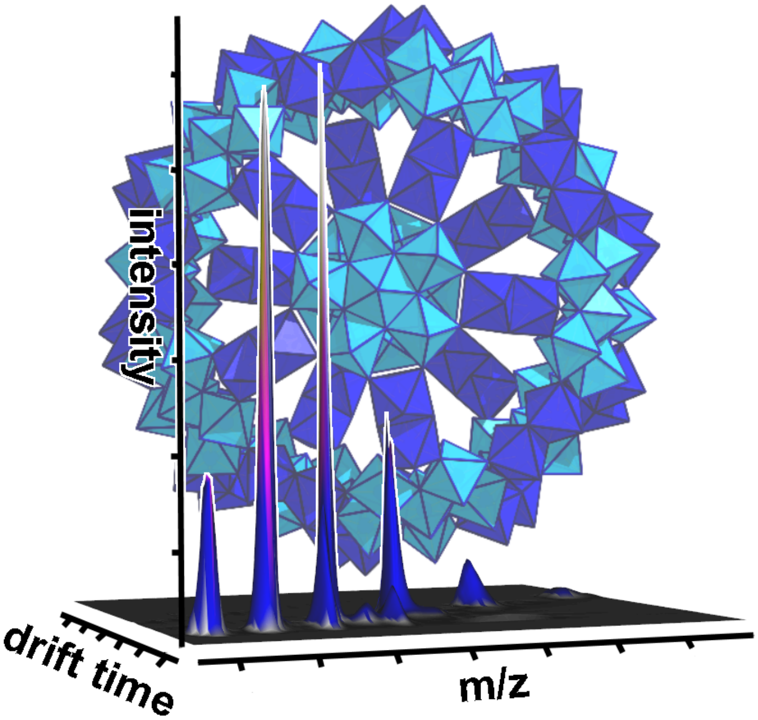
SUPPLEMENTARY INFORMATION

Table of Contents

Ion-mobility mass spectrometry of polyoxometalate Keplerate clusters and their supramolecular assemblies



Philip J. Robbins, Andrew J. Surman, Johannes Thiel, Deliang Long, Leroy Cronin*
Email: Lee.Cronin@glasgow.ac.uk ; website: http://www.croninlab.com

WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK
*To whom correspondence should be addressed.

1. General Materials and Methods

1.1 Analyte preparation

Compounds **1**[1], **2**[2] and **3**[3] were synthesized according to literature procedures. The precursor of compound **4** was synthesized according to literature procedure[4] and compound **4** was precipitated from aqueous solution with tetra(*n*-butyl)ammonium chloride.

1.2 Mass Spectrometry

Sample Preparation

Negative mode high-resolution and ion-mobility mass-spectrometry measurements were performed on a Synapt™ G2 HDMS™ from Waters. For compounds **1**, **2** and **3**, aqueous solutions with a concentration of 10^{-3} M were diluted with acetonitrile by a factor of one hundred. Compound **4** was directly dissolved in acetonitrile at a concentration of 10^{-5} M. The analyte solutions were filtered through a syringe filter (0.2 µm) before injected into the spectrometer via a syringe pump at a flow rate of 5 µL·min^{-1}. Ion-voltages were adjusted for optimum ionization in HRES-mode and kept constant for IMS-MS measurements.

Ionization settings

Compound	Capillary voltage / [V]	Cone Voltage / [kV]	Sampling Cone / [V]
1	2.50	30	2.5
2	2.75	40	4
3	2.50	30	2.5
4	2.7	20	4.3

TWIMS Settings

For comparability of the IMS-MS measurements, all spectra* were recorded under the same conditions: (**nb. ATD reported in Section 5, Fig S10, recorded with IMS Wave Height = 36.5 V*)

Trap Gas Flow (mL/min)	4.00
Helium Cell Gas Flow (mL/min)	180.00
IMS Gas Flow (mL/min)	90.00
IMS Wave Velocity (m/s)	750
IMS Wave Height (V)	40.0

CCSs were estimated following calibration with Equine Cytochrome C, and T10 olgiothymidine (both obtained from Sigma Aldrich; used as solutions in 1:1 acetonitrile/water, pH adjusted with conc. NH_4OH) to determine the instrument-dependent parameters A and B from published CCSs data[5] as previously described in the literature.[6] To obtain IMS spectra the instrument was operated in 'Sensitivity' mode, so charges were assigned with reference to the high resolution MS previously obtained, and, in the case of 'clusters of clusters', by inference from 'monomer' assignment and unchanged *m/z* on aggregation.

