Electronic Supplementary Material (ESI) for ChemComm.

## Supporting Information

# Exploiting the Equilibrium Dynamics in the Self-Assembly of Inorganic Macrocycles based upon Polyoxothiometalate Building Blocks

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## Synthesis of compounds

### Synthesis of $[N(CH_3)_4]K_3[Mo_2O_2S_2]_8(OH)_{16}(C_4O_4)_2 \cdot 34H_2O$ $\{Mo_{16}\}$ (1)

*Method 1*:

The solution containing crystals of $\{Mo_{14}\}$ was filtered and kept at 18 °C for approximately one month during which period yellow block crystals suitable for X-ray diffraction were formed.

*Method 2*:

Compound $\{Mo_{14}\}$ (75 mg, 0.025 mmol) was dissolved in 15 mL aqueous solution of KCl (0.5 M) and then ultrasonicated for 30 min. The solution was adjusted to pH ca. 5 using 1 M $K_2CO_3$, filtered and kept at 18°C for 22 days. Yellow block crystals suitable for X-ray were isolated. Yield: 67mg, 73.1%.

*Method 3*:

Squaric acid (0.22 g, 1.9 mmol) and 7 mL (0.14 M) $[Mo_2O_2S_2(H_2O)_6]X_2$ (where X = $Cl^-$ and/or $I^-$) were dissolved in 20 mL of distilled water. Then KCl (2.0 g, 26.8 mmol) was added into the above solution. The pH of the solution was adjusted to 5.0 with 1 M $K_2CO_3$. The solution was stirred at room temperature for 1 h, and kept at 18°C for 28 days. Yellow block crystals were isolated from the mother liquor. (Yield: 90 mg, 20.4%). Elemental Analysis ($C_{12}H_{96}K_3Mo_{16}NO_{74}S_{16}$, FW: 3604.24 g/mol) EA (cal.): C:

4.00; H: 2.68; N: 0.39; S: 14.23, K: 3.25, Mo: 42.59; EA (exp.): C: 4.17; H: 2.34; N: 0.36; K: 3.56; Mo: 42.92. IR (KBr, cm$^{-1}$): 3408.6 (m), 1628.6 (m), 1513.9 (s), 941.1 (sh), 491.8 (m).

**Synthesis of $[N(CH_3)_4]_2\{(Mo_2O_2S_2)_6(OH)_{12}(CH_3COO)_2\}\cdot 24H_2O$ $\{Mo_{12}(Ac)_2\}$ (2)**

$CH_3COONa$ (0.223 g, 2.72 mmol) was dissolved in 10 mL deionized water. 7 mL $[Mo_2O_2S_2(H_2O)_6]X_2$ (where X = $Cl^-$ and/or $I^-$) diluted with 5 mL deionized water was added dropwise into the above solution. The solution was adjusted with 1 M $K_2CO_3$ to pH= 4.5 and the solution was stirred at room temperature for 1 hour. The solution was kept in a 50 mL conical flask at 18 °C for 2 weeks where orange block crystals were isolated. Yield: 100 mg, 24.0 % based on $Mo^V$. Elemental analysis for $C_{12}H_{90}Mo_{12}O_{52}S_{12}N_2$, FW: 2630.90 g/mol, EA(cal.): C: 5.48; H: 3.45; Mo: 43.76; N: 1.06 % ; EA (exp.): C: 5.42; H: 3.52; Mo: 44.35; N: 0.99%. IR (KBr, cm$^{-1}$): 3357.5 (m), 1515.8 (m), 1481.1 (m), 1418.4 (m), 942.1 (sh), 667.3 (w), 520.7 (sh).

## Synthesis of $(NMe_4)_4\{[(Mo_2S_2O_2)(OH)_2]_7(C_4O_4)_2(H_2O)_2\}\cdot 13H_2O$ $\{Mo_{14}\}$ (3)

The $\{Mo_{14}\}$ (3) ring has been synthesized according to the previously described procedure [*J. Am. Chem. Soc.*, 2012, **134**, 11376-11379] as follows:

$C_4O_4H_2$ (0.2 g, 1.8 mmol) was dissolved in 10 mL distilled water and the pH was adjusted to 7 by addition of 1M $K_2CO_3$. $[Mo_2S_2O_2(H_2O)_6]X_2$ (where X = $Cl^-$ and/or $I^-$) solution 7.4 mL diluted with 10 mL was added dropwise into the above solution giving an orange and clear solution. The pH of the solution was adjusted to (c.a.) 5 with 1M $K_2CO_3$ and heat it at 60 °C under stirring for 1h. Then the reaction mixture was filtered and the filtrate was kept at 18 °C for 50 days during which period of time yellow plate-shaped crystals suitable for X-ray crystallography were isolated.

