771(s), 630(vs), 603(vs).

**Synthesis of (TBA)<sub>2</sub>[Er(V<sub>12</sub>O<sub>32</sub>(Cl))(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (5):** Compound **5** could be prepared using exactly the same method as described for **1** but replacing GdCl<sub>3</sub>·6H<sub>2</sub>O with ErCl<sub>3</sub>·6H<sub>2</sub>O (76mg, 0.2mmol). Yield = 79mg (41% based on V). Elemental analysis for C<sub>36</sub>H<sub>82</sub>ClErN<sub>4</sub>O<sub>34</sub>V<sub>12</sub> (calculated values in brackets): C: 20.77 (22.42), H: 4.26 (4.29), N: 1.50 (2.91). The discrepancy in the experimental values can be accounted for by the loss of the 2 CH<sub>3</sub>CN ligands under air-drying. Characteristic IR bands (in cm<sup>-1</sup>): 3621(w), 3275(w,b), 2964(m), 2937(m), 2874(m), 1644(m), 1591(m), 1465(s), 1379(m), 998(vs), 805(s), 768(s), 635(vs), 607(vs).

## **Methods**

**Single Crystal X-Ray Diffraction:** Single crystal datasets and unit cell data were collected at 150(2)K on a *Bruker Apex II Quasar* CCD diffractometer equipped with a graphite monochromator ( $\lambda$  (Mo $\kappa\alpha$ ) = 0.71073 Å). Absorption effects were corrected for using an empirical method.<sup>2</sup> Structural solution and refinement was carried out using SHELLX-97<sup>3</sup> and WinGX<sup>4</sup> via a full matrix least-squares on F<sup>2</sup> method. DFIX instructions for C-C and C-N distances have been applied to the disordered parts of the tetrabutylammonium cations and solvent acetonitrile moieties. Atoms in these disordered areas have only been isotropically refined and in all cases no hydrogen atoms were added. The Platon SQUEEZE procedure was applied to estimate the remaining solvent area content. A total potential solvent accessible void volume of 262.7 Å<sup>3</sup> and an additional electron count of 24 per unit cell were found and subsequently used when determining the reported crystallographic formula. The crystallographic formula contains considerably more solvent molecules than that found in the chemical analysis as most of the solvent molecules were lost rapidly on removal of the crystals from the mother liquor.

**Microanalysis:** Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHN, CE-440 Elemental Analyser.

**Fourier Transform Infrared (FT-IR) Spectroscopy:** IR Spectra of compounds **1-5** were collected in transmission mode using a *Shimadzu FTIR 8400s* spectrometer fitted with a *golden gate* ATR attachment. Characteristic IR bands are reported in cm<sup>-1</sup>; intensities denoted as vs = very strong, s = strong, m = medium, w = weak, b = broad.

**Mass Spectrometry:** Electrospray ionisation (ESI) measurements were carried out on a *Waters Synapt G2* HDMS instrument operating in sensitivity mode equipped with a quadrupole and time of flight (Q/ToF) module for MS analysis. All samples were prepared by dissolving in HPLC grade acetonitrile to a concentration of *ca.*  $1 \times 10^{-5}$  mol L<sup>-1</sup> and injected at a sample flow rate of 5  $\mu$ L min<sup>-1</sup> using a *Harvard* syringe pump. All spectra were collected in negative ion mode and analysed using the MassLynx v4.1 Software supplied by *Waters*.

For all measurements the following parameters were used: ESI capillary voltage: 2.2 kV; sample cone voltage: 20 V; extraction cone voltage: 2 V; source temperature: 80 °C; desolvation temperature: 120 °C; cone gas flow: 19 l h<sup>-1</sup> (N<sub>2</sub>); desolvation gas flow: 500 l h<sup>-1</sup> (N<sub>2</sub>); source gas flow: 0 ml min<sup>-1</sup>; trap gas flow: 2.5 ml min<sup>-1</sup>; helium cell gas flow: 180 ml min<sup>-1</sup>.

