

Supplementary Information

Sizing and Discovery of Nanosized Polyoxometalate Clusters by Mass Spectrometry

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1. Calibrant set

Compound **1** (Keggin cluster, $(C_{16}H_{36}N)_3 \cdot [PW_{12}O_{40}]$) and Compound **2** (Dawson cluster – $(C_{16}H_{36}N)_6 \cdot [P_2W_{18}O_{62}]$) were synthesised as tetrabutylammonium (TBA) salts according to standard literature procedures (see manuscript refs 30 and 31), whilst compounds **3** and **4** – the TBA salts of Mn-Anderson clusters ' $(C_{16}H_{36}N)_3 \cdot [MnMo_6O_{24}(C_4H_8N)_2]$ ' and ' $(C_{16}H_{36}N)_3 \cdot [MnMo_6O_{24}(C_{20}H_{38}NO)_2]$ ' respectively – were supplied by our co-workers Drs Mali Rosnes and Carine Yvon respectively.^{1,2} All 4 compounds were associated with tetra(*n*-butyl)ammonium (TBA) cations permitting dissolution directly into analytical grade acetonitrile to a working concentration of 0.1mg/ml. Analyte solutions were passed through a 0.2µm filter before injection into the spectrometer *via* syringe pump at 5µl/min.

2. Linear Field Drift Tube Ion Mobility Mass Spectrometry

Experiments were performed on a home built ion mobility drift tube coupled to a commercial MS platform (QToF, Micromass, Manchester, UK) was described elsewhere.³ A 0.1 mg/mL acetonitrile solution of sample was sprayed from home-made nano-electrospray tips (Sutter Instruments, Novato, CA) with the application of 1-1.5 kV. Ions were directed into a Z-spray ion source (Micromass, Manchester, UK) and trapped in a hexapole guide for 20 ms (1e-3 Torr, 50-300 Vp-p, 500 kHz) prior to injection (typically 35V offset) into the drift cell containing 3.5 Torr Helium held at 300K. Pressure of the drift gas is monitored with a capacitance manometer (MKS Baratron) and temperature is monitored with two thermocouples. In order to accurately measure the mobility of ions in helium buffer gas, arrival times were measured at several electric fields (3-9 Td) and the linear correlation of arrival time vs P/V obtained, where the slope is proportional to the mobility K and the intercept provides the time spent in the QToF prior detection (dead time).^{4,5} Fundamental ion mobility equation⁶ (1) was used to calculate the collision cross sections at effective ion temperature⁷ T_{eff} (2):

$$K \approx \frac{3}{16} \frac{q}{N} \left(\frac{1}{M} + \frac{1}{m} \right)^{1/2} \left(\frac{2\pi}{k_B T_{eff}} \right)^{1/2} \frac{1}{\Omega_D(T_{eff})} \quad (1)$$

$$T_{eff} = T + \frac{M(KE)^2}{3k_B} \quad (2)$$

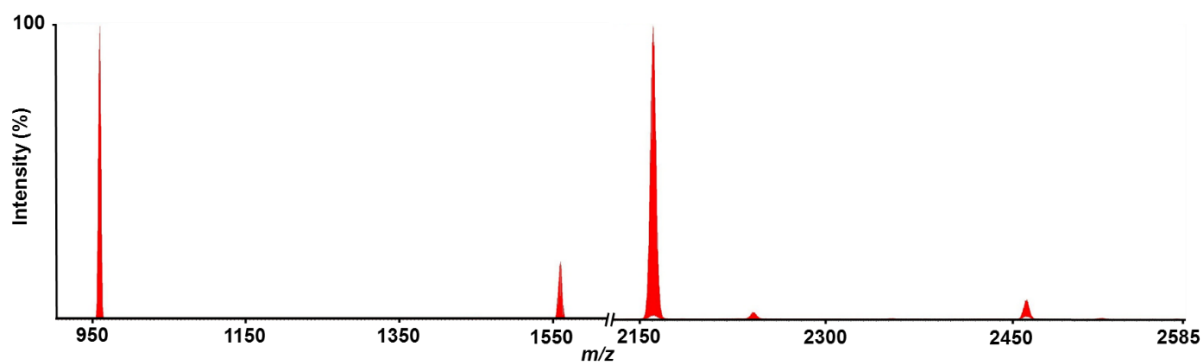
Where: q – charge of the ion, N – gas number density, M – mass of the gas molecule, m – mass of the ion, k_B – Boltzmann Constant, T – temperature of the buffer gas, $\Omega_D(T_{eff})$ – collision cross section at the effective ion temperature (CCS).

3. Calibrant set and TW Ion-Mobility Mass Spectrometry

TW-IM-MS data reported here corresponds to that shown in Fig 3, and is typical of a number of calibrations using the same calibrant set and different TW-IM-MS settings (wave height, wave velocity) depending on IM properties of the chosen analyte. Standard deviations in drift time (t_D) refer to deviation of three repetitions of the same measurement, using the same settings.

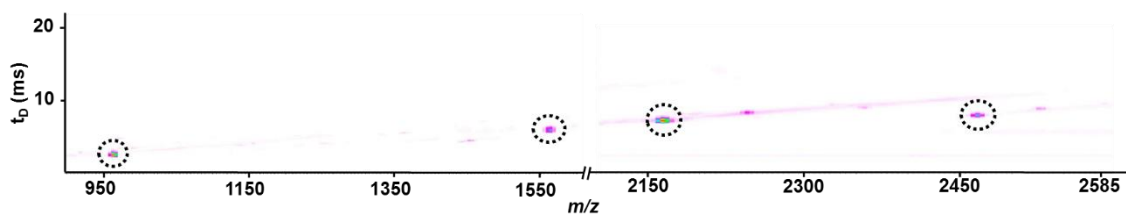
Data were acquired using MassLynx v4.1 and initially processed using DriftScope v2.2. IMS-MS spectra are displayed with a linear intensity scale using the color-coding shown in the accompanying key; no filtering is applied to limit signals (e.g., no filtering of signals <5% in 2D map; that is, few other signals are visible in the raw data with no manipulation). To determine drift times (t_D) of species of interest in the IMS arrival time distribution (ATD), data were extracted from Driftscope/Masslynx, and fit to Gaussian curves using Fityk v0.9.8 to determine a representative retention times peak center. Typical TW-IM-MS settings were: ESI capillary voltage, 2.7 kV; sample cone voltage, 30 V; extraction cone voltage, 4.0 V; source temperature, 80 °C; desolvation temperature, 180 °C; cone gas (N₂) flow, 15 L/h; desolvation gas (N₂) flow, 750 L/h; IMS gas flow, 90 mL/min. The results in this section utilise: IMS wave velocity, 1000 m/s; IMS wave height, 40 V.