2. High-resolution mass spectra and putative assignments

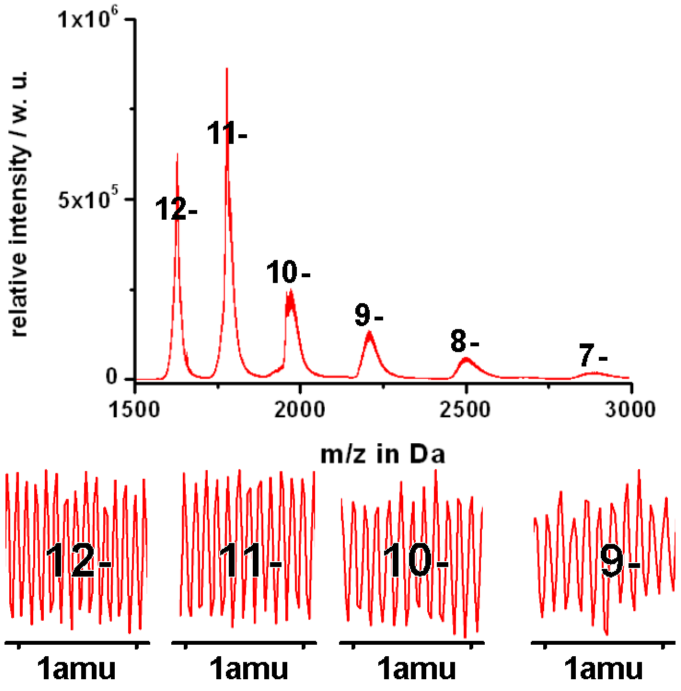


Figure S1. HRES-MS of compound **1**.

m/z	Charge	Putative Ion Composition
1627.2	12-	$(NH_4)_{12}[Mo_{132}O_{372}(CH_3COO)_{12}]$
1777.5	11-	$(NH_4)_{13}[Mo_{132}O_{372}(CH_3COO)_{12}]$
1958.4	10-	$(NH_4)_{14}[Mo_{132}O_{372}(CH_3COO)_{12}]$
2207.8	9-	$(NH_4)_{18}[Mo_{132}O_{372}(CH_3COO)_{15}(CH_3CN)]$
2501.9	8-	$(NH_4)_{21}[Mo_{132}O_{372}(CH_3COO)_{17}]$
2888.6	7-	$(NH_4)_{24}[Mo_{132}O_{372}(CH_3COO)_{19}(CH_3CN)]$

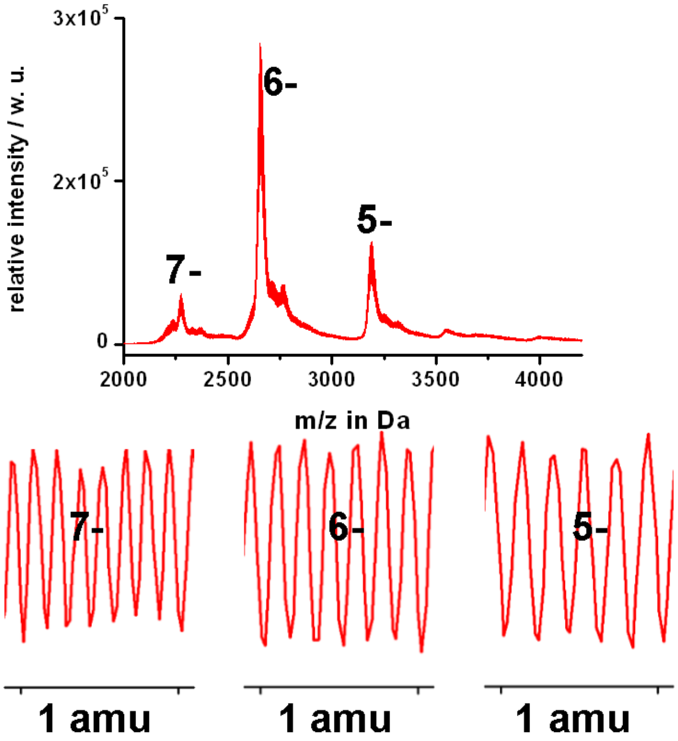


Figure S2. HRES-MS of compound **2**.