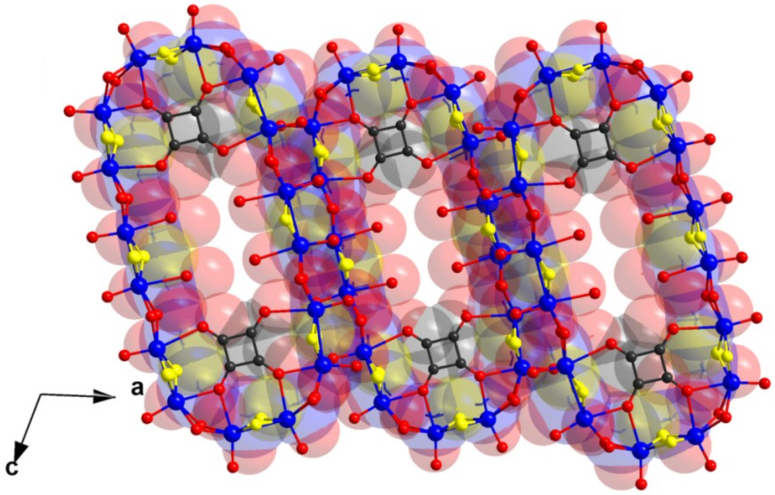

**Fig. S1** The packing mode for **1** $\{Mo_{16}\}$ along the b axis.

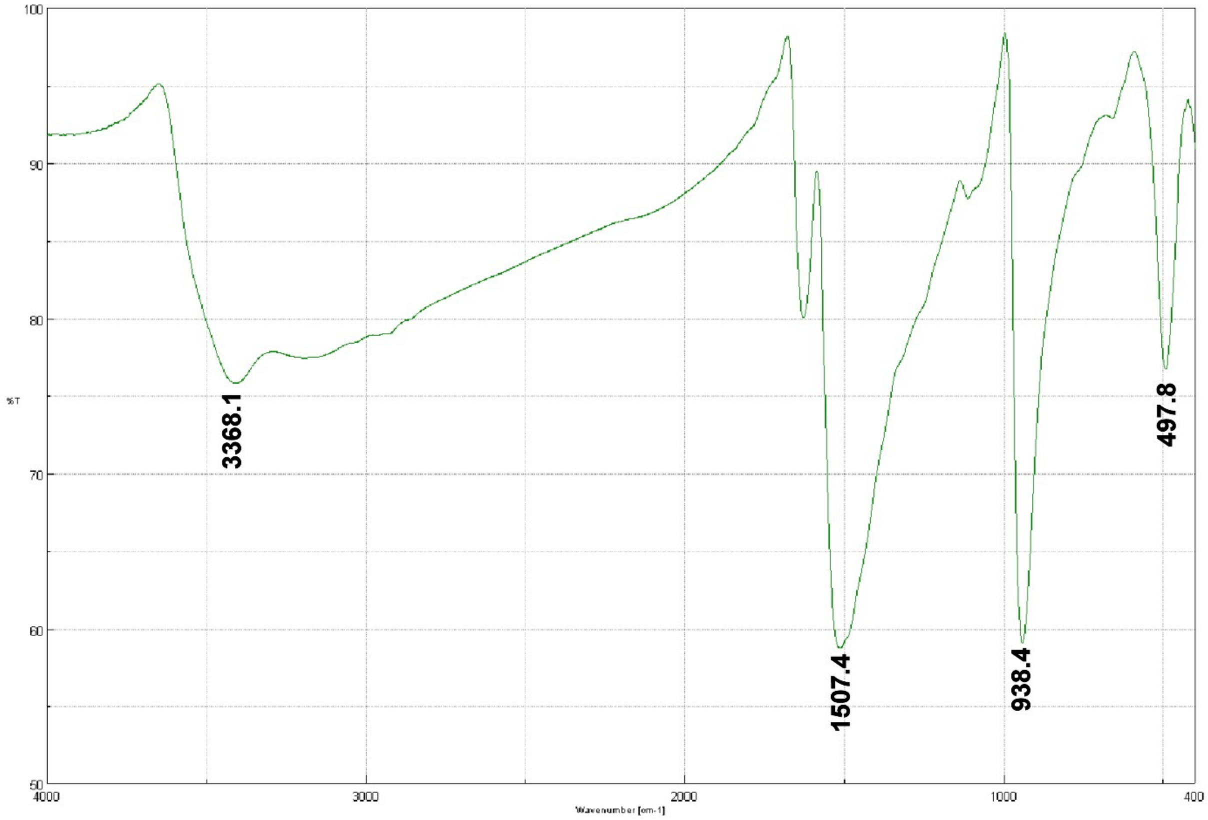

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**Fig. S2** IR spectrum for compound **1**.