**Magnetic Susceptibility Measurements:** Variable-temperature magnetic susceptibility measurements were carried out on manually powdered single-crystalline samples using a Quantum Design MPMS-XL SQUID magnetometer. Pascal's constants were used to determine the necessary diamagnetic corrections.

**Electrochemistry:** All measurements were performed on either a 600D or 740D model electroanalysis system supplied by CH Instruments using the classic three electrode set-up. All solutions were deaerated thoroughly for at least 30 min with dry nitrogen or argon and kept under a positive pressure of this gas during the experiment. The glassy carbon working electrodes had a diameter of 3 mm and were polished with alumina (3  $\mu$ m) on a polishing pad, rinsed with distilled water and sonicated in acetone before each use. Potentials are quoted against an Ag/AgCl reference electrode. Platinum foil/wire was used as the counter electrode. All experiments were performed at room temperature.

Coulometry of **1'** was performed at +1.0V (quoted against Ag/AgCl) on a 0.1mM solution of **1'** in N,N-dimethylformamide (DMF) containing TBA PF<sub>6</sub> as electrolyte with a platinum net as the working electrode. The circuit was closed via a salt bridge (paper supported saturated TBA PF<sub>6</sub> solution in DMF) and platinum wire was used as a counter electrode.

**Photochemistry:** A small powdered sample of **1** was irradiated in air for 3 days under a 140W Xenon arc lamp UV light source (no filter was applied) and manually agitated several times a day in order to maximise the homogeneity of the sample to yield **1'** as a dark green powder. Infrared spectroscopy was used to confirm the purity of **1'** (Fig. S10).

**Thermogravimetric Analysis (TGA):** TGA was performed on a TA Instruments Q 500 Thermogravimetric Analyzer at a heating rate of 10 °C min<sup>-1</sup> in a platinum pan.

## Crystallographic Data

**Table S1:** Selected crystallographic data for compound **1**

Crystallographic Formula	$((C_4H_9)_4N)_2[Gd(V_{12}O_{32}(Cl))(H_2O)_2(CH_3CN)_2] \cdot 4CH_3CN$
$M_r$ (g mol <sup>-1</sup> )	2083.26
Crystal System	Orthorhombic
Space Group	$P 2_1 2_1 2$
$a$ (Å)	15.6592(14)
$b$ (Å)	25.175(2)
$c$ (Å)	10.2383(9)
$\alpha, \beta, \gamma$ (°)	90.0(0)
$Z$	2
$V$ (Å <sup>3</sup> )	4036.1(6)
$\rho_{\text{calcd.}}$ (g cm <sup>-3</sup> )	1.714
$\mu$ (Mo $K_{\alpha}$ ) (mm <sup>-1</sup> )	2.24
$T$ (K)	150(2)
Rflns. (measd.)	17042
Rflns. (uniq.)	7447 ( $R_{\text{int}} = 0.0351$ )
No. params.	434
$R1$ ( $I > 2\sigma(I)$ )	0.0391
$wR2$ (all)	0.1011
$S$	1.037
Flack Parameter	-0.009(11)
Extrema	0.91 and -0.49 e $\cdot$ Å <sup>-3</sup>

