Electronic Supplementary Information

Microwave Assisted Synthesis of a Mono Organo-imido Functionalised Anderson Evans Polyoxometalate

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Experimental Section

Materials and Analytical Methods

$(TBA)_4[Mo_8O_{26}]$ was prepared as previously published,[1] all other reagents and solvents were used as purchased. (KBr Disc) FT-IR spectroscopy was performed on a Bruker Tensor 27 FT-IR spectrometer. Signals are listed as wavenumbers (cm^{-1}) with the following abbreviations: s = strong, m = medium, w = weak and b = broad. Chemical analysis was performed on a Carlo Erba Elemental Analyser EA 1108. The synthesis of **(1)** was conducted in a Biotage Intiator Microwave reactor. UV-Vis spectroscopy was performed on an Agilent Technologies Cary 60 UV-Vis using standard quartz cuvettes (d = 1 cm). ESI-MS spectra were recorded on a high resolution Agilent QTOF LCMS 6520. ^{1}H NMR spectroscopy was performed on a Varian 400 MHz NMR Spectrometer at room temperature and referenced to the residual proton resonance of the deuterated solvent.

Small angle X-ray scattering (SAXS) measurements were conducted using a Bruker MicroCalix, using Cu Ka radiation at a wavelength of 1.54 Å. The instrument was run in high flux mode, with the X-ray microsource running at 50 W. Scattered light was detected using a Pilatus 100 k detector. Solutions of known concentration were measured in 1.5 mm diameter quartz X-ray capillaries with 10 μm wall thickness (Hilgenberg, Germany). Scattering and transmission measurements were made for each of the samples, as well as for a sample containing only the solvent. Scattering patterns were collected for between 1-4 hours depending on sample scattering, and transmission measurements were collected for 5 s. Data analysis (normalization, primary beam masking, background subtraction) were carried out in fit-2D. No smoothing was used, and the fit results were not significantly affected by normalization. Shape analysis was carried out using SasView (http://www.sasview.org/). Scattering Length Densities (SLDs) for the molecules and solvents were calculated from crystallographic data and used as inputs, though the fits are insensitive to small changes in the SLDs. Cylinder and/or Spherical models were fit to the data. Other appropriate models were also trialled without yielding good fits.

In addition to the full fits, low Q Guinier analyses were also carried out, yielding a measure of the Radius of gyration (R_g) which is not model dependent. For a solid sphere the relationship between R_g and R is:

$$R_g = \sqrt{\frac{3}{5}}R$$

For a cylinder or radius R and Length L the relationship is:

$$R_g^2 = \frac{R^2}{2} + \frac{L^2}{12}$$

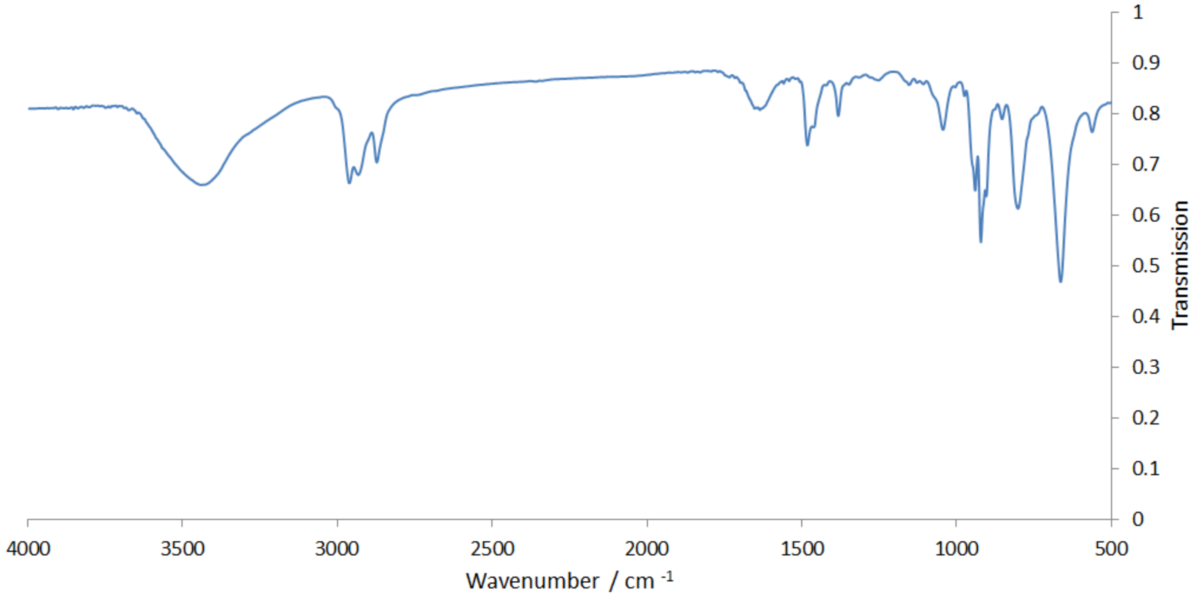
The low q Guinier fits were used as checks of the appropriateness of the models.