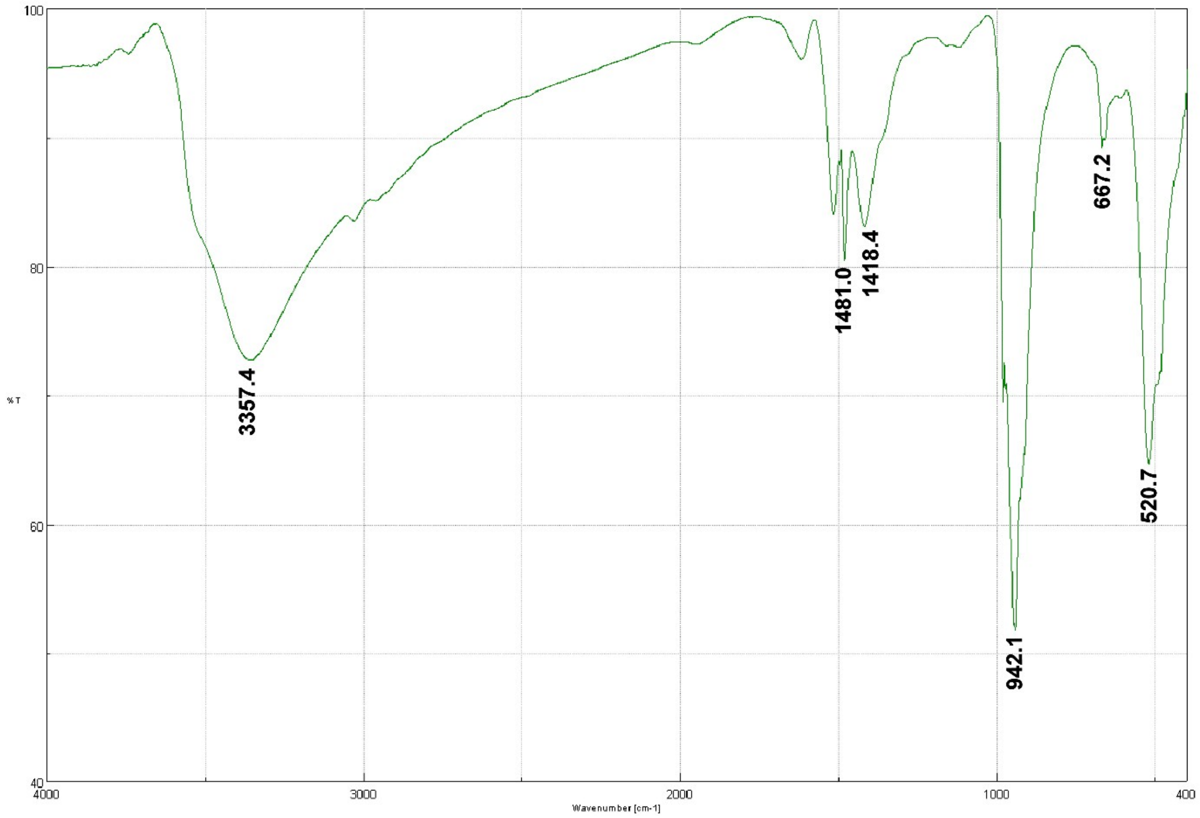


**Fig. S3** IR spectrum for compound **2**.

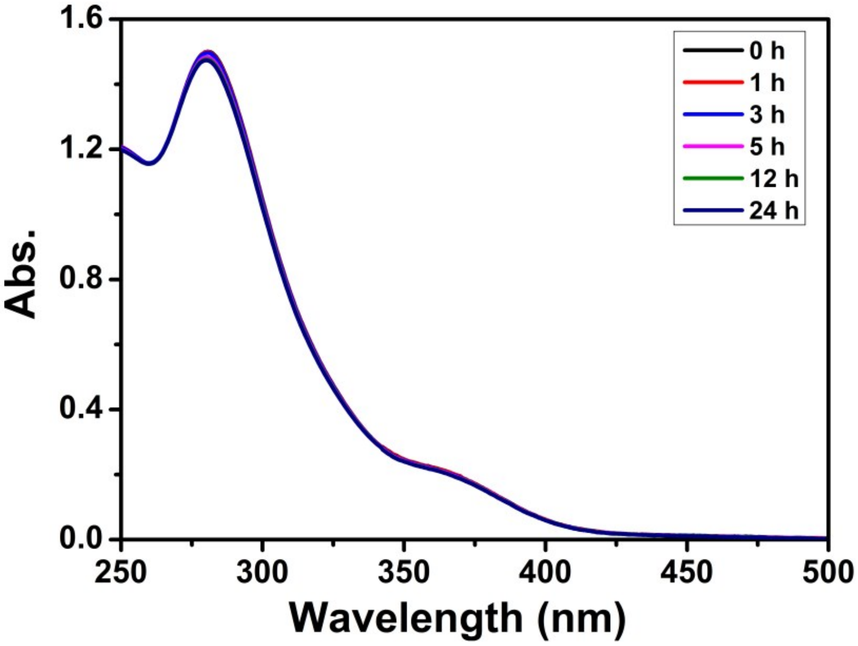


**Fig. S4** UV-vis spectra for compound **1** $\{Mo_{16}\}$ in 0.1 M KOAc-HOAC solution (concentration $10^{-4}$ M). One strong absorption peak at 280 nm and a shoulder centred at 365 nm,] were observed, respectively. The location and intensity of the peaks remained unchanged as a function of the time demonstrating the stability of the cluster in solution.