m/z	Charge	Putative Ion Composition
2274.1	7-	$SiMo_{12}O_{40}Mo_{72}Fe_{30}O_{252}(CH_3COO)_{16}(CH_3CN)_{13}$
2655.8	6-	$NaSiMo_{12}O_{40}Mo_{72}Fe_{30}O_{252}(CH_3COO)_{16}(CH_3CN)_{13}$
3191.3	5-	$Na_2SiMo_{12}O_{40}Mo_{72}Fe_{30}O_{252}(CH_3COO)_{16}(CH_3CN)_{13}$

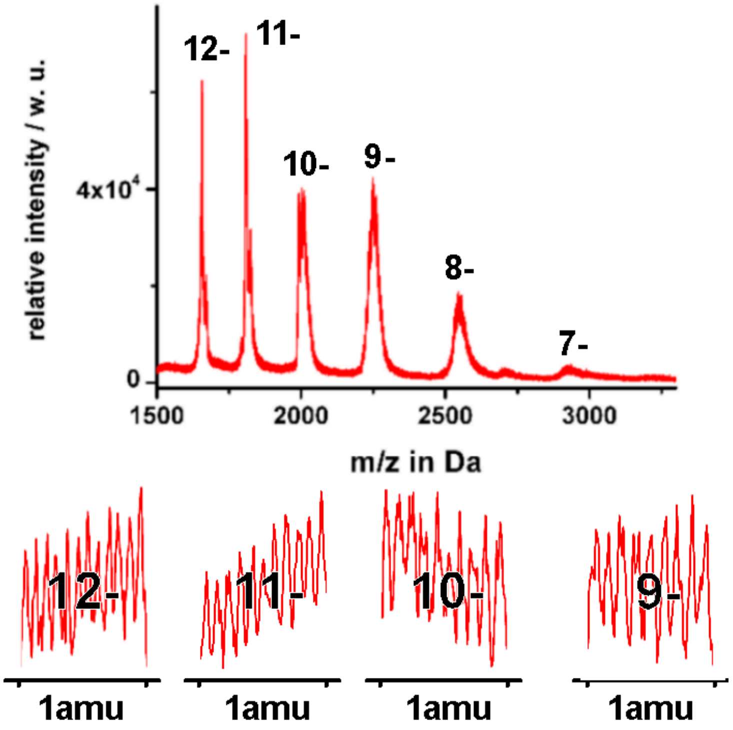


Figure S3. HRES-MS of compound **3**.

m/z	Charge	Putative Ion Composition
1656.4	12-	$(NH_4)_{12}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH_3CN)$
1809.0	11-	$(NH_4)_{13}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH3CN)$
1992.0	10-	$(NH_4)_{14}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH3CN)$
2249.3	9-	$(NH_4)_{15}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH3CN)_8$
2544.9	8-	$(NH_4)_{16}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH3CN)_{10}$
2920.9	7-	$(NH_4)_{17}[Mo_{132}O_{372}(C_3H_5COO)_{12}](CH3CN)_{12}$

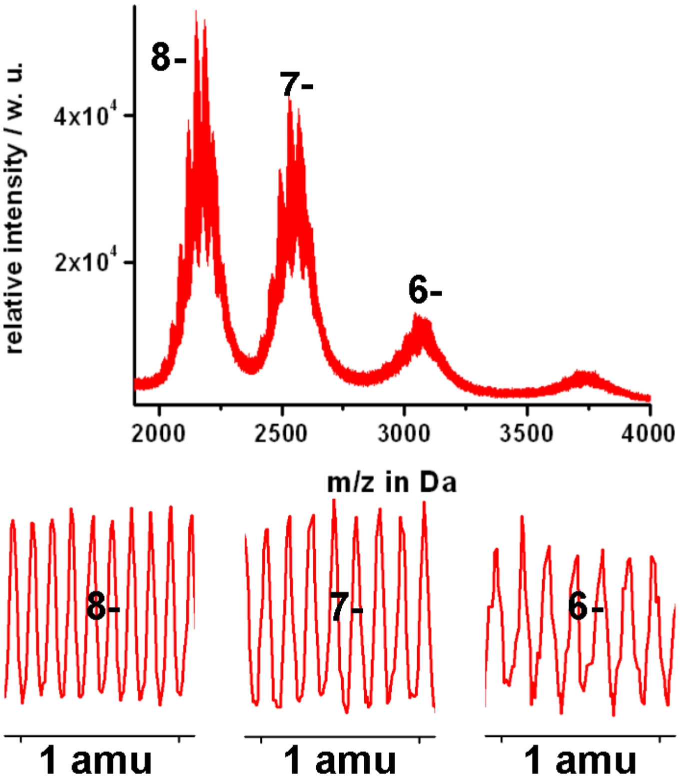


Figure S4. HRES-MS of compound **4**.