3.1 Compound 1 – PW₁₂O₄₀



<i>m/z</i>	<i>assignment</i>	<i>z</i>	<i>m/z(calc)</i>
959	PW ₁₂ O ₄₀	3	958.73
1560	(TBA)PW ₁₂ O ₄₀	2	1559.23
2161	(TBA) ₃ (PW ₁₂ O ₄₀) ₂	3	2160.41
2461	(TBA) ₅ (PW ₁₂ O ₄₀) ₃	4	2460.74

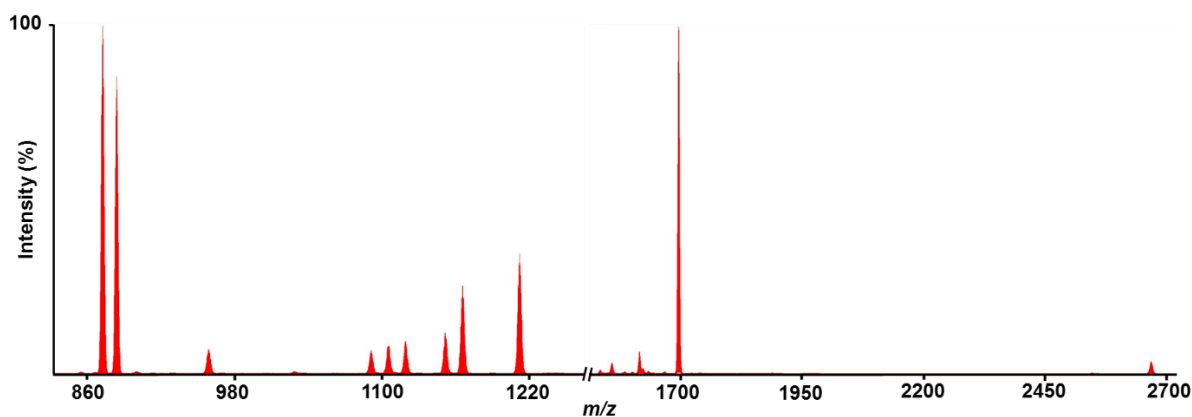
Fig. S1. HRES-ESI-MS of compound 1 – PW₁₂O₄₀ and assignment table



<i>m/z</i>	<i>assignment</i>	<i>t_D (ms)</i>	<i>stndev(t_D)</i>	^{TW} <i>CCS</i> _{N₂→He}	^{DT} <i>CCS</i> _{He}
959	PW ₁₂ O ₄₀	2.426	0	161.04	150
1560	(TBA)PW ₁₂ O ₄₀	5.843	0	212.60	207
2161	(TBA) ₃ (PW ₁₂ O ₄₀) ₂	7.497	0	386.17	368
2461	(TBA) ₅ (PW ₁₂ O ₄₀) ₃	8.269	0.063509	551.72	524

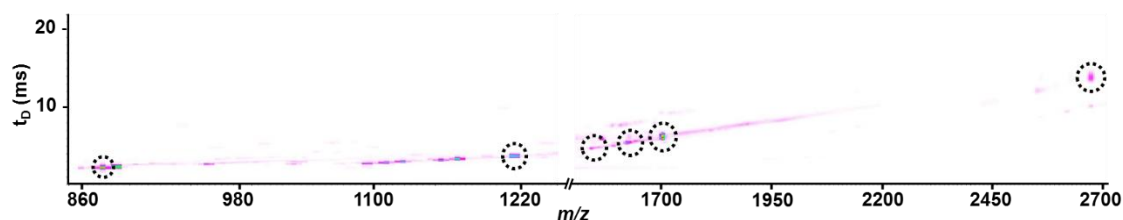
Fig. S2. TW-IM-MS of compound 1 – PW₁₂O₄₀ and assignment table

3.2 Compound 2 – P₂W₁₈O₆₂



<i>m/z</i>	<i>assignment</i>	<i>z</i>	<i>m/z(calc)</i>
872	H ₁ (P ₂ W ₁₈ O ₆₂)	5	872.75
1212	(TBA) ₂ (P ₂ W ₁₈ O ₆₂)	4	1211.83
1536	H ₂ (TBA) ₁ (P ₂ W ₁₈ O ₆₂)	3	1535.68
1616	H ₁ (TBA) ₂ (P ₂ W ₁₈ O ₆₂)	3	1616.11
1697	(TBA) ₃ (P ₂ W ₁₈ O ₆₂)	3	1696.87
2666	(TBA) ₄ (P ₂ W ₁₈ O ₆₂)	2	2666.45

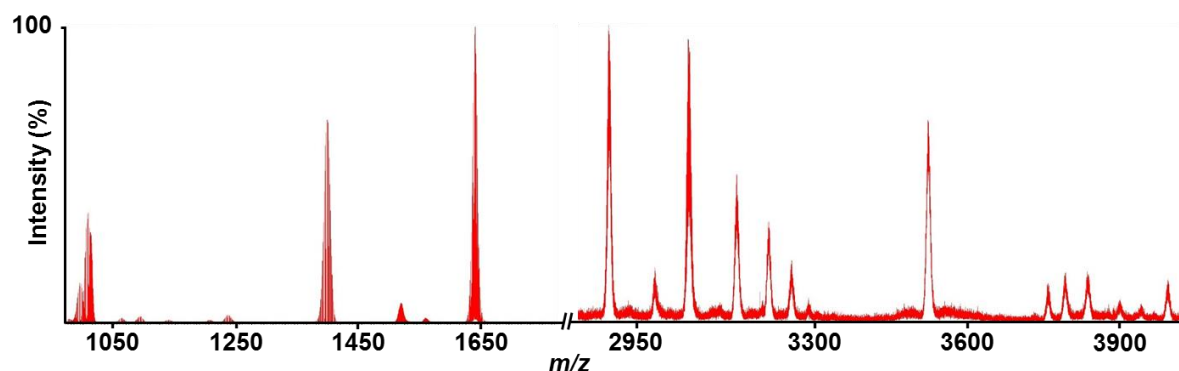
Fig. S3. HRES-ESI-MS of compound 2 – P₂W₁₈O₆₂ and assignment table



<i>m/z</i>	<i>assignment</i>	<i>t_D (ms)</i>	<i>stndev(t_D)</i>	^{TW} <i>CCS</i> _{N₂→He}	^{DT} <i>CCS</i> _{He}
872	H ₁ (P ₂ W ₁₈ O ₆₂)	2.095	0	235.57	209
1212	(TBA) ₂ (P ₂ W ₁₈ O ₆₂)	3.528	0.092376	283.80	314
1536	H ₂ (TBA) ₁ (P ₂ W ₁₈ O ₆₂)	4.631	0.063509	263.41	245
1616	H ₁ (TBA) ₂ (P ₂ W ₁₈ O ₆₂)	5.402	0	297.19	310
1697	(TBA) ₃ (P ₂ W ₁₈ O ₆₂)	6.064	0	325.31	357
2666	(TBA) ₄ (P ₂ W ₁₈ O ₆₂)	13.892	2.18E-15	414.38	412

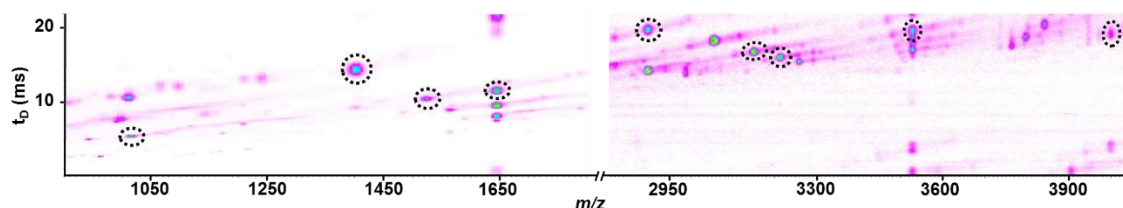
Fig. S4. TW-IM-MS of compound 2 – P₂W₁₈O₆₂ and assignment table

3.3 Compound **3** – tris-substituted MnMo₆O₂₄



<i>m/z</i>	<i>assignment</i>	<i>z</i>	<i>m/z(calc)</i>
1012	(TBA) ₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	3	1012.21
1398	H ₁ (TBA) ₁ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂)	1	1397.67
1519	H ₁ (TBA) ₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	2	1518.81
1640	(TBA) ₄ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	2	1639.95
2894	(TBA) ₁₂ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₅	3	2894.45
3145	(TBA) ₂₂ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₉	5	3145.34
3208	(TBA) ₂₇ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₁₁	6	3208.15
3522	(TBA) ₅ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	1	3522.19
3992	(TBA) ₂₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₉	4	3992.50