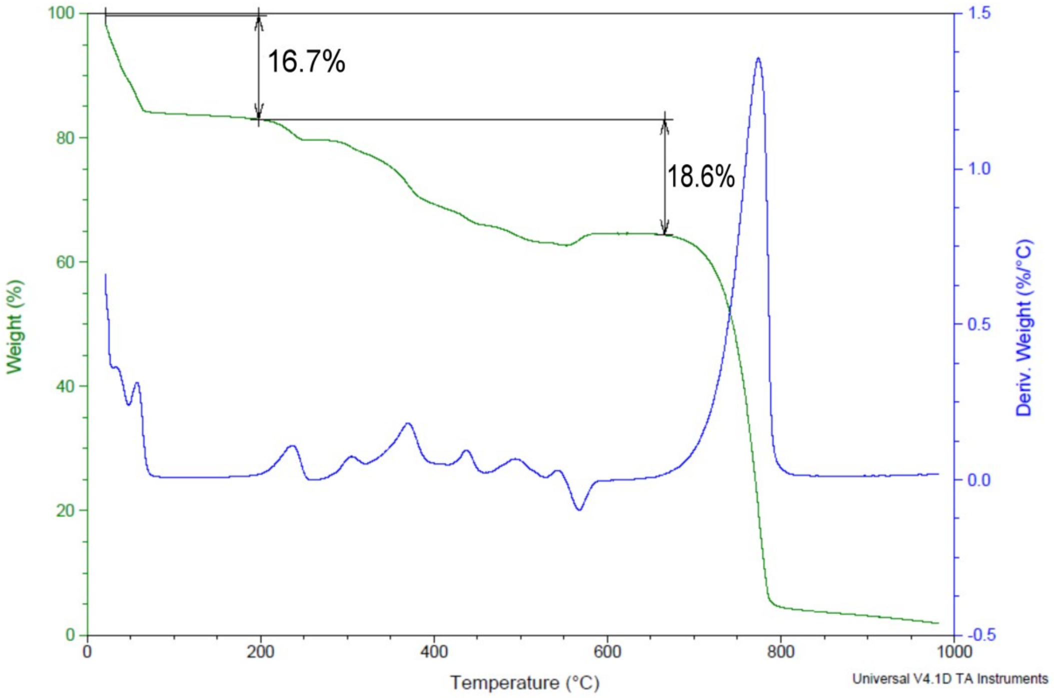


**Fig.S5** Thermogravimetric analysis for compound **1**. The first weight loss of 16.7 % can be attributed to the loss of 34 crystal lattice water molecules followed by the loss of 11.7 % attributed to the loss of the organic content ($Me_4N^+$ and $C_4O_4^{2-}$) in the form of $C_xH_y$, $NH_3$ and $CO_2$ and 7.1% attributed to the partial elimination of the sulphur content as 4 x $SO_2$ in three overlapping steps. Finally, at 795 $^{o}$C we can observe a phase change as expected associated to the formation of $MoO_3$.

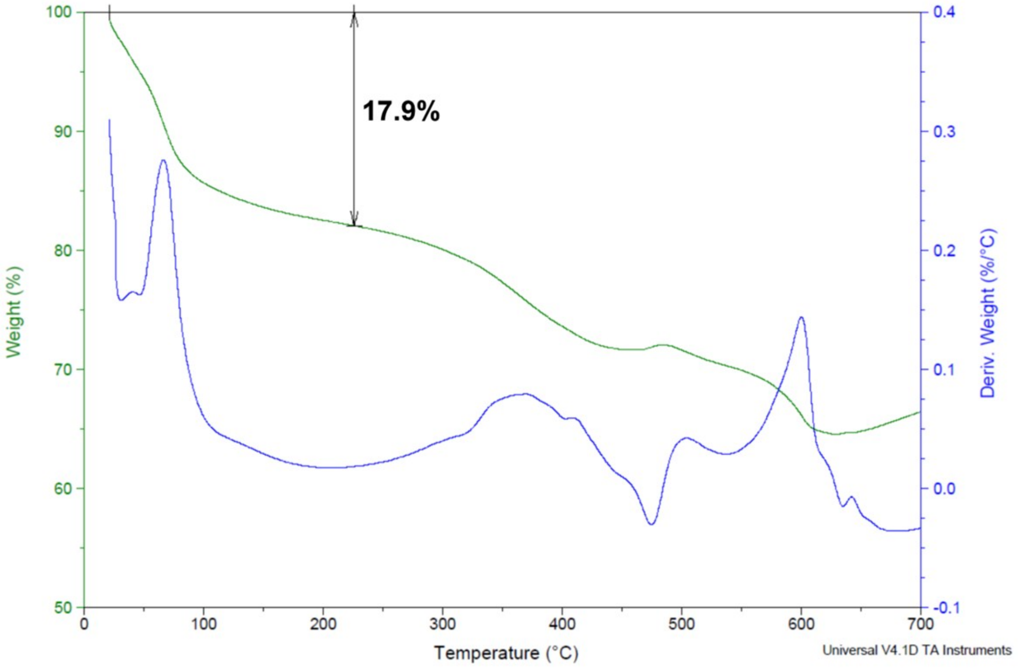


**Fig. S6** Thermogravimetric analysis for compound **2**. The first weight loss of 17.9 % can be attributed to the loss of 25 water molecules followed by the loss of 10.0 %

attributed to the loss of the organic content ($Me_4N^+$ and $CH_3COO^-$) in the form of $C_xH_y$, $NH_3$ and $CO_2$ whilst the final loss of 8% can be attributed to the partial elimination of the sulphur content as $SO_2$ (8%).