m/z	Charge	Putative Ion Composition
2148.6	8-	$(N(C_4H_9)_4)_{15}KMo_{72}V_{30}O_{282}(SO_4)_6$
2183.4	8-	$(N(C_4H_9)_4)_{14}K_4Mo_{72}V_{30}O_{282}(SO_4)_7$
2533.3	7-	$(N(C_4H_9)_4)_{14}K_{11}Mo_{72}V_{30}O_{282}(SO_4)_{10}$
2569.9	7-	$(N(C_4H_9)_4)_{14}K_{13}Mo_{72}V_{30}O_{282}(SO_4)_{11}(CH_3CN)_2$
3045.1	6-	$(N(C_4H_9)_4)_{15}K_{13}Mo_{72}V_{30}O_{282}(SO_4)_{11}(CH_3CN)_3$

nb. In all spectra (**S1**-**S4**) peaks are broad, resulting from a range of ions being formed with a varying mix of cations (native, and others present in solvent/glassware, such as Na^+, H^+), associated solvents (H_2O, acetonitrile) and dissociation of ligands (acetate/butyrate loss). Putative composition assignments are based on plausible ion compositions with calculated *m/z* close to intensity maximum observed in each peak envelope; many other compositions will undoubtedly contribute to these peak envelopes and these compositions are meant as a guide to understanding, not a definitive assignment.

3. Ion-mobility mass spectra

Spectra are plotted with *m/z* on the x-axis and drift time (t_D) on the y-axis. The intensity of the signals is represented by color-coded log scale on a white background, where yellow represents the highest intensity and blue can be disregarded as noise.

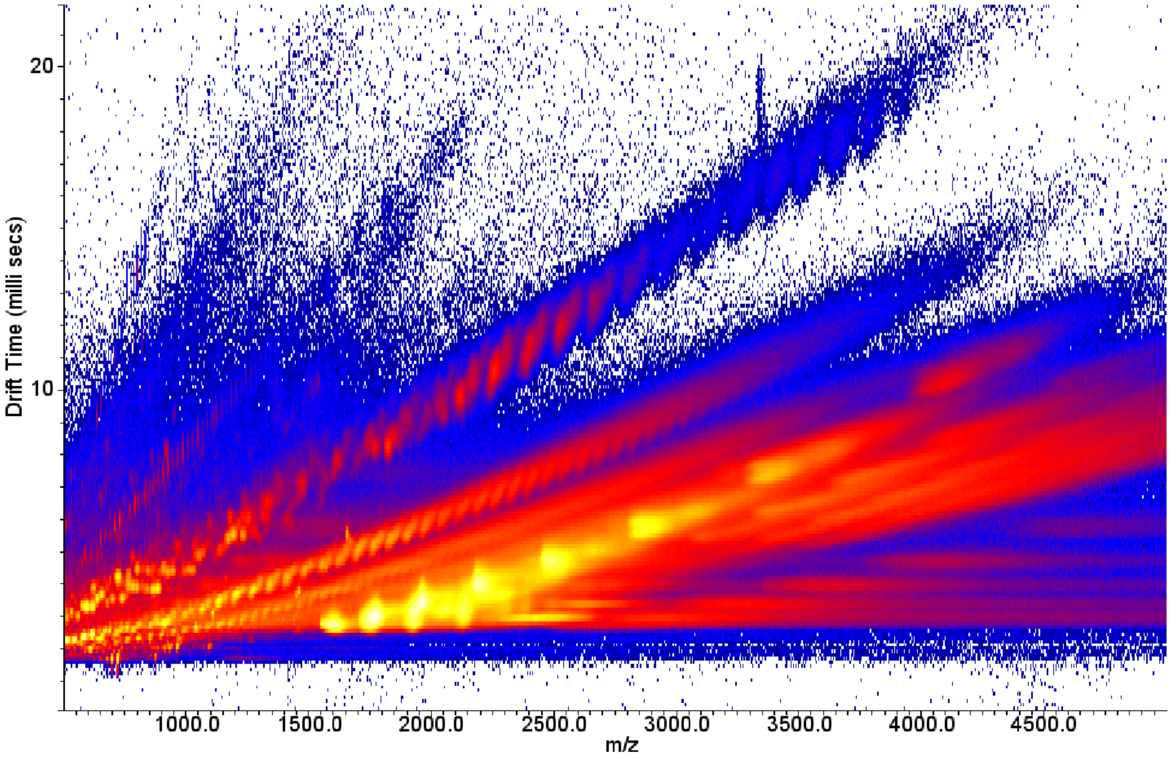


Figure S5. IMS-MS of compound **1**.