Single crystal X-ray data was collected using an Agilent Technologies SuperNova Dual Wavelength single crystal X-ray diffractometer at 130 K using Cu-Kα radiation (λ = 1.5418 Å) fitted with a mirror monochromator. The data was reduced using CrysAlisPro software (Version 1.171.36.28) using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Data was solved using direct methods by SHELXT and refined using a full-matrix least square procedure based upon F^2.[2] All non-hydrogen atoms of the main polyanion were refined anisotropically, with all other atoms refined isotropically. Data was refined using the OLEX2 software package Version 1.2.6.[3] Significant crystallographic disorder was observed for **1** with the positions of, and the bonding within the organic cations being restrained. Furthermore, we were unable to crystallographically locate all the TBA cations, with the use of a solvent mask being required to account for the residual electron density.

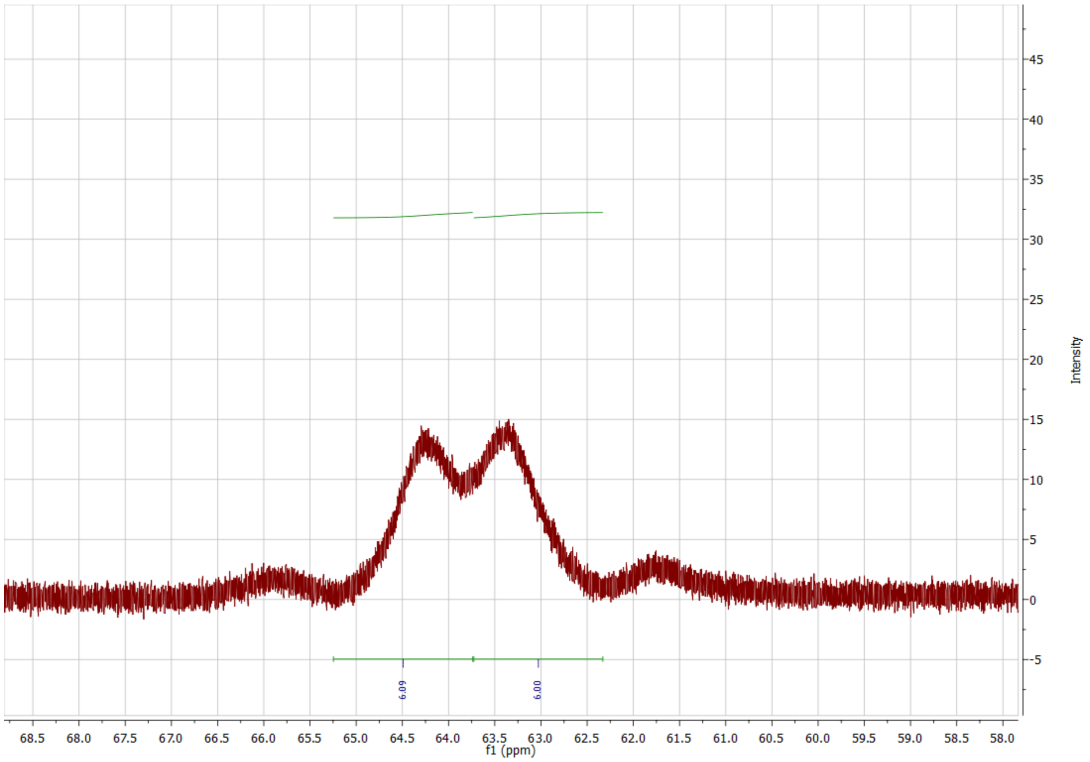
Synthesis of $\mathbf{TBA_5[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_2]}$ (1)