### Mass spectra study

Sample Preparation

Compounds **1** and **2** were dissolved in methanol at approx. 0.1 mg/ml (traces of acetonitrile present; less than 0.5 vol%). The analyte solution was filtered through a syringe filter (0.2 µm) before infused into the spectrometer using a syringe pump at a flow rate of 5 $\mu L \cdot min^{-1}$.

MS and IMS-MS Settings (Compound **1**)

Negative mode mass-spectrometry (MS) and ion-mobility mass-spectrometry (IMS-MS) measurements were performed on a Synapt™ G2 HDMS™ from Waters in 'Sensitivity' mode with the following settings:

| | |
|---|---|
| **Ionization** | Capillary voltage = 2.7 kV; Source temperature = 80 °C; Sampling cone = 20 V; Extraction cone = 4 V; Desolvation temperature = 120 °C; Trap collision energy = 0.0 V, except where noted ("CID" experiments); Transfer Collision energy = 0.0 V. |
| **TWIMS** | Trap Gas Flow = 4 mL/min; Helium Cell Gas Flow = 180 mL/min; IMS Gas Flow 90 mL/min; IMS Wave Velocity 750 m/s; IMS Wave Height 40 V. |

MS spectrum

The spectrum below is typical of those observed for **1**. Most of the major peaks observed are broad and plausibly assigned as a continua resulting from a single anion with a range of different cations and/or neutral addenda (particularly solvent ions). IMS-MS and CID studies (*vide infra*) support the assignment of the broad peaks ca. 1000 Da ($z = -3$) and 1500 Da ($z = -2$) as corresponding to the intact $\{Mo_{16}\}$ cluster with a variety of cations/solvent molecules (listed in blue), and most other peaks are assigned as fragments (some of the largest listed in red).

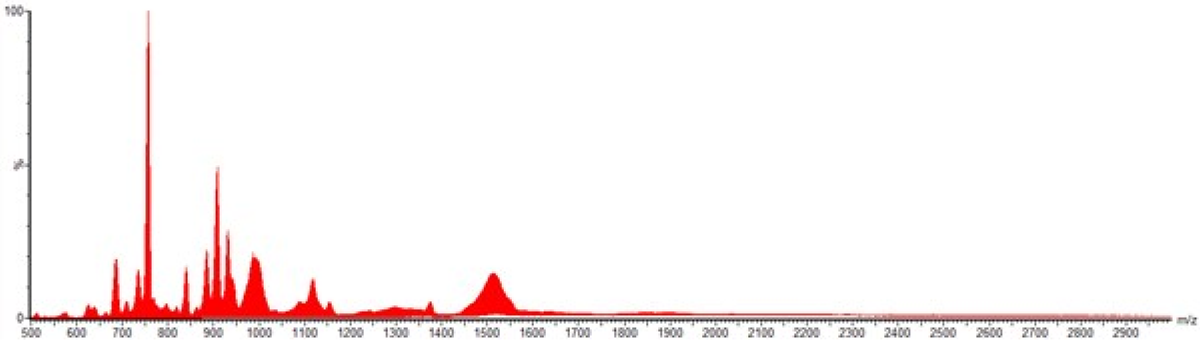
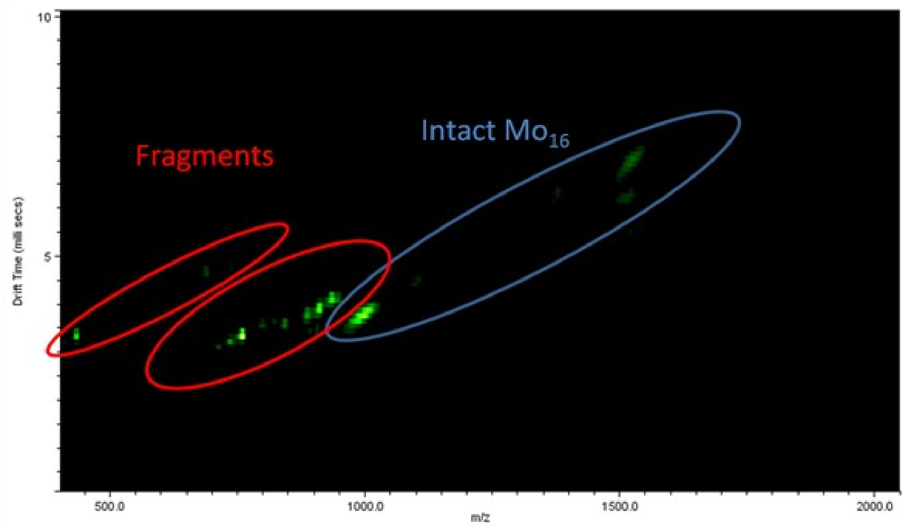