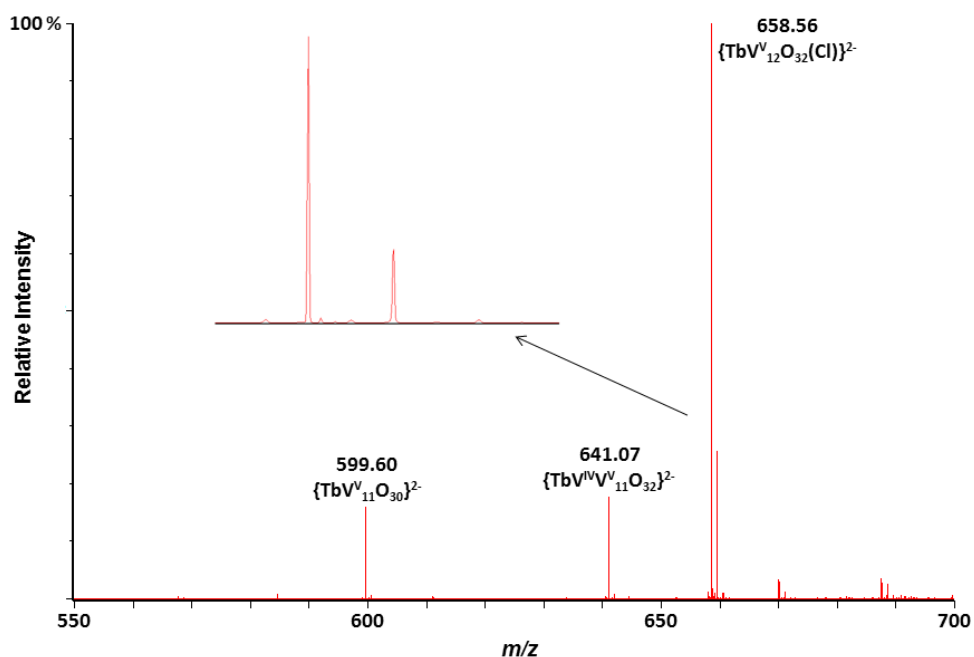
**Table S2:** Bond valence sums for compound **1**

Gd	3.014
V1	4.919
V2	4.890
V3	4.856
V4	4.916
V5	4.997
V6	5.037

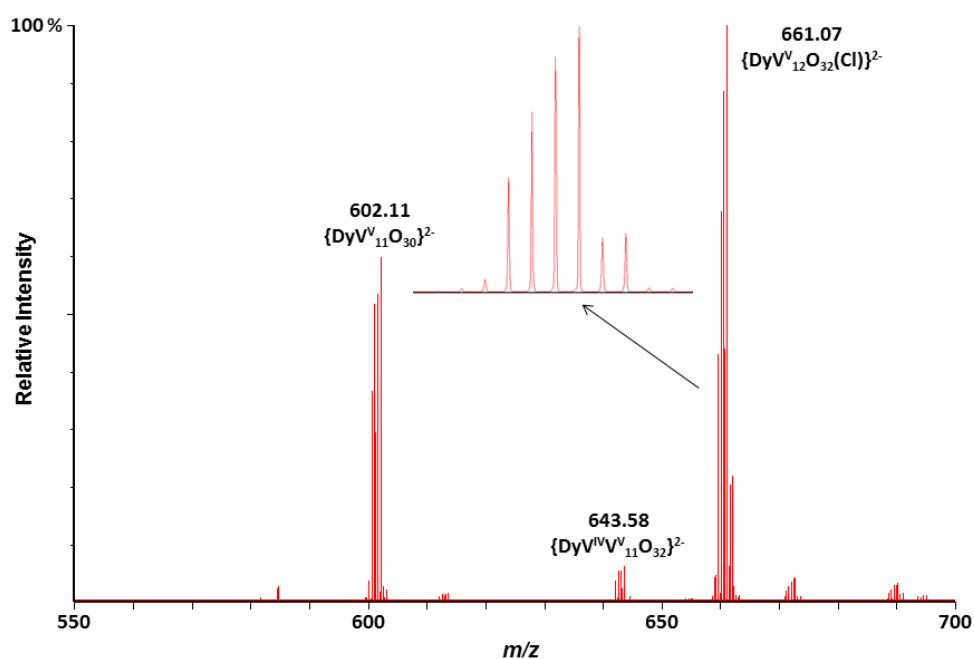
**Table S3:** Unit cell dimensions for compounds **2-5**

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\beta$	$\gamma$	$V$ (Å <sup>3</sup> )
<b>2</b>	10.22	15.48	24.84	90°	90°	90°	3930
<b>3</b>	10.25	15.82	25.08	90°	90°	90°	4067
<b>4</b>	10.24	16.10	24.62	90°	90°	90°	4058
<b>5</b>	10.19	16.13	24.34	90°	90°	90°	4001