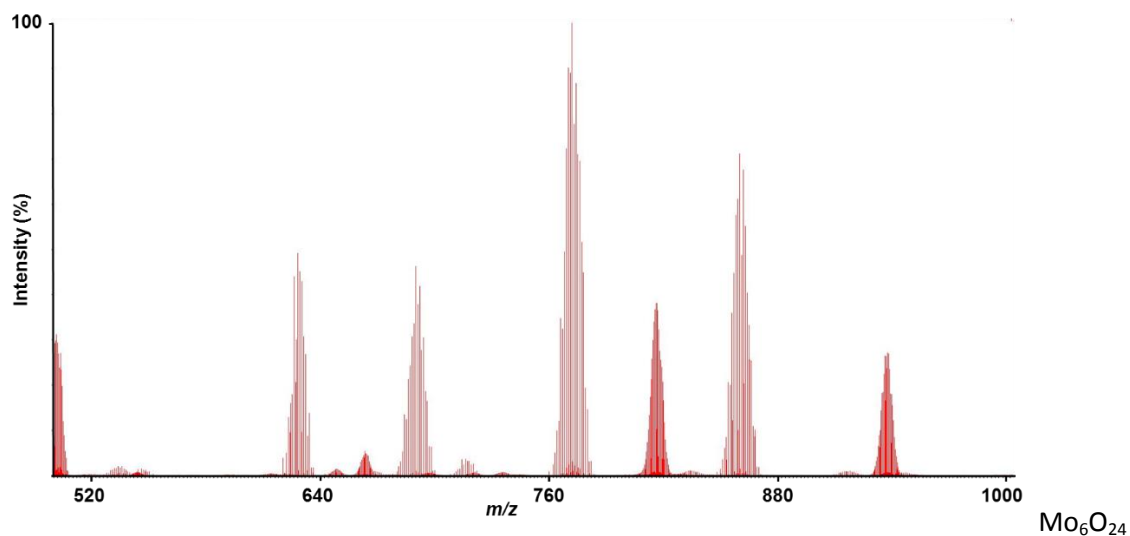
Fig. S5. HRES-ESI-MS of compound **3** – tris-substituted MnMo₆O₂₄ and assignment table



<i>m/z</i>	<i>assignment</i>	<i>t_D</i> (ms)	<i>stndev(t_D)</i>	^{TW} <i>CCS</i> _{N₂→He}	^{DT} <i>CCS</i> _{He}
1012	(TBA) ₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	5.292	0	293.44	326
1398	H ₁ (TBA) ₁ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂)	14.333	0.063509	214.10	213
1519	H ₁ (TBA) ₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	10.474	0	333.38	353
1640	(TBA) ₄ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	11.577	0	360.32	333
2894	(TBA) ₁₂ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₅	19.732	0.271932	816.52	740
3145	(TBA) ₂₂ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₉	16.759	0	1196.98	1181
3208	(TBA) ₂₇ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₁₁	15.987	0	1384.16	1371
3522	(TBA) ₅ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₂	19.699	0	272.37	274
3992	(TBA) ₂₃ (MnMo ₆ O ₂₄ (C ₄ H ₈ N) ₂) ₉	19.141	0.11	1061.81	1125

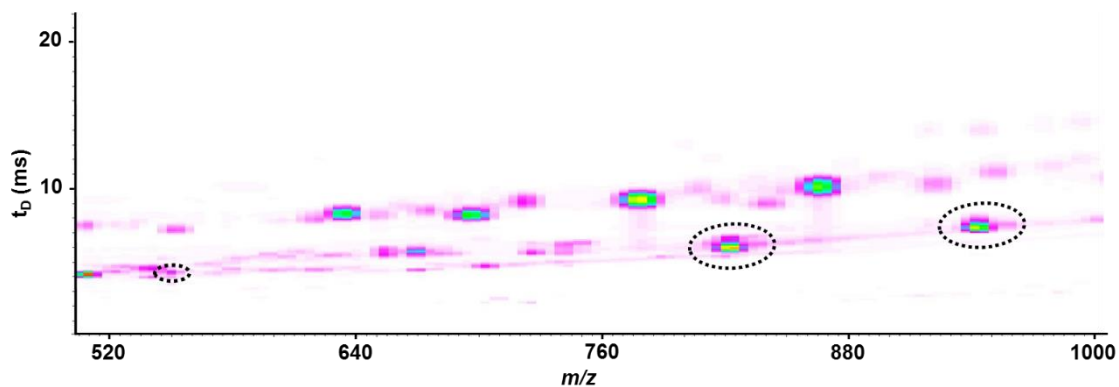
Fig. S6. TW-IM-MS of compound **3** – tris-substituted $\text{MnMo}_6\text{O}_{24}$ and assignment table

3.4 Compound **4** – aliphatic-substituted Mn



<i>m/z</i>	<i>assignment</i>	<i>z</i>	<i>m/z(calc)</i>
544	$(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})_2)$	3	543.95
817	$(\text{TBA})(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})(\text{C}_4\text{H}_8\text{N}))$	2	817.95
937	$(\text{TBA})(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})_2)$	2	937.06

Fig. S7. HRES-ESI-MS of compound **4** – aliphatic-substituted $\text{MnMo}_6\text{O}_{24}$ and assignment table



<i>m/z</i>	<i>assignment</i>	<i>t_D (ms)</i>	<i>stndev(t_D)</i>	<i>^{TW}CCS_{N₂→He}</i>	<i>^{DT}CCS_{He}</i>
544	$(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})_2)$	4.19	0	245.82	253
817	$(\text{TBA})(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})(\text{C}_4\text{H}_8\text{N}))$	5.843	0.063509	212.37	242
937	$(\text{TBA})(\text{MnMo}_6\text{O}_{24}(\text{C}_{20}\text{H}_{38}\text{NO})_2)$	7.277	0	251.78	247

Fig. S8. TW-IM-MS of compound **4** – aliphatic-substituted $\text{MnMo}_6\text{O}_{24}$ and assignment table

4. Ion Mobility-Mass Spectrometry of 3 giant Tungstate POMs (incl. charge assignments)

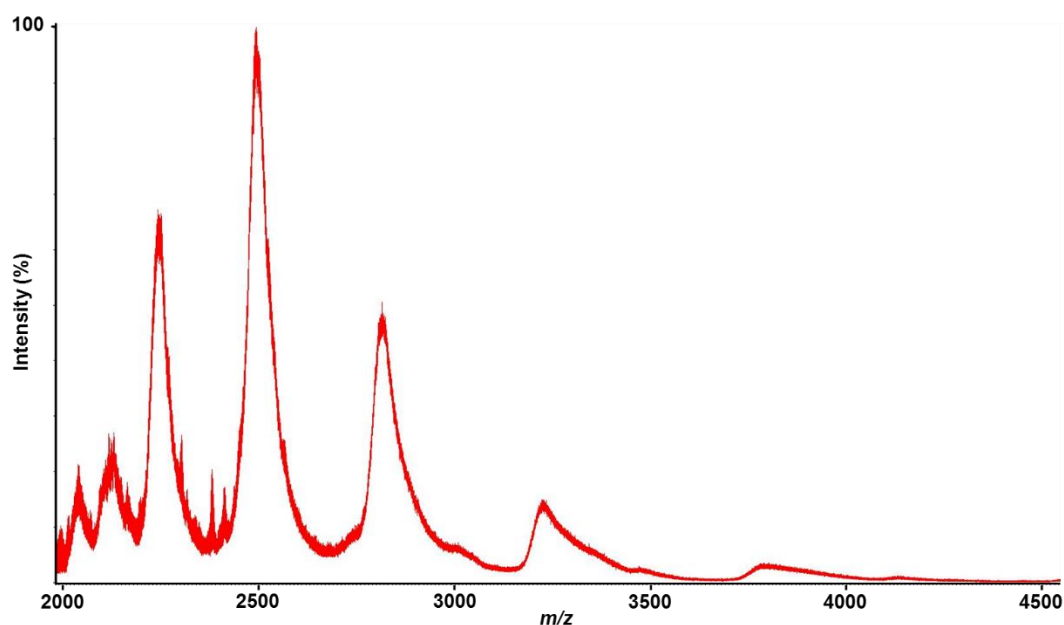
Compounds A-C were synthesised as reported in ref 8 and the anion compositions are as follows:

A - POW 'trimer' $\{\text{Se}_8\text{W}_{86}\text{O}_{299}\}$, full formula is $[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]^{40-}$

B – POW 'tetramer' $\{\text{Se}_8\text{W}_{116}\text{O}_{408}\}$, full formula is $[\text{H}_{26}\text{Mn}_2\text{W}_2\text{O}_4(\text{H}_2\text{O})_4(\text{Se}_2\text{W}_{29}\text{O}_{102})_4]^{44-}$

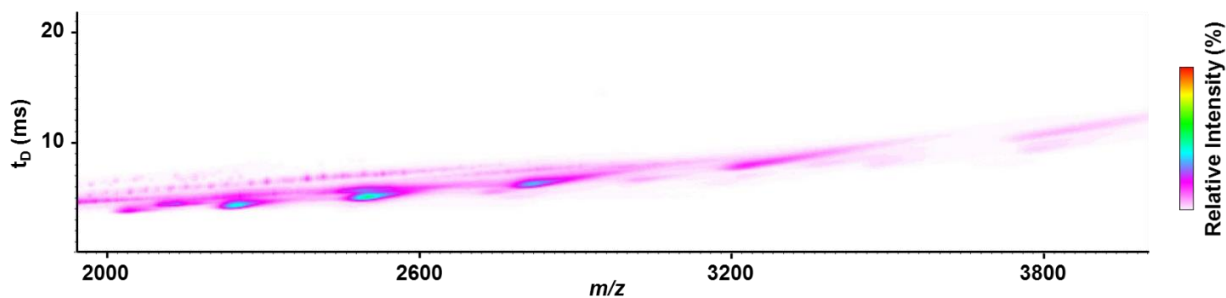
C – $\{\text{Se}_{12}\text{W}_{174}\text{O}_{612}\}$, full formula is $[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]^{99-}$

4.1 Mass Spectrum of compound A - POW 'trimer' $\{\text{Se}_8\text{W}_{86}\text{O}_{299}\}$



<i>m/z</i>	<i>Assignment</i>	<i>z</i>	<i>m/z(calc)</i>
2039	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_5\text{H}_7$	11	2040.39
2243	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_5\text{H}_8$	10	2244.53
2494	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_5\text{H}_9$	9	2494.04
2814	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{19}(\text{C}_2\text{H}_8\text{N})_5\text{H}_8$	8	2815.53
3227	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{22}(\text{C}_2\text{H}_8\text{N})_4\text{H}_7$	7	3227.73
3789	$[\text{H}_4\text{CoWO}(\text{H}_2\text{O})_3(\text{Se}_2\text{W}_{26}\text{O}_{85})(\text{Se}_3\text{W}_{30}\text{O}_{107})_2]\text{K}_{21}(\text{C}_2\text{H}_8\text{N})_8\text{H}_5$	6	3789.56

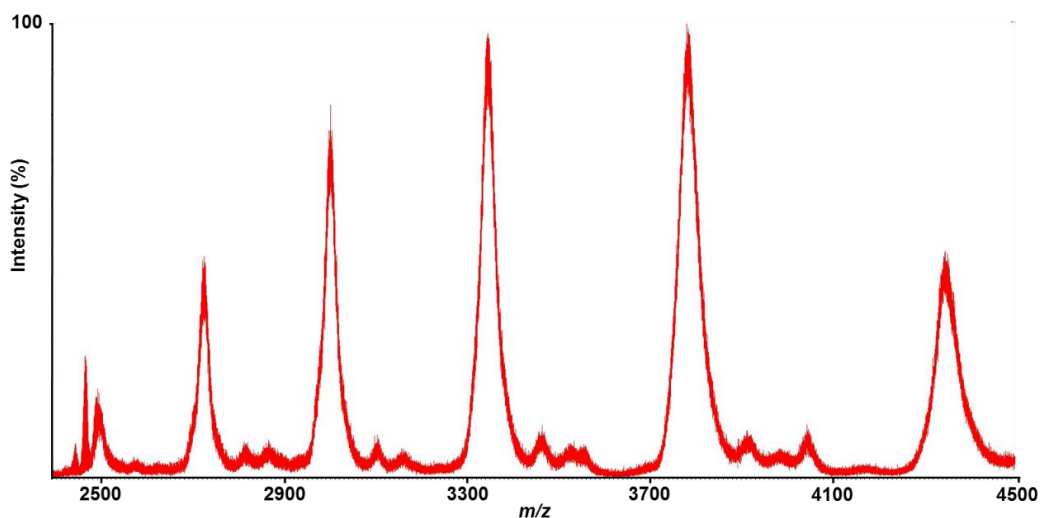
Fig. S9. HRES-ESI-MS of compound A - $\{\text{Se}_8\text{W}_{86}\text{O}_{299}\}$ and assignment table



m/z	assignment	t_D (ms)	$^{TW}CCS_{N_2 \rightarrow He}$
2039	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{17}(C_2H_8N)_5H_7$	3.75	824.65
2243	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{17}(C_2H_8N)_5H_8$	4.19	817.3
2494	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{17}(C_2H_8N)_5H_9$	4.961	838.88
2814	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{19}(C_2H_8N)_5H_8$	6.23	890.21
3227	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{22}(C_2H_8N)_4H_7$	8.049	950.64
3789	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]K_{21}(C_2H_8N)_8H_5$	10.97	1036.61

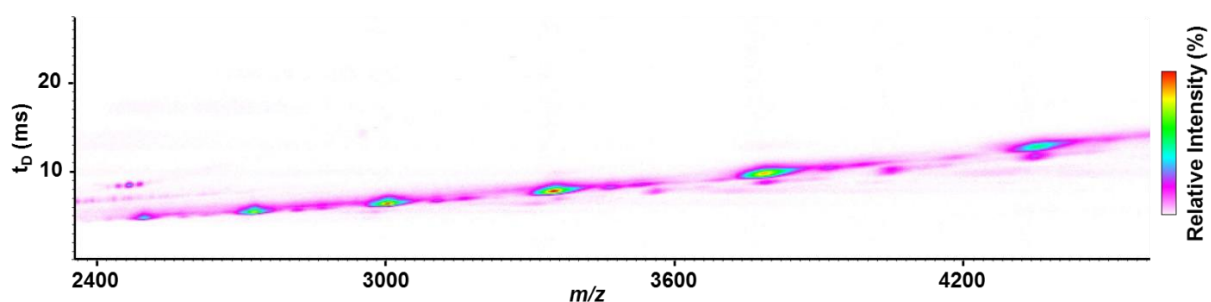
Fig. S10. TW-IM-MS of compound A - $\{Se_8W_{86}O_{299}\}$ and assignment table