$(TBA)_4[Mo_8O_{26}]$ (800 mg, 0.372 mmol), $Mn(CH_3COO)_3{\cdot}2H_2O$ (66 mg, 0.246 mmol) and $C_4H_{11}NO_3$ (60 mg, 0.496 mmol) was dissolved in 12 mL of acetonitrile and placed in a 20 mL microwave reaction vessel. With stirring the reaction mixture was heated to 110 °C at 4 bar for 3 hours and subsequently allowed to cool to room temperature prior to opening of the reaction vessel. Diethyl ether was diffused into the deep orange solution until the solution became colourless and the resulting crystalline mixture filtered and dried. An acetone slurry of the solid was then prepared and filtered to yield a dark yellow solution into which was diffused diethyl ether resulting in a pure crystalline sample of **(1)** over a few hours in (220 mg, 0.068 mmol, 28 % yield). ^1H NMR ([D_6]acetone, 400 MHz), δ 1.01 (t, 60H, $-CH_3$ $[Bu_4N]^+$), 1.50 (m, 40H, $-CH_2$ $[Bu_4N]^+$), 1.83 (m, 40H, $-CH_2$ $[Bu_4N]^+$), 3.43 (m, 40H, $-CH_2$ $[Bu_4N]^+$), 62.50-63.75 (s, 6H, $-CH_2$, $Mo{\equiv}N\text{-}C(C\mathbf{H_2}O)_3$), 63.75 – 65.00 (s, 6H, $-CH_2$, $NH_2C(C\mathbf{H_2}O)_3$). Elemental analysis (%) calculated, (found) for $C_{88}H_{194}MnMo_{12}N_7O_{42,}$ C, 32.70 (32.70); H, 6.06 (6.14); N, 3.04 (3.10). Selected IR data (KBr, cm^{-1}): 3441 (b), 2961 (s), 2933 (s), 2873 (s), 1635 (m), 1482 (m), 1382 (m), 1068 (w), 1044 (m), 974 (w), 940 (m), 921(m), 904 (w), 853 (s), 664 (s), 562 (m). MS (ESI): *m/z* calcd for $\{[Bu_4N]_1[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_3]\}^{3-}$: 753.33 $[M^{3-}]$; found, 753.33. MS (ESI): *m/z* calcd for $\{[Bu_4N]_2[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_2]\}^{3-}$: 834.43 $[M^{3-}]$; found, 834.42. MS (ESI): *m/z* calcd for $\{[Bu_4N]_2[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_3]\}^{2-}$: 1251.15 $[M^{2-}]$; found, 1251.14. MS (ESI): *m/z* calcd for $\{[Bu_4N]_3[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_2]\}^{2-}$: 1372.78 $[M^{2-}]$; found, 1372.77.