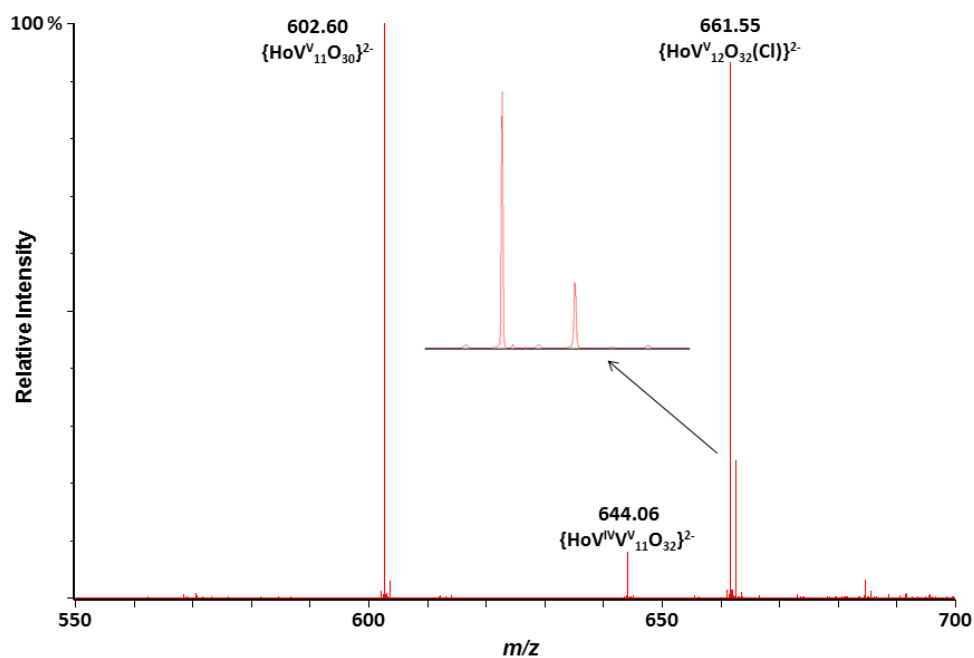
## Mass Spectrometry



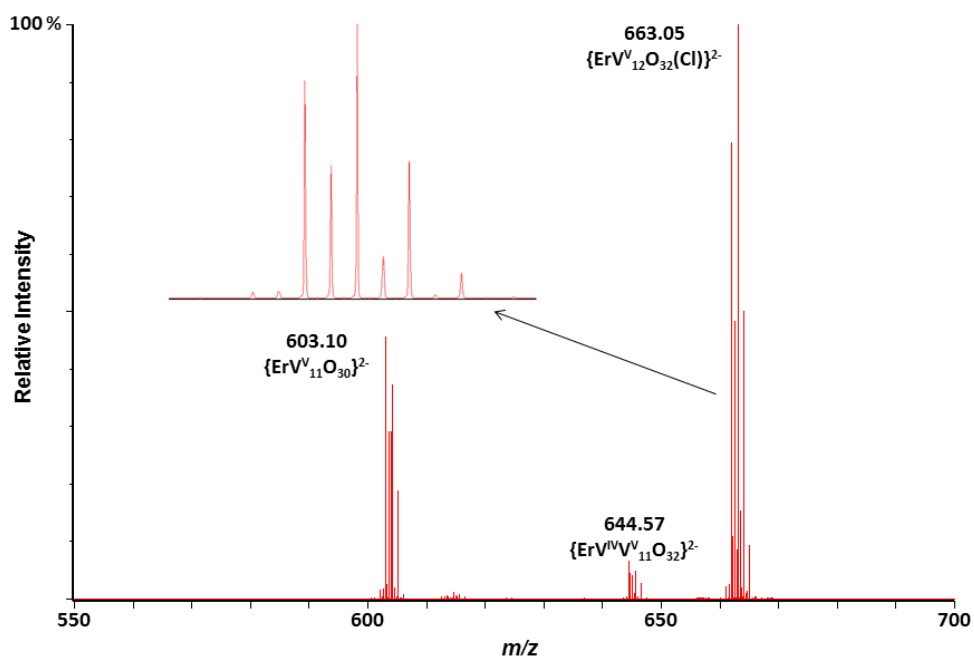
**Figure S1:** Negative ion mass spectrum of **2** shown in the 550 to 700  $m/z$  range highlighting the three primary  $2^-$  peaks. Expansion of the peak centred at  $m/z = 658.56$  is shown inset.