4.2 Mass Spectrum of compound B— POW 'tetramer' $\{Se_8W_{116}O_{408}\}$



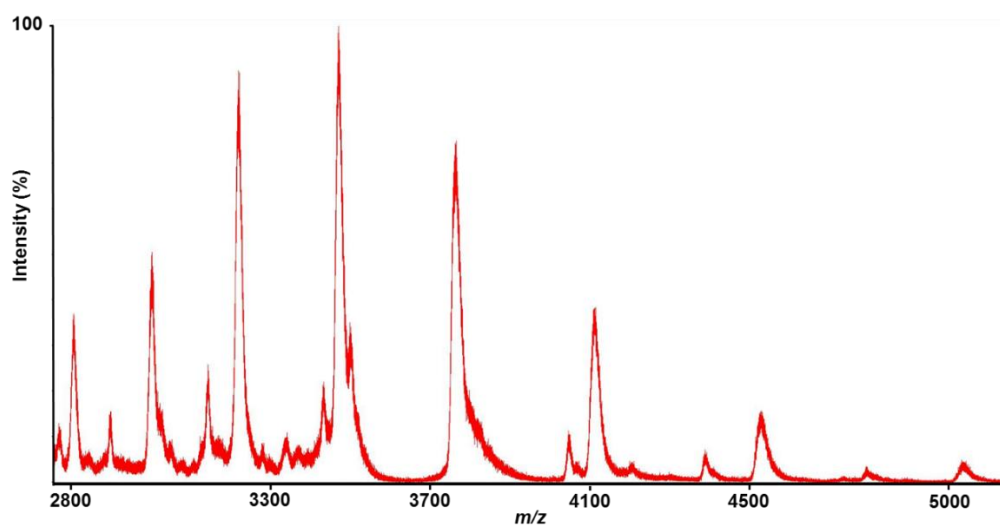
m/z	assignment	z	m/z (calc)
2493	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{13}(C_2H_8N)_6H_{13}$	12	2493.55
2723	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{14}(C_2H_8N)_6H_{13}$	11	2723.78
3000	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{15}(C_2H_8N)_6H_{13}$	10	3000.06
3346	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{11}(C_2H_8N)_{12}H_{12}$	9	3346.68
3781	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{12}(C_2H_8N)_{14}H_{10}$	8	3781.15
4346	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]K_{13}(C_2H_8N)_{17}H_7$	7	4346.19

Fig. S11. HRES-ESI-MS of compound **B** – {Se₈W₁₁₆O₄₀₈} and assignment table



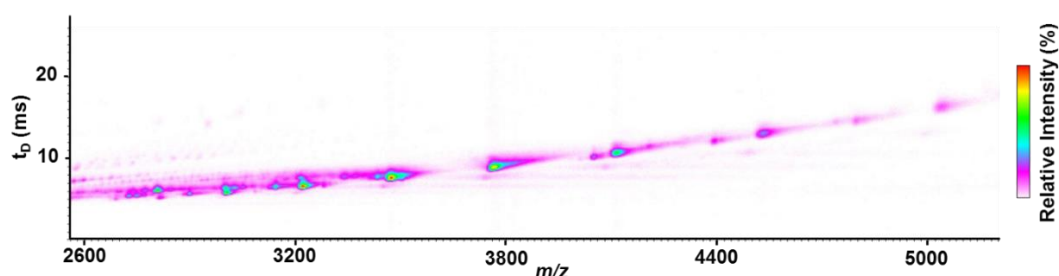
<i>m/z</i>	<i>assignment</i>	<i>t_D</i> (ms)	^{TW} CCS _{N₂→He}
2493	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₃ (C ₂ H ₈ N) ₆ H ₁₃	4.701	1072.36
2723	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₄ (C ₂ H ₈ N) ₆ H ₁₃	5.392	1093.69
3000	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₅ (C ₂ H ₈ N) ₆ H ₁₃	6.36	1130.54
3346	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₁ (C ₂ H ₈ N) ₁₂ H ₁₂	7.604	1169.15
3781	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₂ (C ₂ H ₈ N) ₁₄ H ₁₀	9.678	1253.61
4346	[H ₂₆ Mn ₂ W ₂ O ₄ (H ₂ O) ₄ (Se ₂ W ₂₉ O ₁₀₂) ₄]K ₁₃ (C ₂ H ₈ N) ₁₇ H ₇	12.79	1362.41

Fig. S12. TW-IM-MS of compound **B** – {Se₈W₁₁₆O₄₀₈} and assignment table



<i>m/z</i>	<i>assignment</i>	<i>z</i>	<i>m/z(calc)</i>
2804	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_{20}\text{H}_{46}$	16	2804.32
3001	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{15}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{44}$	15	3001.3
3217	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{18}(\text{C}_2\text{H}_8\text{N})_{23}\text{H}_{44}$	14	3217.44
3469	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{44}$	13	3469.03
3794	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{20}(\text{C}_2\text{H}_8\text{N})_{32}\text{H}_{35}$	12	3794.05
4114	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{20}(\text{C}_2\text{H}_8\text{N})_{26}\text{H}_{42}$	11	4114.48
4529	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{22}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{42}$	10	4529.12
5032	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{22}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{43}$	9	5032.46

Fig. S13. HRES-ESI-MS of compound **C** – $\{\text{Se}_{12}\text{W}_{174}\text{O}_{612}\}$ and assignment table



<i>m/z</i>	<i>assignment</i>	<i>t_D</i> (ms)	^{TW} CCS _{N₂→He}
2804	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_{20}\text{H}_{46}$	5.945	1715.85
3001	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{15}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{44}$	5.668	1550.04
3217	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{18}(\text{C}_2\text{H}_8\text{N})_{23}\text{H}_{44}$	6.498	1608.99
3469	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{17}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{44}$	7.604	1688.36
3794	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{20}(\text{C}_2\text{H}_8\text{N})_{32}\text{H}_{35}$	8.848	1753.39
4114	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{20}(\text{C}_2\text{H}_8\text{N})_{26}\text{H}_{42}$	10.646	1855.94
4529	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{22}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{42}$	13.134	1986.49
5032	$[\text{H}_{18}\text{Cu}_9\text{Cl}_3(\text{H}_2\text{O})_{18}(\text{Se}_2\text{W}_{29}\text{O}_{102})_6]\text{K}_{22}(\text{C}_2\text{H}_8\text{N})_{25}\text{H}_{43}$	16.314	2116.09

Fig. S14. TW-IM-MS of compound **C** – $\{\text{Se}_{12}\text{W}_{174}\text{O}_{612}\}$ and assignment table

4.4 Inferred charge assignments of the 3 POWs

Since it sufficient resolution to directly determine the charge state for each ion observed to form from the POW series (compounds **A-C**) was not always available, the following method was employed as a check:

- The first peak in a structures charge series was identified.
- For a series of possible charges, an *m/z* value was calculated based on the core anion (as observed in XRD) and Na^+ cations.