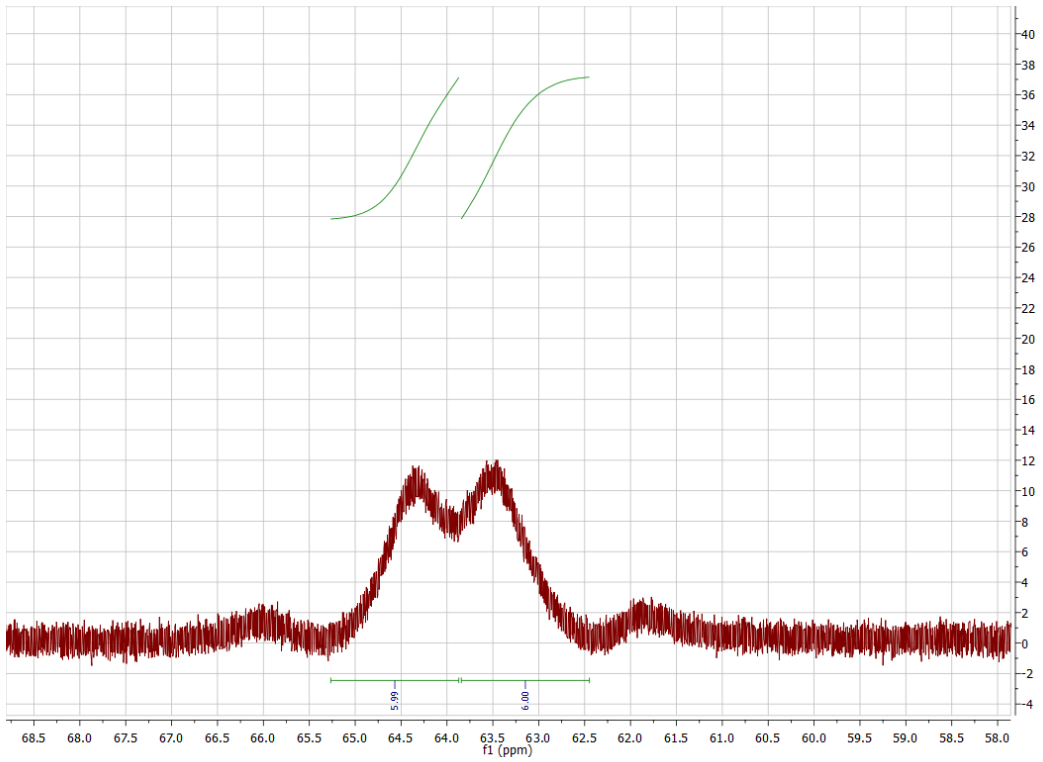
Characterization and Data Analysis



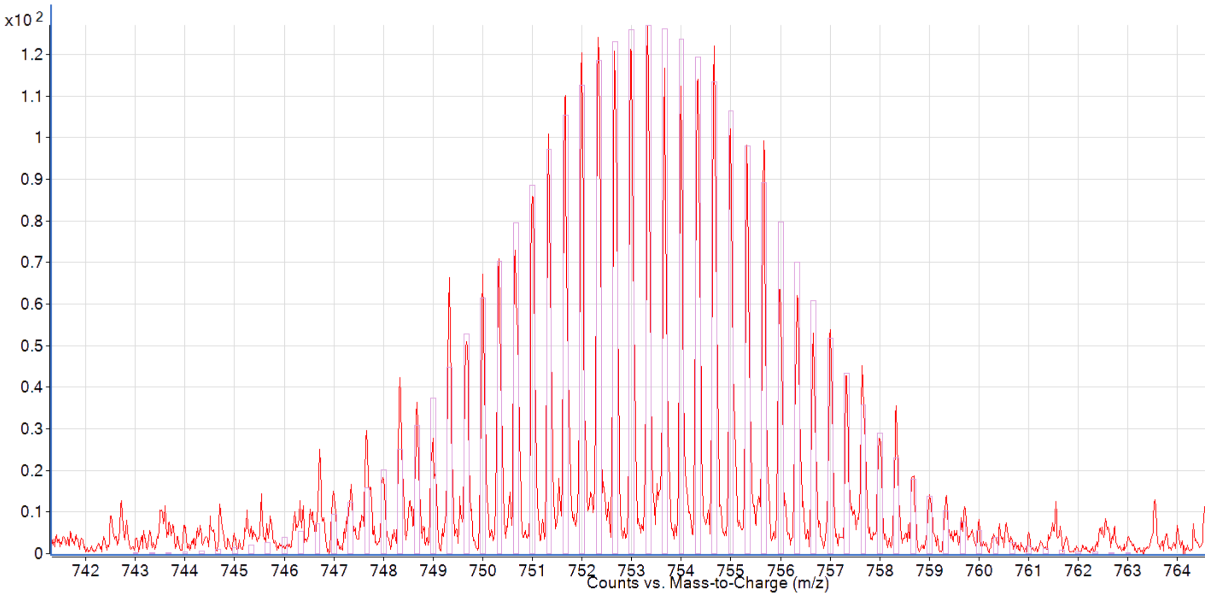
S1. FTIR spectroscopy of a freshly crystallized sample of **(1)**.



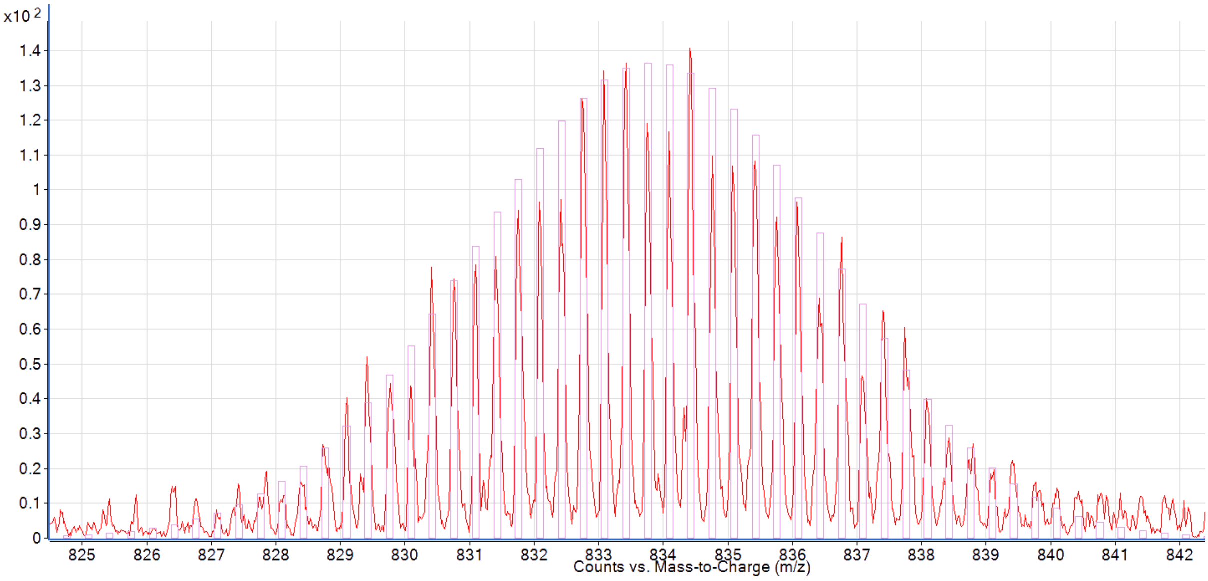
S2. ^{1}H NMR spectra of **[1]** focussing on the Mo≡N-C(CH_2O)$_3$ and NH$_2$C(CH_2O)$_3$ TRIS hydrogen atoms with broad resonances at 62.50-63.75 and 63.75 – 65.00 ppm respectively.