**Figure S2:** Negative ion mass spectrum of **3** shown in the 550 to 700  $m/z$  range highlighting the three primary  $2^-$  peaks. Expansion of the peak centred at  $m/z = 661.07$  is shown inset.

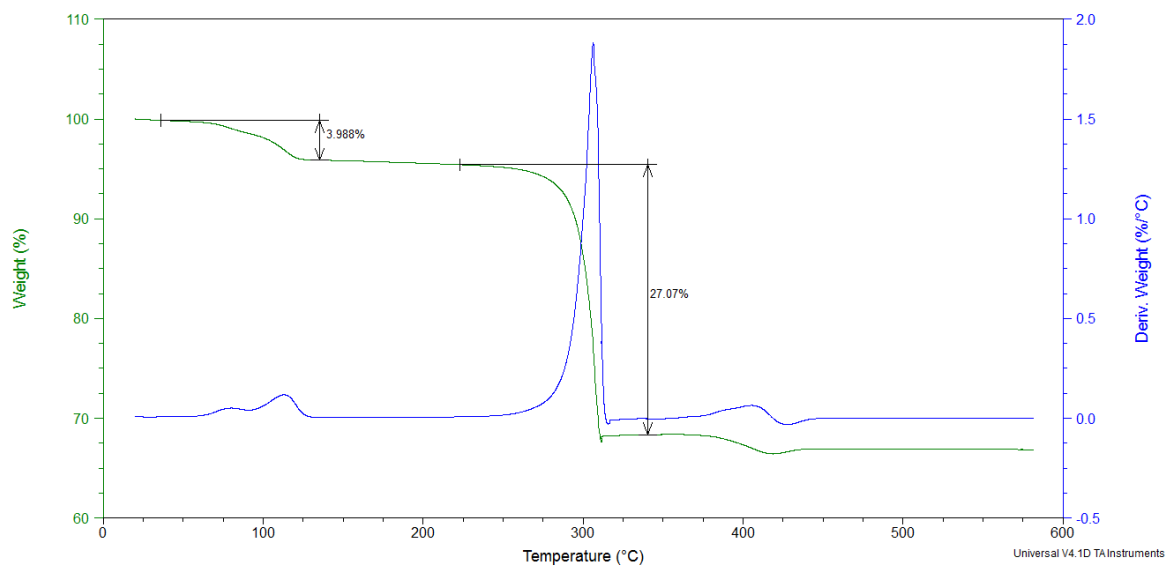


**Figure S3:** Negative ion mass spectrum of **4** shown in the 550 to 700  $m/z$  range highlighting the three primary  $2^-$  peaks. Expansion of the peak centred at  $m/z = 661.55$  is shown inset.