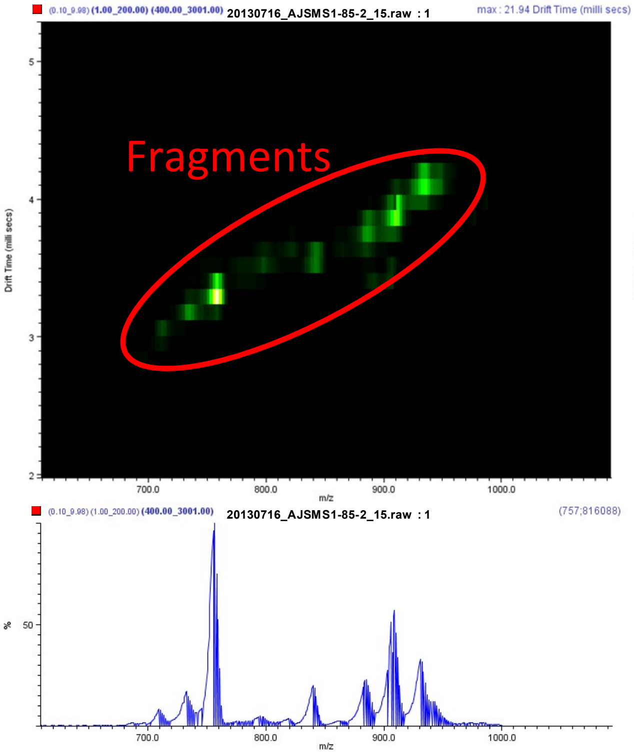
**Figure S7.** MS spectrum of Compound **1** in MeOH.

**Table S1** The peaks assignment for the mass spectra.

| *m/z* | *z* | Putative Ion Composition |
|---|---|---|
| 1506 | -2 | $[N(CH_3)_4]_2[(Mo_2O_2S_2)_8(OH)_{16}(C_4O_4)_2](CH_3OH)_2$ |
| 1508 | -2 | $[N(CH_3)_4]_2[(Mo_2O_2S_2)_8(OH)_{16}(C_4O_4)_2]\ (H_2O)_2(CH_3OH)$ |
| 1510 | -2 | $[N(CH_3)_4]_2((Mo_2O_2S_2)_8(OH)_{16}(C_4O_4)_2)(H_2O)_4$ |
| 994 | -3 | $[N(CH_3)_4][(Mo_2O_2S_2)_8(OH)_{16}(C_4O_4)_2](H_2O)_2(CH_3OH)(CH_3CN)$ |
| 993 | -3 | $[N(CH_3)_4][(Mo_2O_2S_2)_8(OH)_{16}(C_4O_4)_2](H_2O)_4(CH_3OH)$ |
| 907 | -3 | $K[(Mo_2O_2S_2)_5(OH)_{11}(C_4O_4)](H_2O)_2$ |
| 906 | -3 | $[N(CH_3)_4][(Mo_2O_2S_2)_5(OH)_{11}(C_4O_4)]$ |
| 756 | -3 | $K_2\ [(Mo_2O_2S_2)_4(OH)_{10}(C_4O_4)]$ |

### IMS-MS spectrum


Fragments
Intact Mo16
Drift Time (milli secs)
10
5
500.0
1000.0
1500.0
2000.0
m/z


(0.10_9.98) (1.00_200.00) (400.00_3001.00) 20130716_AJSMS1-85-2_15.raw : 1
max : 21.94 Drift Time (milli secs)
Fragments
Drift Time (milli secs)
5
4
3
2
700.0
800.0
900.0
1000.0
m/z
(0.10_9.98) (1.00_200.00) (400.00_3001.00) 20130716_AJSMS1-85-2_15.raw : 1
(757;816088)
%
50
700.0
800.0
900.0
1000.0
m/z

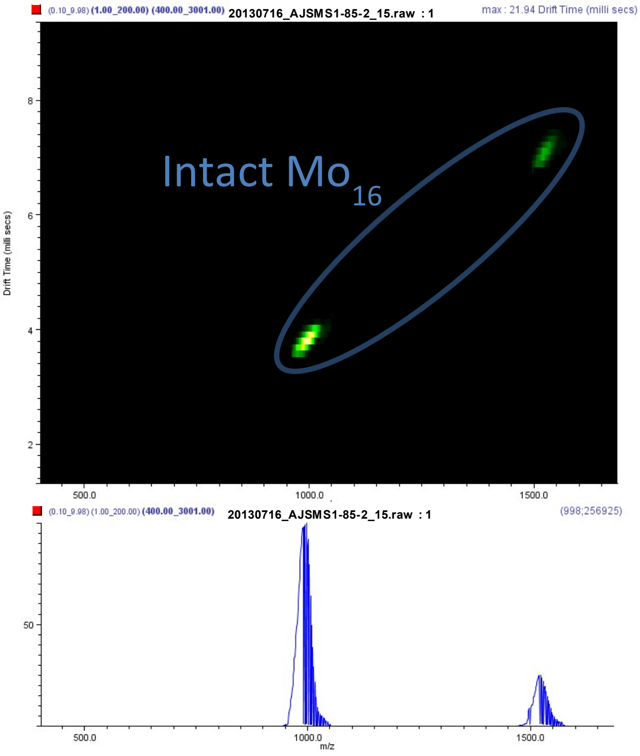

(0.10_9.98) (1.00_200.00) (400.00_3001.00) 20130716_AJSMS1-85-2_15.raw : 1
max : 21.94 Drift Time (milli secs)
Intact Mo16
Drift Time (milli secs)
8
6
4
2
500.0
1000.0
1500.0
(0.10_9.98) (1.00_200.00) (400.00_3001.00) 20130716_AJSMS1-85-2_15.raw : 1
(998;256925)
50
500.0
1000.0
1500.0
m/z

**Fig. S8.** IMS-MS spectrum of compound **1** in MeOH showing the relevant areas along with the associated spectra which can be assigned to the intact {$Mo_{16}$} cluster and its building block-based fragments.