Aggregation	*m/z*	Charge	t_D (ms)	Estimated CCS (Å^2)
x 1	2864	7	5.73	1051
x 1	2486	8	4.63	1045
x 1	2189	9	3.86	1045
x 1	1959	10	3.31	1050
x 1	1771	11	2.87	1053
x 1	1602	12	2.6	1077

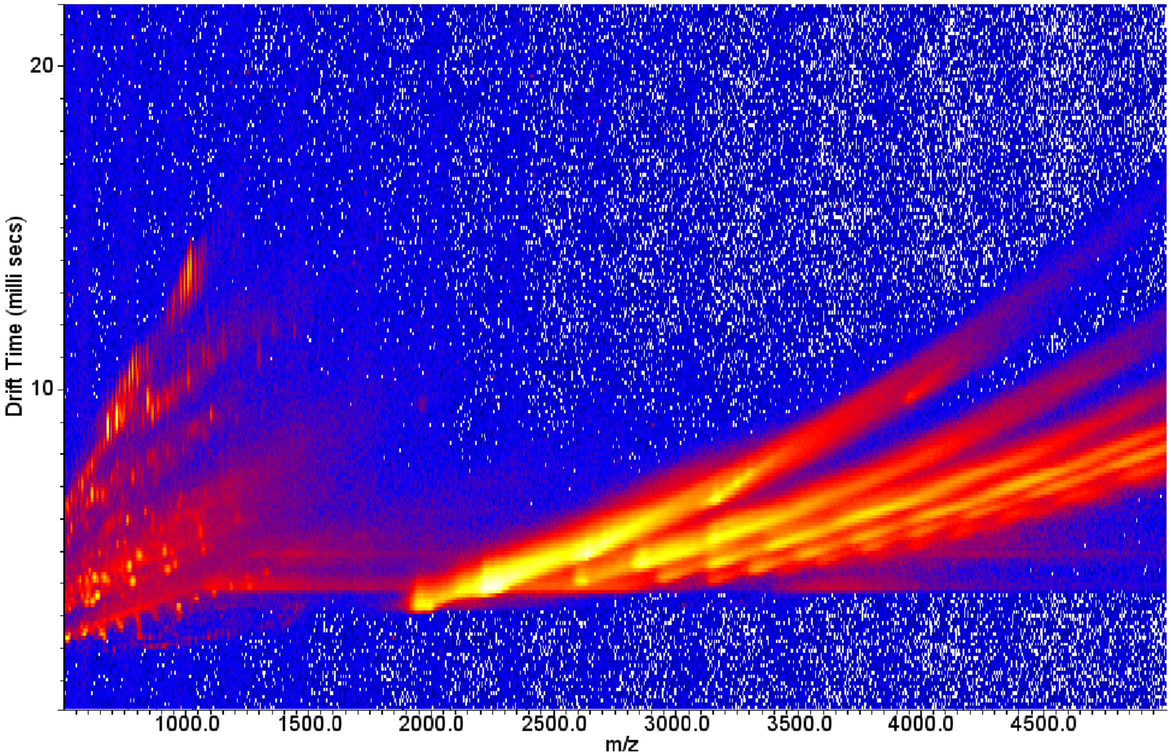


Figure S6. IMS-MS of compound **2**.