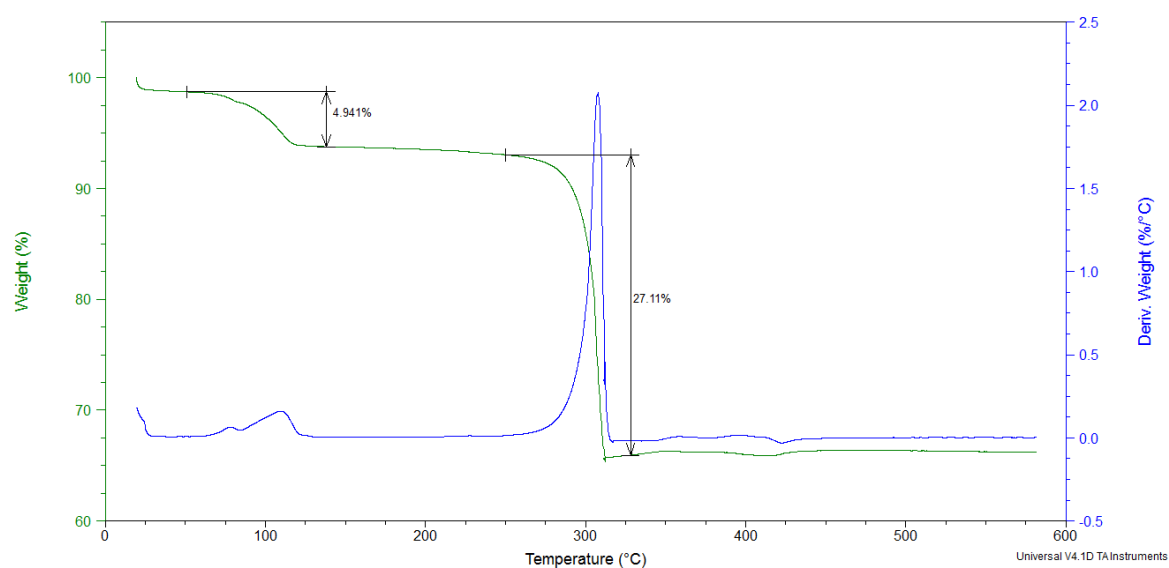


**Figure S4:** Negative ion mass spectrum of **5** shown in the 550 to 700  $m/z$  range highlighting the three primary  $2^-$  peaks. Expansion of the peak centred at  $m/z = 663.05$  is shown inset.