- For each of these values, the discrepancy (“sum error”) between the observed m/z and calculated value was determined.
- The correct charge was assigned as that for which the smallest discrepancy was observed – in each case this was clear.
(n.b. A small discrepancy is observed even in correct assignments, since this model presumes homogenous counterions and no associated solvent molecules; assignments were checked in more than one case where the isotopic pattern was resolved for at least one peak in a series)

4.4.1 Compound A charge assignment

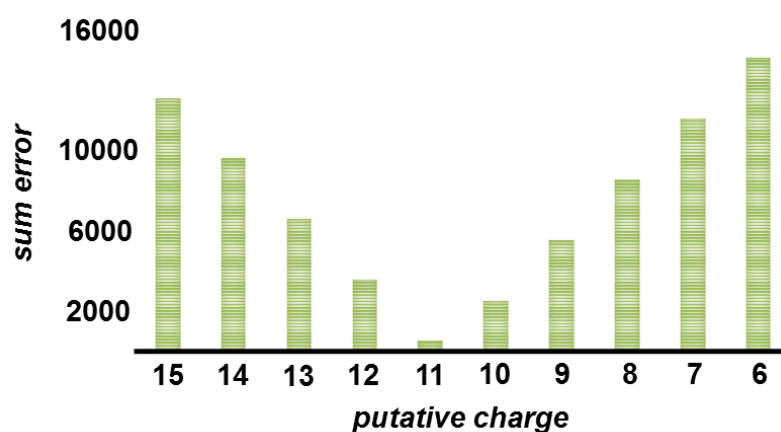


Fig. S15. Charge assignment for the first peak in the compound A series (=11)

4.4.2 Compound B charge assignment

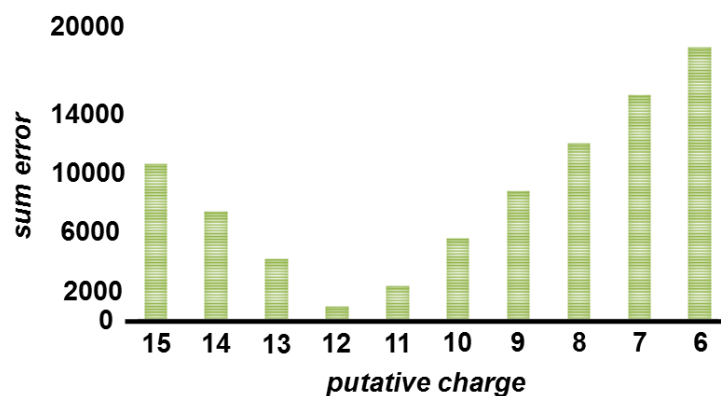


Fig. S16. Charge assignment for the first peak in the compound **B** series (=12)

4.4.3 Compound **C** charge assignment

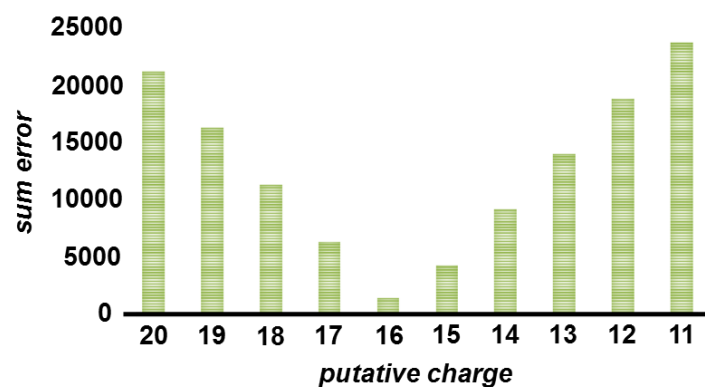


Fig. S17. Charge assignment for the first peak in the compound **C** series (=16)

5. Ion-Mobility Mass Spectrometry of two literature standards – oligothymidine and Cytochrome C

5.1 Mass spectrum of oligothymidine (T10)

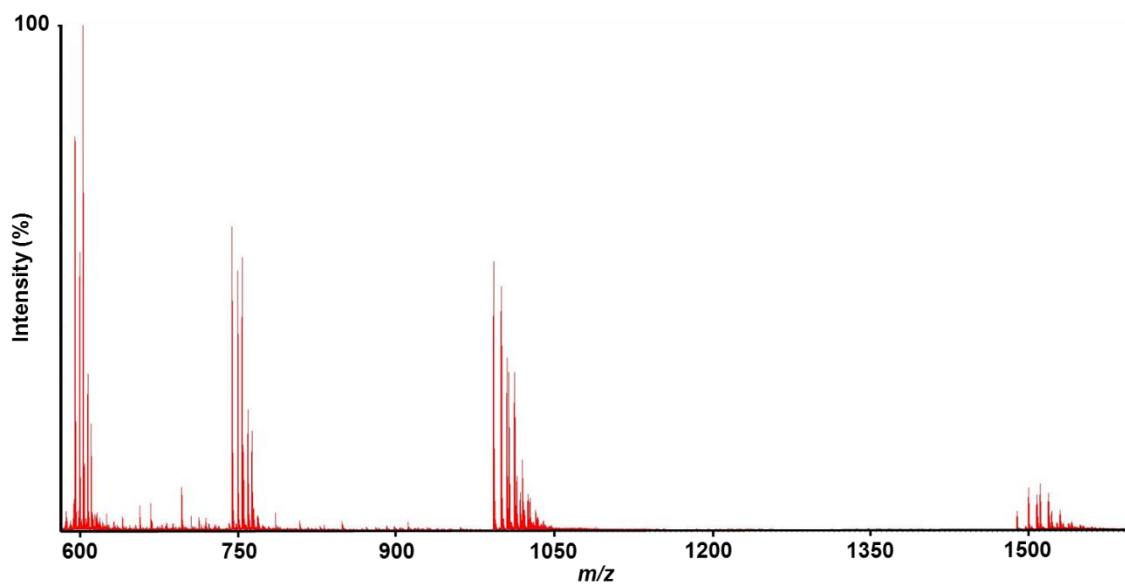
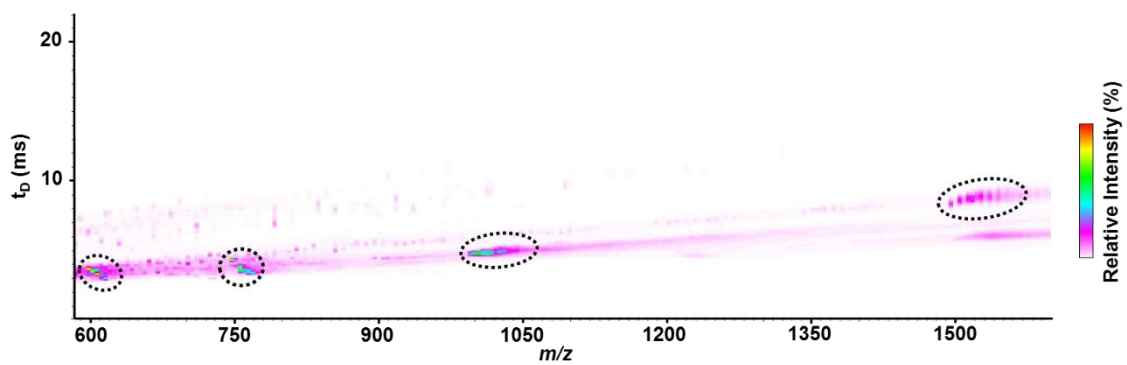


Fig. S18. HRES-ESI-MS of the literature standard T10



m/z	z	t_D (ms)	$^{TW}CCS_{N_2 \rightarrow He}$	$^{DT}CCS_{He}$ (lit)
594	5	3.638	553	627
743	4	4.19	493	537
992	3	4.631	399	446
1488	2	8.269	413	447