Aggregation	*m/z*	Charge	t_D (ms)	Estimated CCS (Å^2)
x 1	3157	5	6.59	822
x 1	2633	6	4.83	806
x 1	2250	7	3.83	808
x 2	3157	10*	5.31	1428
x 2	2633	12*	3.99	1422
x 3	3157	15*	4.57	1941

*inferred from assignment of aggregation state, ie. as ‘clusters of clusters’

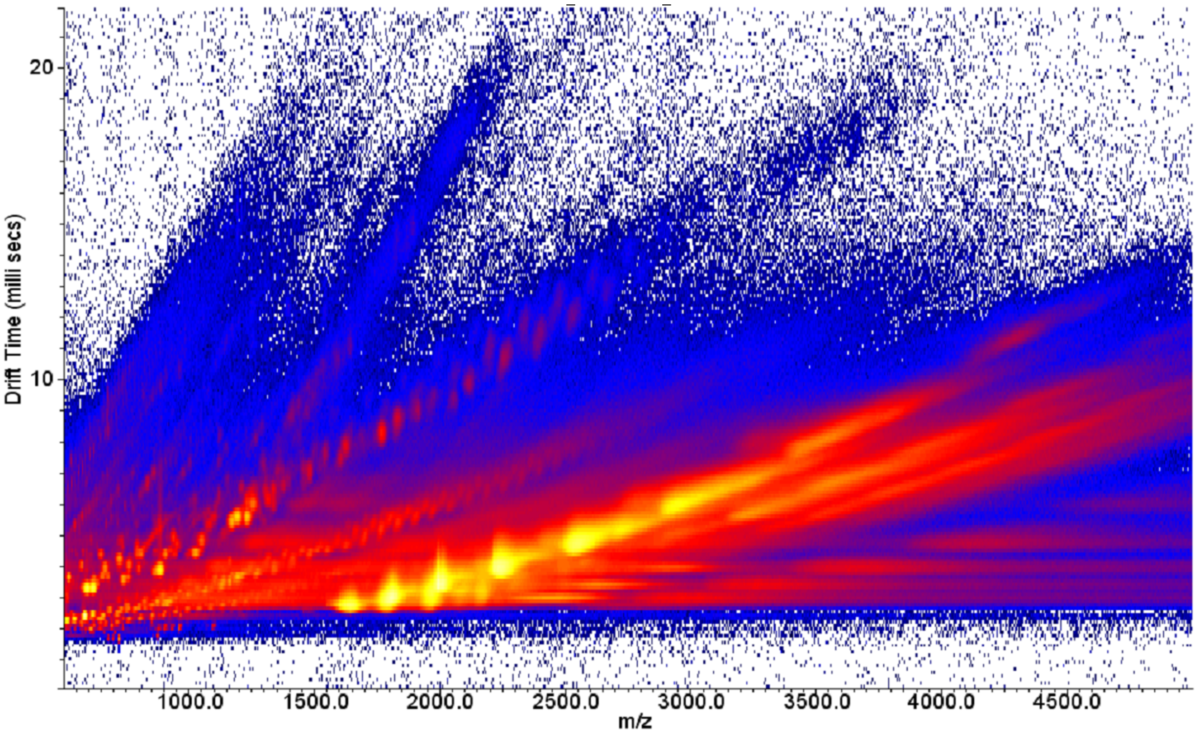


Figure S7. IMS-MS of compound **3**.

Aggregation	*m/z*	Charge	t_D (ms)	Estimated CCS (Å^2)
x 1	1656	7	5.84	1060
x 1	1809	8	4.64	1042
x 1	1992	9	3.86	1038
x 1	2249	10	3.32	1045
x 1	2545	11	2.90	1052
x 1	2921	12	2.64	1080