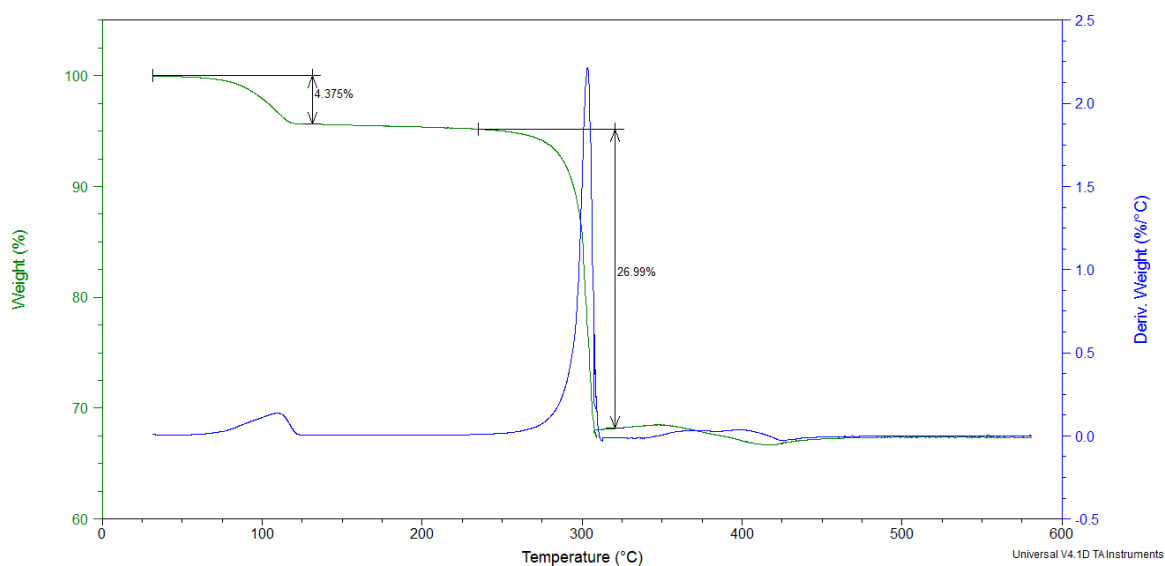
## Thermogravimetric Analysis



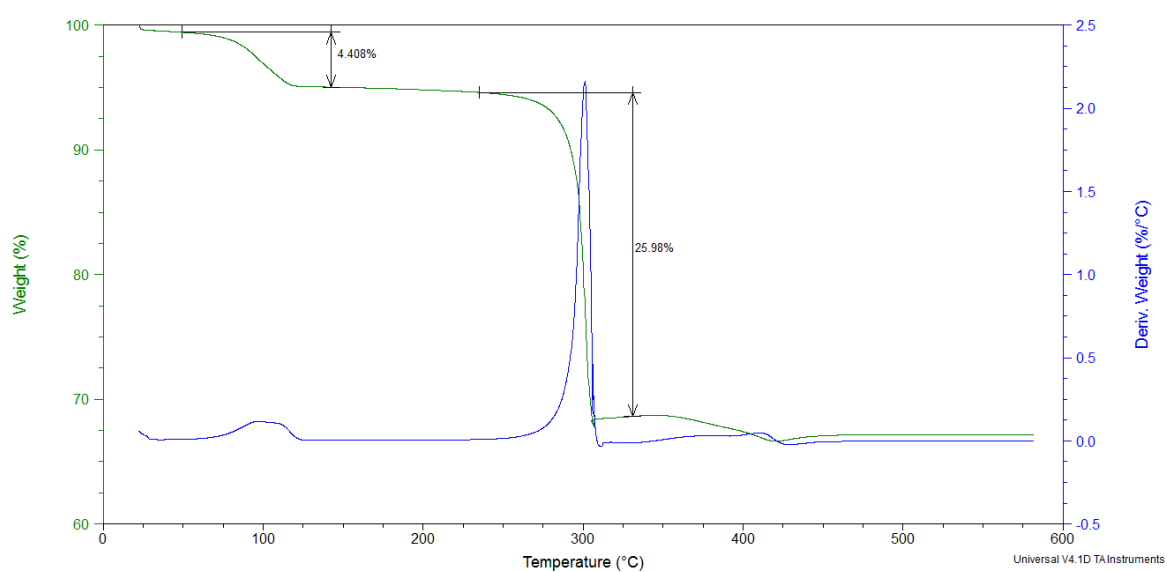
**Figure S5:** Thermogravimetric analysis of **1** showing the loss of ca. 4 H<sub>2</sub>O molecules between 30 - 120°C (3.99%, calc'd: 3.85%) and 2 TBA cations between 250 - 320°C (27.07%, calc'd: 26.91%).



**Figure S6:** Thermogravimetric analysis of **2** showing the loss of ca. 5 H<sub>2</sub>O molecules between 30 - 120°C (4.94%, calc'd: 4.78%) and 2 TBA cations between 250 - 320°C (27.11%, calc'd: 26.87%).