## Fragmentation (MS/MS) demonstrates presence of solvent molecules

In order to further confirm the putative assignment of peaks incorporating the intact {Mo16} cluster as including a neutral solvent molecules, a narrow range of the peak at 1506 +/- 3 Da was selected using the instrument's quadrupole and subjected to collision-induced dissociation (CID) conditions (Trap Collision Energy = 15 V), leading to fragmentation. It is clear that the principal neutral loss (without fragmentation of the {$Mo_{16}$} cluster) correspond to species of mass 32 ($\Delta m/z = 16$; $z = 2$), consistent with loss of associated methanol molecules from the selected ions.

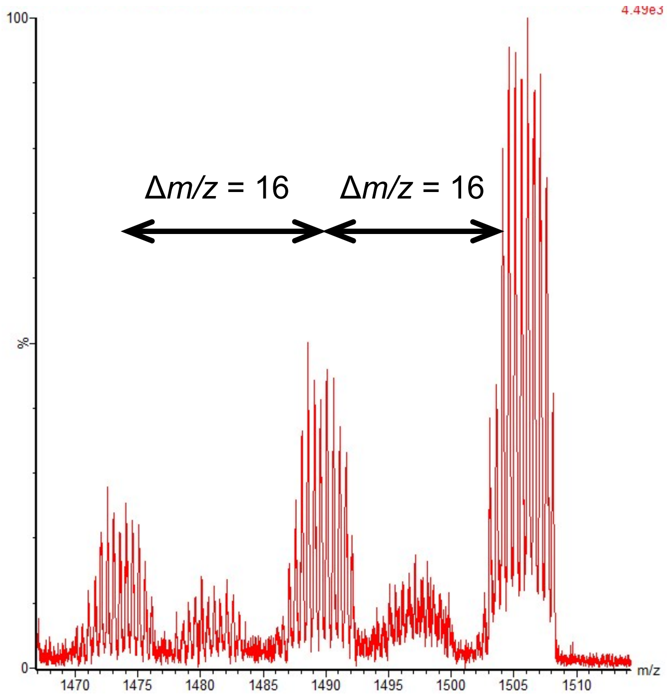


**Fig. S9** MS/MS spectrum of Compound **1** in MeOH (CID @ 15 V).

MS spectrum (Compound **2**)

Electrospray Ionisation Mass Spectrometry (ESI-MS) was performed using a Bruker micrOTOF-Q quadrupole time-of-flight mass spectrometer. Samples were dissolved in MeOH introduced into the MS at a dry gas temperature of 180 °C. The ion polarity for all MS scans recorded was negative, with the voltage of the capillary tip set at 4500 V, end plate offset at −500 V, funnel 1 RF at 400 Vpp and funnel 2 RF at 400 Vpp, hexapole RF at 200 Vpp, ion energy 5.0 eV, collision energy at 15 eV, collision cell RF at 2100 Vpp, transfer time at 120.0μs, and the pre-pulse storage time at 20.0 μs.ode and analysed using the Bruker Daltonics v4.1 software.