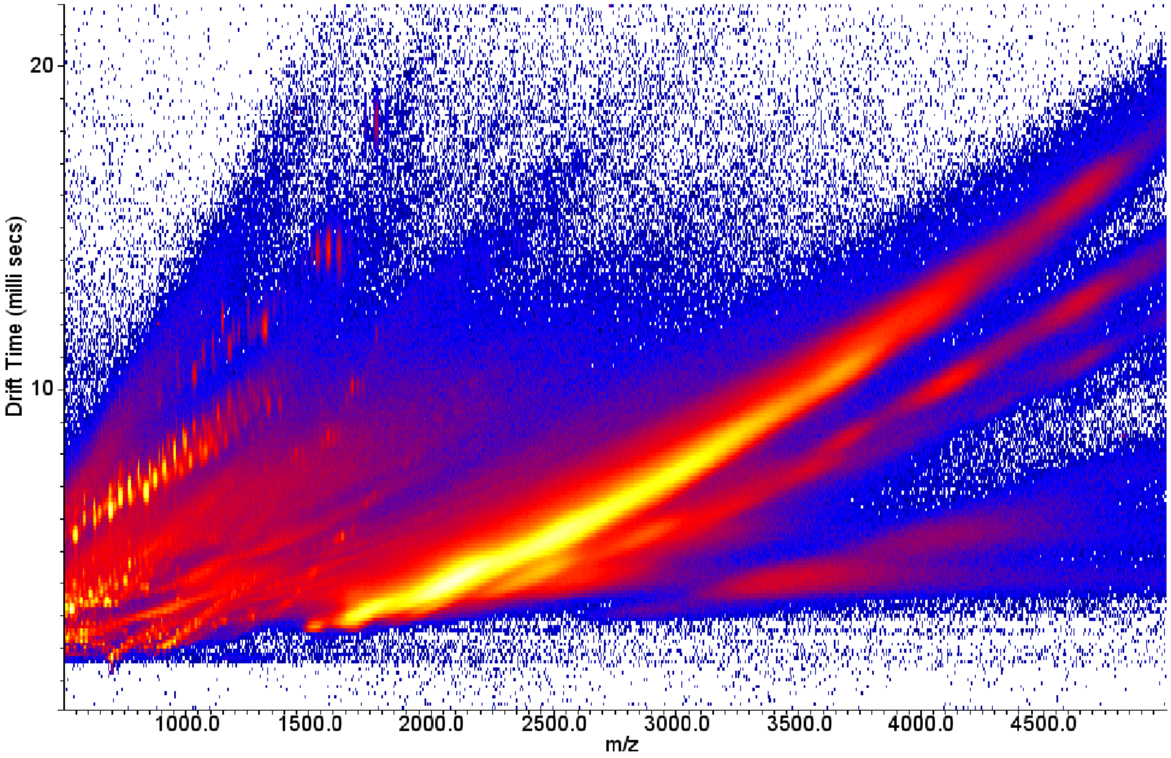


Figure S8. IMS-MS of compound **4**.

Aggregation	*m/z*	Charge	t_D (ms)	Estimated CCS (Å^2)
x 1	3045	6	11.69	1436
x 1	2569	7	8.6	1372
x 1	2533	7	8.27	1337
x 1	2184	8	6.39	1292
x 1	2150	8	6.17	1263

4. Fragmentation of clusters in the TWIMS drift tube

To confirm the robustness of POM clusters (cf. more delicate biomolecules) under TWIMS conditions, an MSMS experiment was performed to observe the degree of fragmentation of mass-selected ions assigned to intact clusters following transmission through the TWIMS drift tube. A broad mass-filtered selection of the ions assigned to the intact cluster of compound **2** was allowed to pass through the TWIMS cell configured with the settings used to obtain the IMS-MS spectrum reported above, and the spectrum of all the transmitted ions is shown in Figure S9. Negligible fragmentation consistent with the continued integrity of an intact cluster was observed, with a few slightly lower mass ions probably corresponding to the loss of solvent molecules.

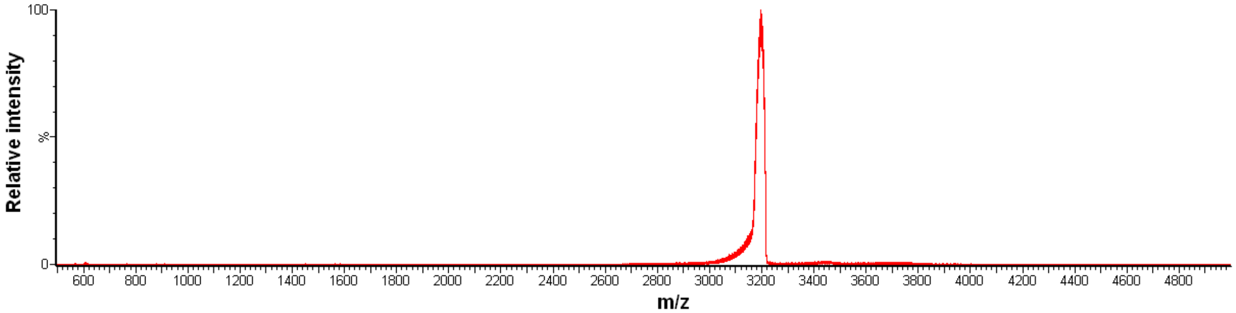


Figure S9. MS of all ions resulting from **2** transmitted through TWIMS drift cell following quadrupole mass selection (m/z = 3180; LM Resolution = 3).