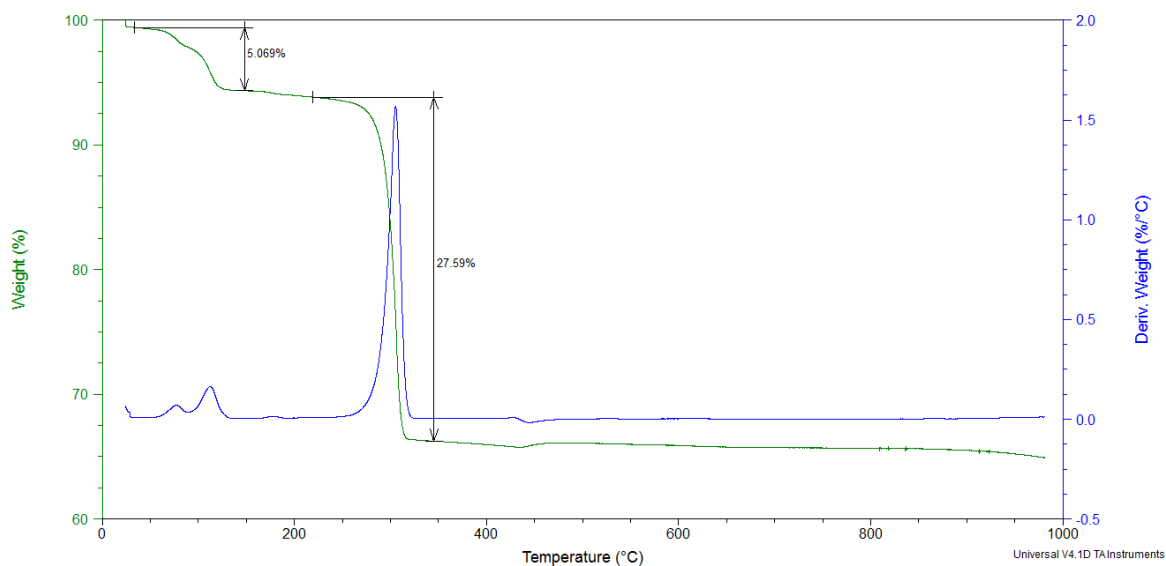


**Figure S7:** Thermogravimetric analysis of **3** showing the loss of ca. 5 H<sub>2</sub>O molecules between 30 - 120°C (4.38%, calc'd: 4.74%) and 2 TBA cations between 250 - 320°C (26.99%, calc'd: 26.80%).

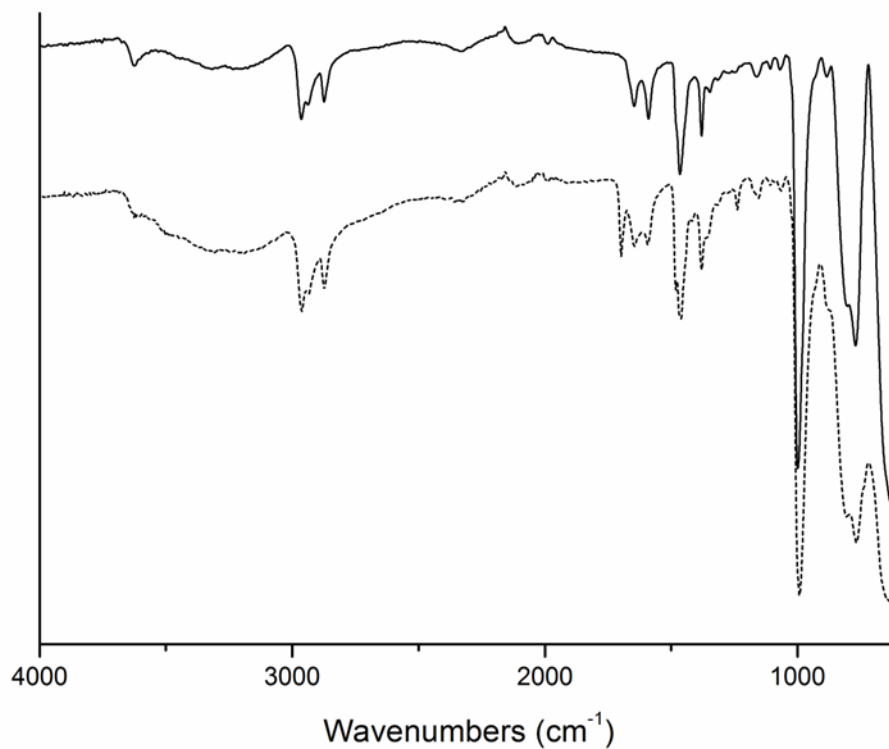


**Figure S8:** Thermogravimetric analysis of **4** showing the loss of ca. 5 H<sub>2</sub>O molecules between 30 - 120°C (4.41%, calc'd: 4.74%) and 2 TBA cations between 250 - 320°C (25.98%, calc'd: 26.77%).





**Figure S9:** Thermogravimetric analysis of **5** showing the loss of ca. 5 H<sub>2</sub>O molecules between 30 - 120°C (5.07%, calc'd: 4.74%) and 2 TBA cations between 250 - 320°C (27.59%, calc'd: 26.76%).



**Figure S10:** Infrared spectra indicating the stability of the cluster on photoreduction from **1** (solid line) to **1'** (dashed line). Characteristic IR bands for **1'** (in cm<sup>-1</sup>): 3628(w), 2963(m), 2936(m), 2874(m), 1698(m), 1645(m), 1590(m), 1464(s), 1379(m), 994(vs), 804(s), 766(s), 632(vs), 605(vs).

## References

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