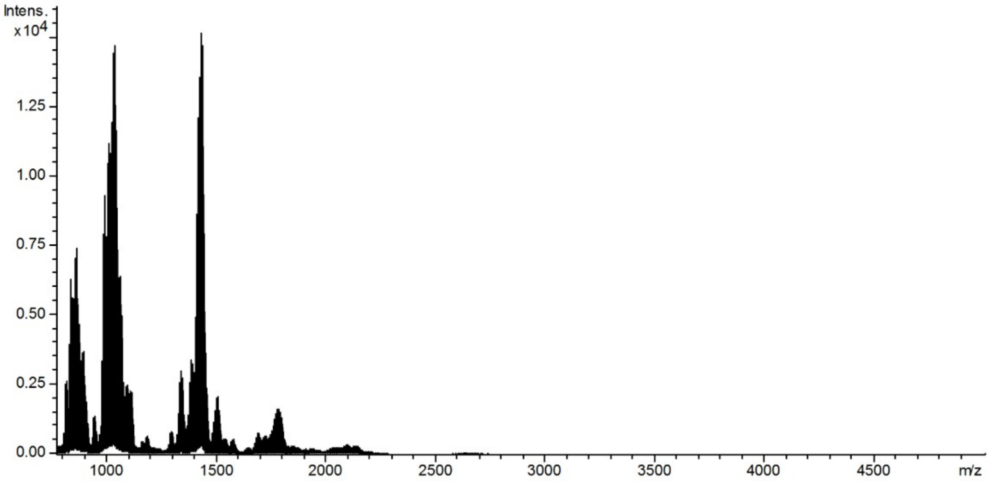


**Fig. S10.** MS spectrum of Compound **2** in MeOH.

**Table S2** The peaks assignment for the mass spectra.

| *m/z* | *z* | Putative Ion Composition |
|---|---|---|
| 1403.13 | -1 | $[N(CH_3)_4][(Mo_2O_2S_2)_4(OH)_{10}](CH_3OH)$ |
| 1505.20 | -1 | $[N(CH_3)_4]_2[(Mo_2O_2S_2)_4(OH)_{12}H]$ |
| 1341.02 | -1 | $[(Mo_2O_2S_2)_4(OH)_{11}H_2]$ |
| 1034.30 | -1 | $[(Mo_2O_2S_2)_3(OH)_8H](CH_3OH)$ |

Electrochemical characterization

The cyclic voltammetry for the three compounds were conducted using The CHI 760D electrochemical equipment. The standard three-electrode arrangement was employed with a Pt mesh auxiliary electrode, 1.5 mm glassy carbon working electrode, and Ag/AgCl reference electrode. All potentials are quoted relative to the Ag/AgCl reference electrode. The glassy carbon working electrodes (diameter 1.5 mm) were polished with alumina (3 µm) on polishing pads, rinsed with distilled water, and sonicated in $H_2O$ and then acetone solution before each experiment.

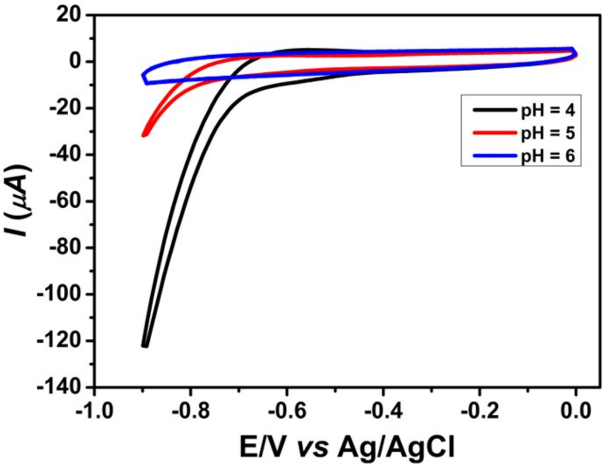


**Fig. 11** Cyclic voltammogram of $3\times10^{-4}$ M of $\{Mo_{16}\}$ taken in 0.1 M KOAc-HOAc aqueous solution at a scan rate of 100 mV/s.

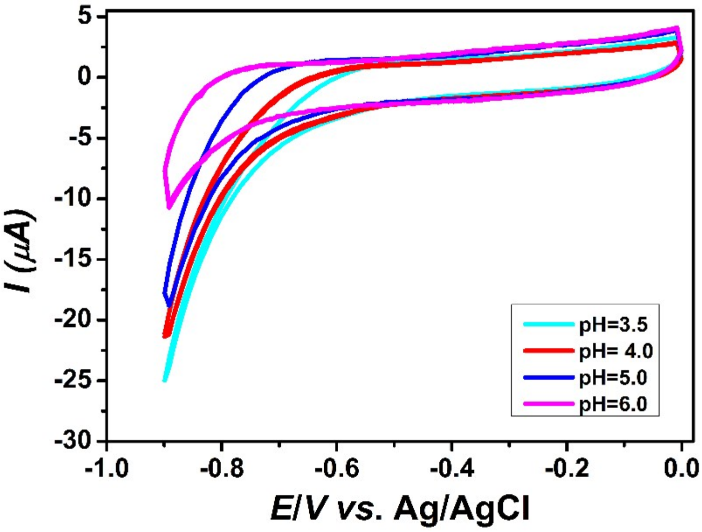


**Fig. 12** Cyclic voltammogram of $3\times10^{-4}$ M of $\{Mo_{12}\}$ taken in 0.1 M KOAc-HOAc aqueous solution at a scan rate of 100 mV/s.

The cyclic voltammograms (CVs) of compound the $\{Mo_{16}\}$ ring was recorded in aqueous medium in the potential window of 0 to −0.90 V *vs*. Ag/AgCl at a scan rate of 100 mV/s. The concentrations of the $\{Mo_{16}\}$ used was $3 \times 10^{-4}$ mol·L$^{-1}$ and the pH was adjusted in the range 4–6 by means of acetic acid (see ESI for further details). During pH 4-6, there are no noticeable reversible electrochemical processes is detected. The CV of compound {$Mo_{16}$} in the range 4-5 exhibit similar patterns when recorded in acidic aqueous electrolytes with a large pluri-electronic irreversible wave mainly attributed to the electrocatalytic reduction of protons into hydrogen. At pH=6, the reduction wave was not obvious; however, this catalytic wave gradually moves towards more positive potentials when the pH decreases, whereas its intensity dramatically grows, thus undergoing an enhanced catalysis in more acidic media. The electrochemistry of {$Mo_{12}$} exhibited a similar behaviour within the same pH range, however the catalytic wave appeared to be weaker.