Fig S19. TW-IM-MS of the literature standard T10 and assignment table

5.2 Mass Spectrum of Cytochrome C

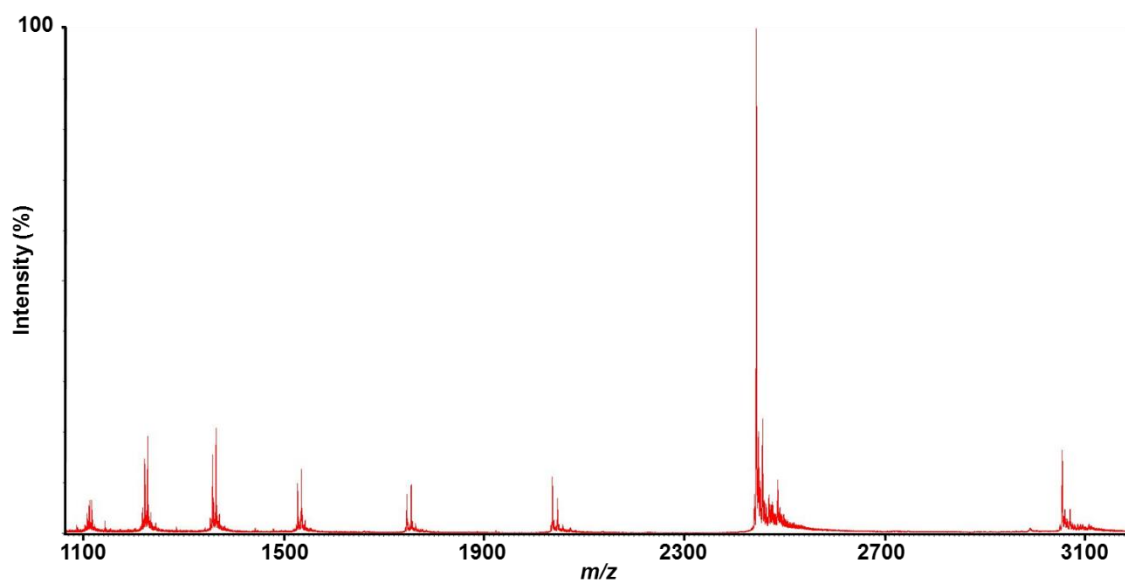
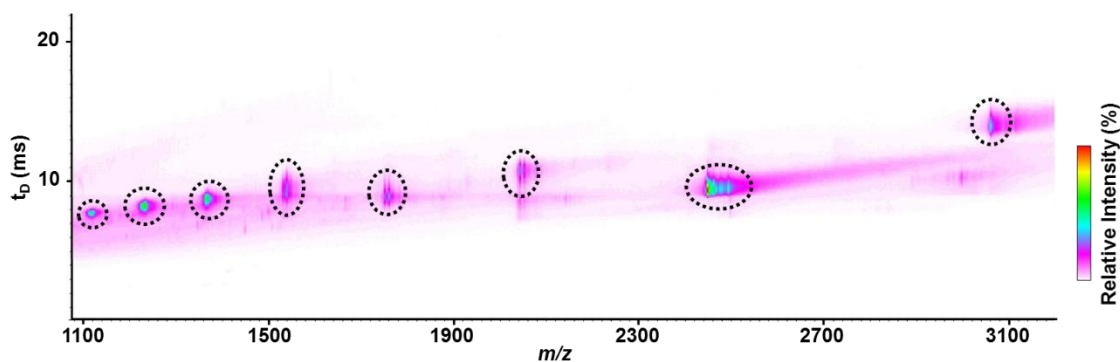


Fig. S20. HRES-ESI-MS of the literature standard cytochrome c



<i>m/z</i>	<i>z</i>	<i>t_D</i> (ms)	^{TW} CCS _{N₂→He}	^{DT} CCS _{He} (lit)
1122	11	7.718	2149	2305
1234	10	8.159	2038	2207
1371	9	8.71	1928	2024
1543	8	9.041	1763	1760
1763	7	8.82	1514	1586
2058	6	10.805	1514	1535
2058	6	8.71	1285	1351
2470	5	9.372	1132	1246
3096	4	14.112	1237	1174

Fig. S21. TW-IM-MS of the literature standard cytochrome c and assignment table

6. Synthesis and Ion-Mobility Mass Spectrometry of Unknown POWs

6.1 Synthesis of “Unknown” POWs

“Unknown” POWs (compounds **D** and **E**), were obtained from reactions analogous to those yielding Compound **B**.

Unknown Structure D

K₂WO₄·2H₂O (1.0 g, 3.07 mmol), H₃PO₃ (0.3 g, 3.6 mmol) and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 40 mL water. The pH of the mixture was adjusted to 3.3 quickly by 37% hydrochloric acid. After the solution was stirred for around 20 min, Co(NO₃)₂·6H₂O (0.08 g, 0.27 mmol) was then added into the solution, whose pH was dropped to 3.1. The pale pink solution was filtered and left for evaporation. Purple block crystals were obtained within two weeks.

Unknown Structure E

K₂WO₄·2H₂O (1.0 g, 3.07 mmol), Na₂TeO₃ (0.064 g, 0.29 mmol), KCl (0.08g, 1.0 mmol) and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 40 mL water. The pH of the mixture was adjusted to 3.3 quickly by 37% hydrochloric acid. After the solution was stirred for around 20 min, it increased to 3.5. MnCl₂·4H₂O (0.08 g, 0.27 mmol) was then added into the solution, whose pH was dropped to 3.3. The pale yellow solution was filtered and left for evaporation. Pale yellow block crystals were obtained within 1 week.

6.2 Mass spectrum of compound **D** – unknown POW

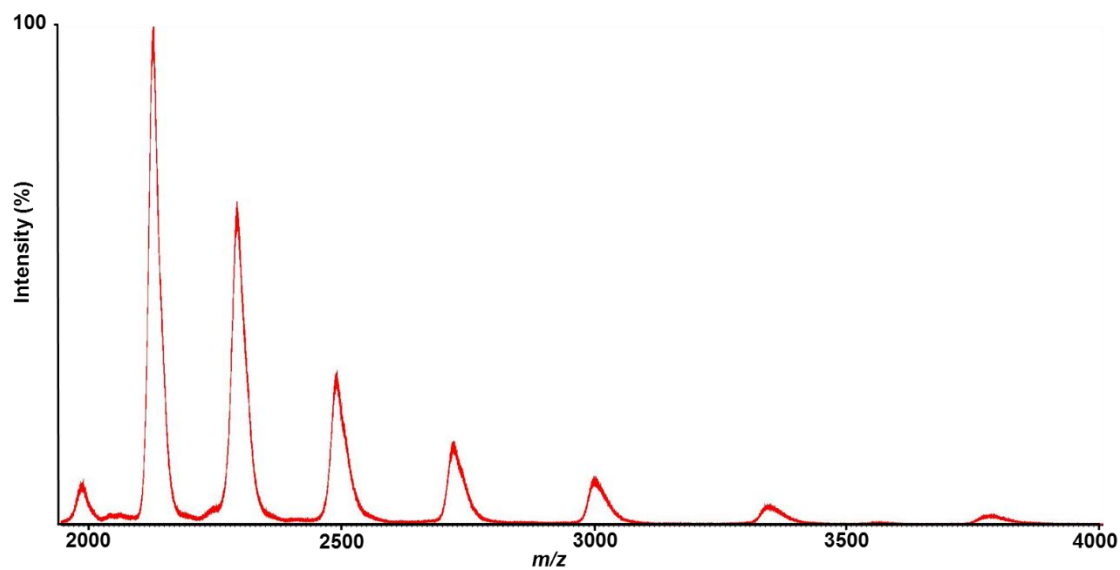
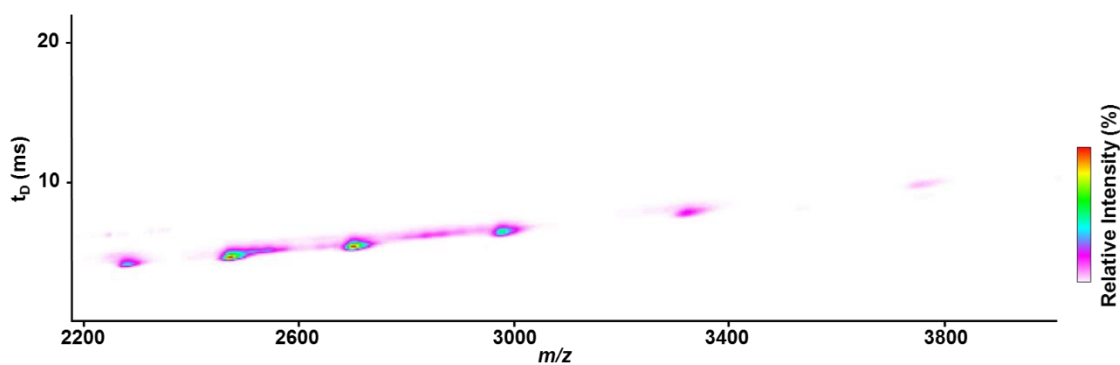