5. Fragmentation of ‘clusters of clusters’ to yield intact clusters

To confirm that large ions observed in IMS-MS spectra do indeed correspond to higher order ‘clusters of clusters’ assemblies, rather than some other structure, collision-induced dissociation (CID) was used to observe the fragments formed on their disintegration (using energies not previously observed to cause fragmentation of POMs). Mass-selected ions assigned to intact clusters (**2**; m/z = 3180; z = -5) were passed through an ion trap with CID turned on at two different collision energies (0V, and 17.5V) prior to entering the TWIMS drift tube, and the arrival time distributions (ATDs; Figure S10(a)) and MS spectra (Figure S10(b)) of transmitted ion populations were acquired. Under these conditions the intact clusters (t_D = 7.9), and putative dimers (t_D = 6.3) were observed in both cases. Where collision energy was raised, the intensity of the ATD peak corresponding to the dimer was halved, while no significant population of fragment ions was observed, strongly suggesting dimer-to-monomer dissociation rather than the fragmentation of some other species.

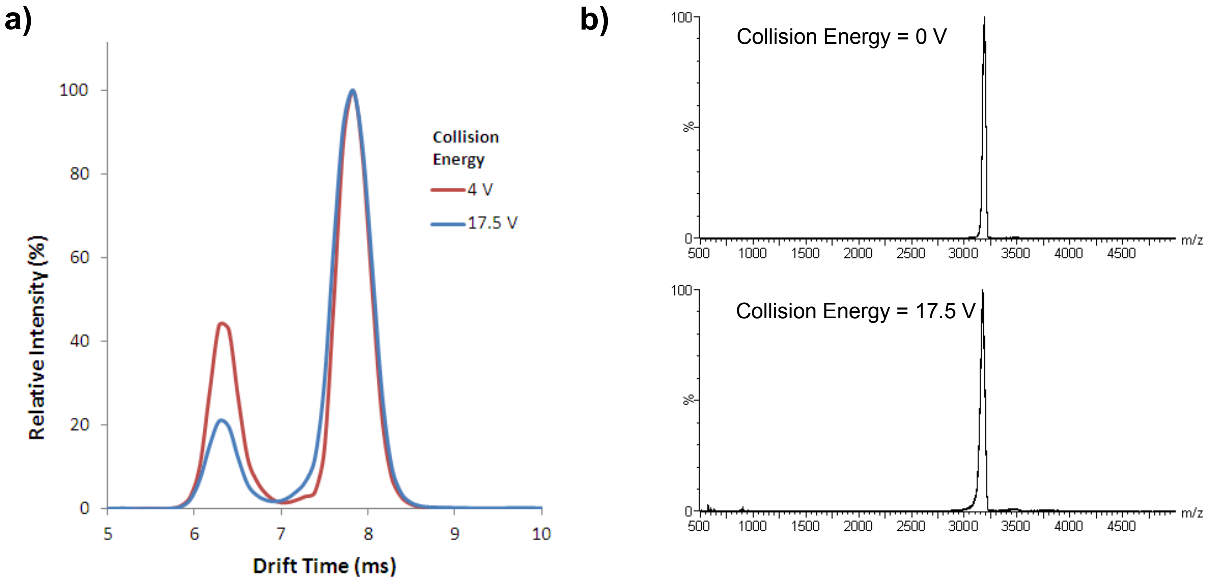


Figure S10. (a) ATD of ions leaving CID cell at high and low energy; intensity normalized to highest peak. **(b)** MS resulting from all ions transmitted through TWIMS drift cell in (a).

References

(1) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann and F. Peters, *Angew. Chem. Int. Ed.,* 1998, **37**, 3359.

(2) A. M. Todea, J. Szakács, S. Konar, H. Bögge, D. C. Crans, T. Glaser, H. Rousselière, R. Thouvenot, P. Gouzerh and A. Müller, *Chem.-Eur. J.*, 2011, **17**, 6635.

(3) C. Schäffer, H. Bögge, A. Merca, I. A. Weinstock, D. Rehder, E. T. K. Haupt and A. Müller, *Angew. Chem. Int. Ed.,* 2009, **48**, 8051.

(4) B. Botar, P. Kögerler and C. L. Hill, *Chem. Commun.,* 2005, 3138.

(5) Clemmer Group Cross Section Database. http://www.indiana.edu/~clemmer/Research/Cross Section Database/cs_database.php

(6) S. I. Merenbloom, T. G. Flick and E. R. Williams, *J. Am. Soc. Mass. Spectrom.,* 2012, **23**, 553.