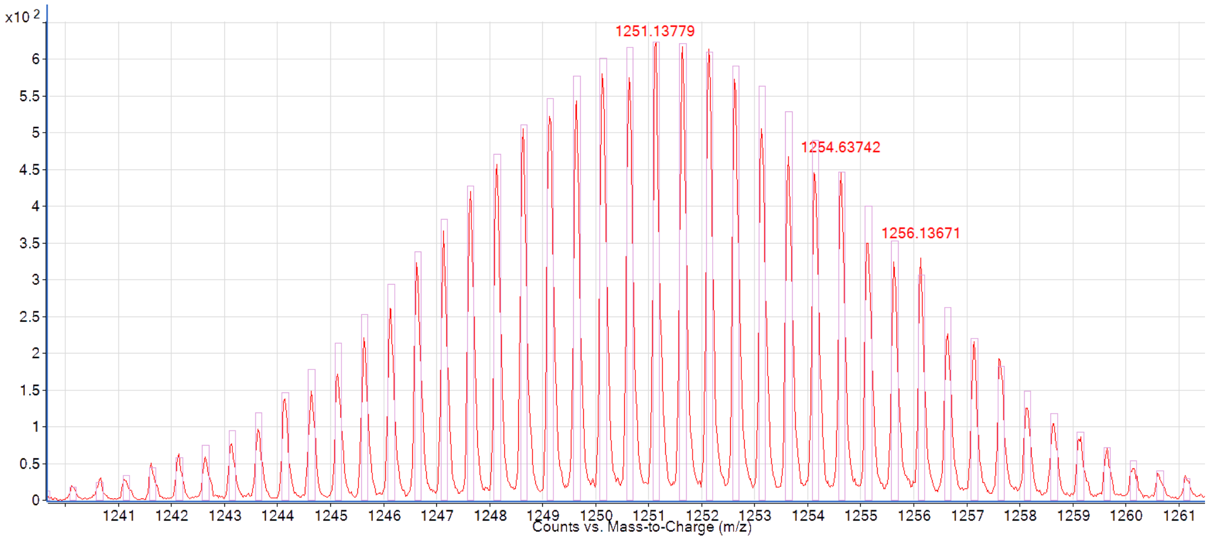
S3. Aged (1 week) ^{1}H NMR spectra of **[1]** focussing on the Mo≡N-C(C$\mathbf{H_2}$O)$_3$ and NH$_2$C(C$\mathbf{H_2}$O)$_3$ TRIS hydrogen atoms with broad resonances at 62.50-63.75 and 63.75 – 65.00 ppm respectively.



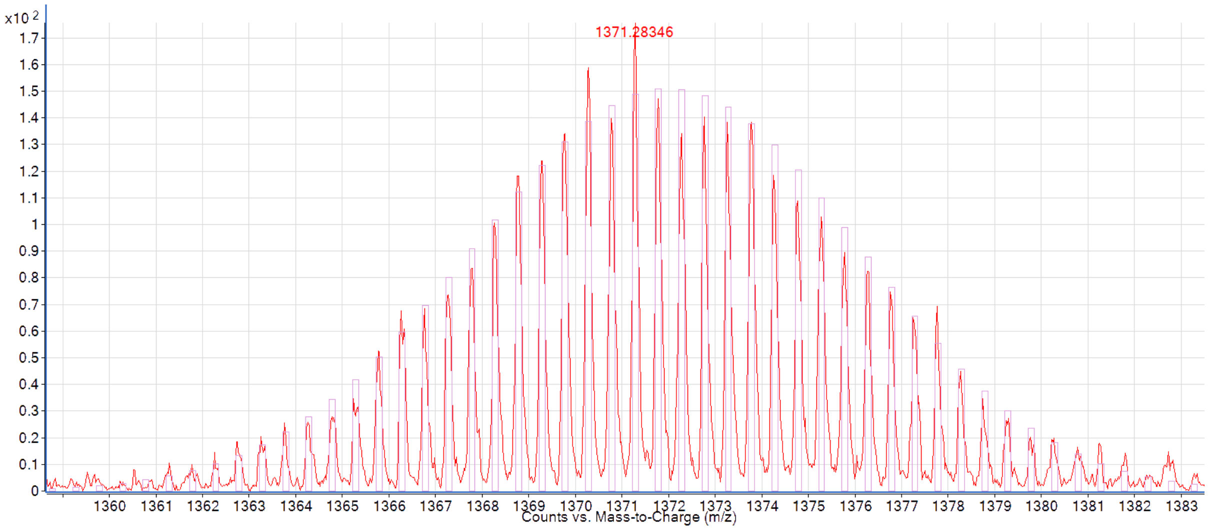
S4. ESI-MS of the molecular ion [M^{3-}] - {[Bu$_4$N]$_1$[Mo$_6$O$_{18}$NC(OCH$_2$)$_3$MnMo$_6$O$_{18}$(OCH$_2$)$_3$CNH$_3$]}$^{3-}$



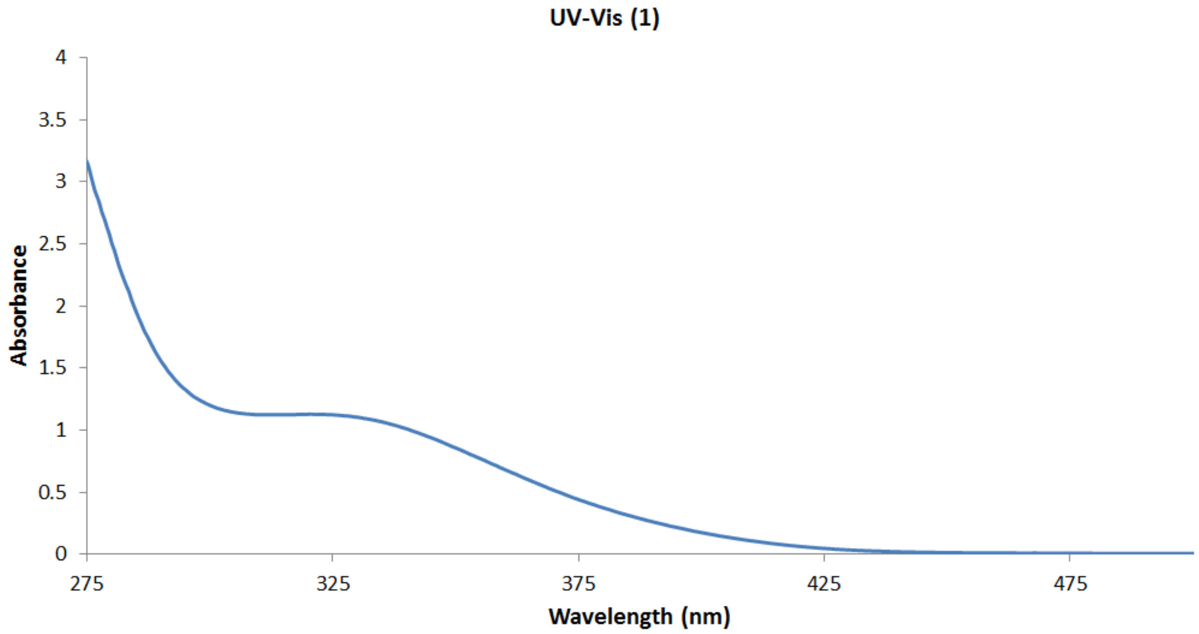
S5. ESI-MS of the molecular ion [M^{3-}] - {$[Bu_4N]_2[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_2]$}$^{3-}$



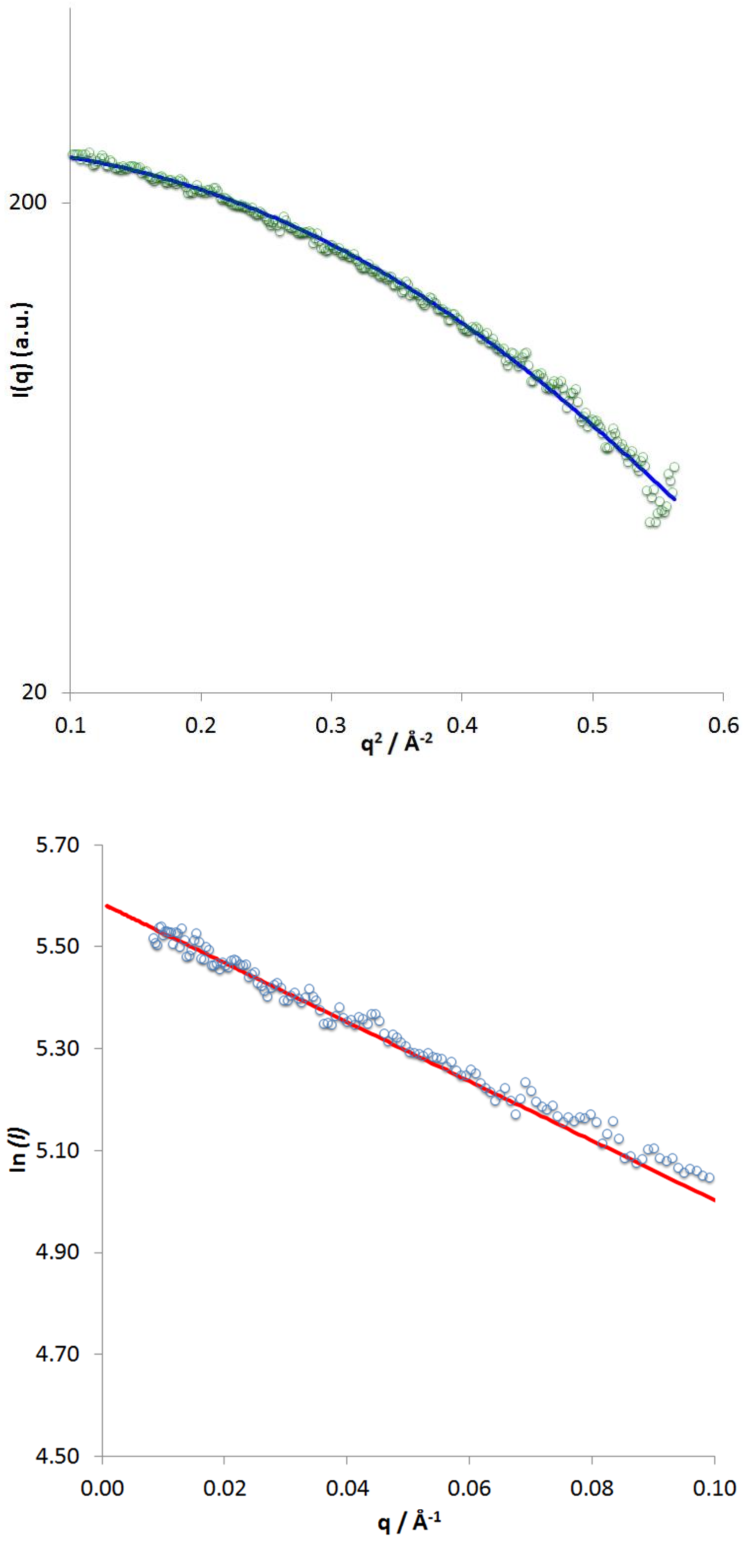
S6. ESI-MS of the molecular ion [M^{2-}] - {$[Bu_4N]_2[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_3]$}$^{2-}$



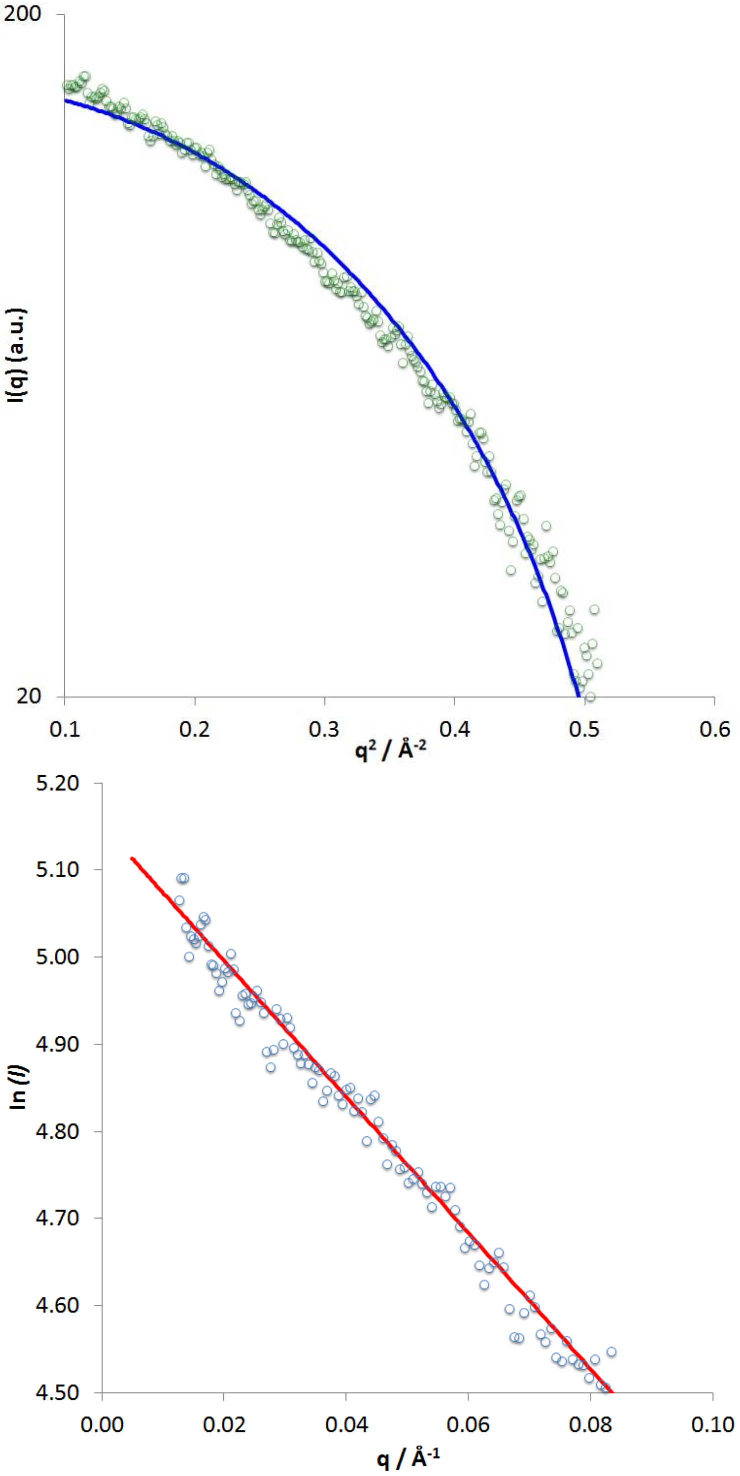
S7. ESI-MS of the molecular ion [M^{2-}] - $\{[Bu_4N]_3[Mo_6O_{18}NC(OCH_2)_3MnMo_6O_{18}(OCH_2)_3CNH_2]\}^{2-}$



S8. UV-Vis spectroscopy of a freshly prepared sample of **(1)** in acetone.



S9. SAXS data for a 0.5 mM acetonitrile solution of $(TBA)_3[MnMo_6O_{18}(NH_2C(CH_2O)_3)_2]$. Top is the best fit over the full data range using a spherical model with R = 5.16 Å, bottom is a low q fit yielding the radius of gyration R_g = 4.18 Å, which gives R = 5.39 Å assuming a spherical model. Given that the molecule is clearly not spherical, and that this model is therefore only an approximation, the agreement between these is very good, and is consistent with values obtained from single crystal X-ray diffraction studies.



S10. SAXS data for a 0.5 mM acetonitrile solution of $(TBA)_2[Mo_6O_{19}]$. A fit over the full data range using a spherical model does not yield a good fit (top - fit with R = 5 Å shown as example). Bottom is a low q fit yielding the radius of gyration R_g = 4.84 Å, which gives R = 6.25 Å assuming a spherical model. This is larger than the size calculated from OLEX2 (Sphere R = 4.75 Å). The fact that a single spherical model cannot fit the data, and the “effective” radius is larger than expected, suggests it is possible that there is conversion of a small proportion to octamolybdate.

REFERENCES

1. Klemperer, W. G. (1990) Tetrabutylammonium Isopolyoxometalates, in Inorganic Syntheses, Volume 27 (ed A. P. Ginsberg), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470132586.ch15
2. Sheldrick, G. M., Acta. Cryst. Sec. A., (2015), **A71**, 3-8.
3. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A . K. and Puschmann, H., J. Appl. Cryst. (2009), **42**, 339-341.