Fig. S22. HRES-ESI-MS of compound **D**



	m/z	z	t_D (ms)	$^{TW}CCS_{N_2 \rightarrow He}$
Compound D	2278	13	3.969	1026
	2472	12	4.52	1043
	2701	11	5.292	1075
	2975	10	6.395	1125
	3317	9	7.718	1164
	3756	8	9.813	1236

Fig. S23. TW-IM-MS of compound **D** and data table

6.3 Mass spectrum of compound **E** – unknown POW

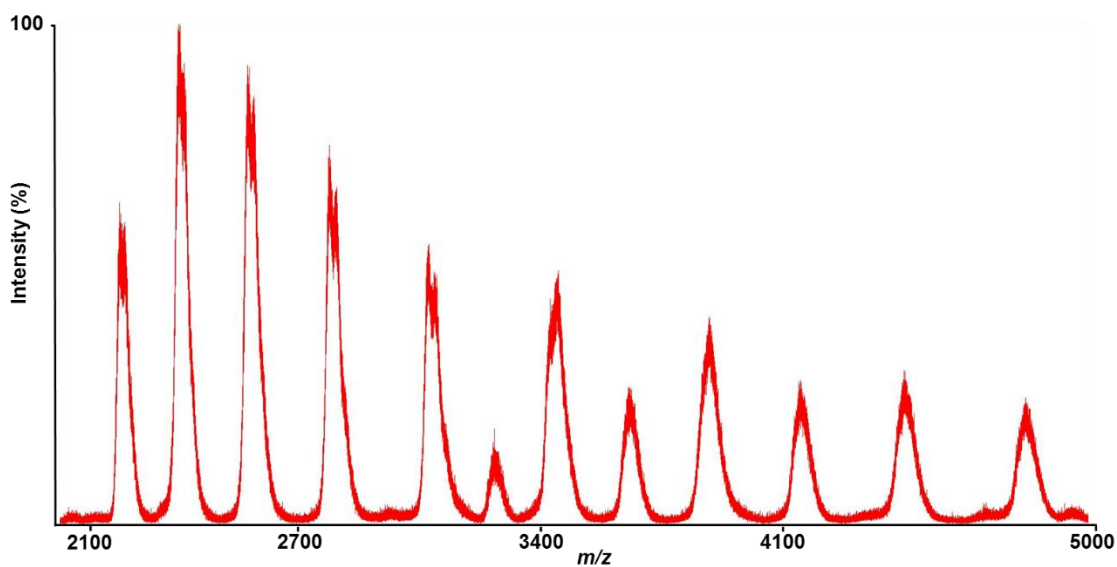
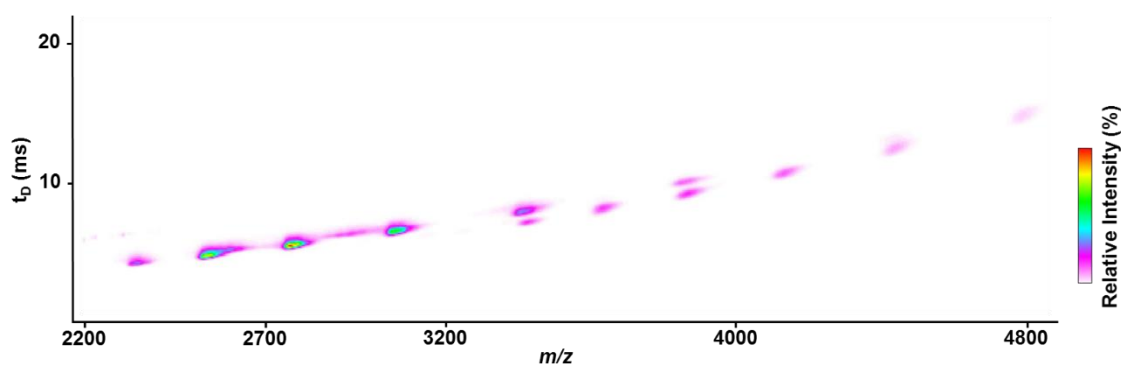


Fig. S24. HRES-ESI-MS of compound E



	m/z	z	t_D (ms)	$^{TW}CCS_{N_2 \rightarrow He}$
Compound E (monomers)	2353	13	4.19	1068
	2546	12	4.741	1081
	2768	11	5.513	1108
	3054	10	6.505	1139
	3403	9	7.938	1188
(dimers)	3844	8	10.033	1257
	3422	18	7.166	2202
	3630	17	8.159	2290
	3866	16	9.261	2368
	4126	15	10.695	2470
	4435	14	12.569	2599
	4789	13	14.884	2735

Fig. S25. TW-IM-MS of compound E data table

6.4 Inferred charge assignments of the Unknown POWs

Same procedure as described in section 2.4

6.4.1 Compound **D** charge assignment

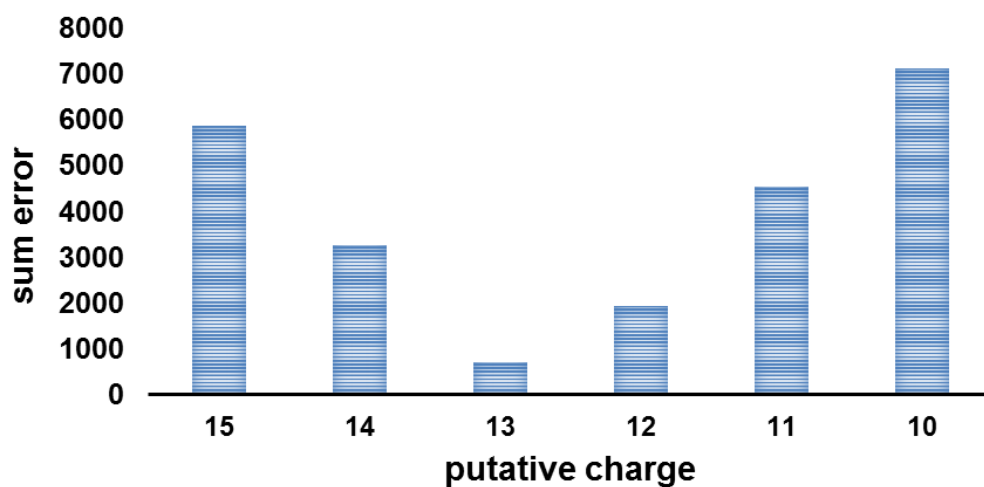


Fig. S26. Charge assignment for the first peak in the compound **D** series (=13)

6.4.2 Compound **E₁** charge assignment (**monomeric** series)

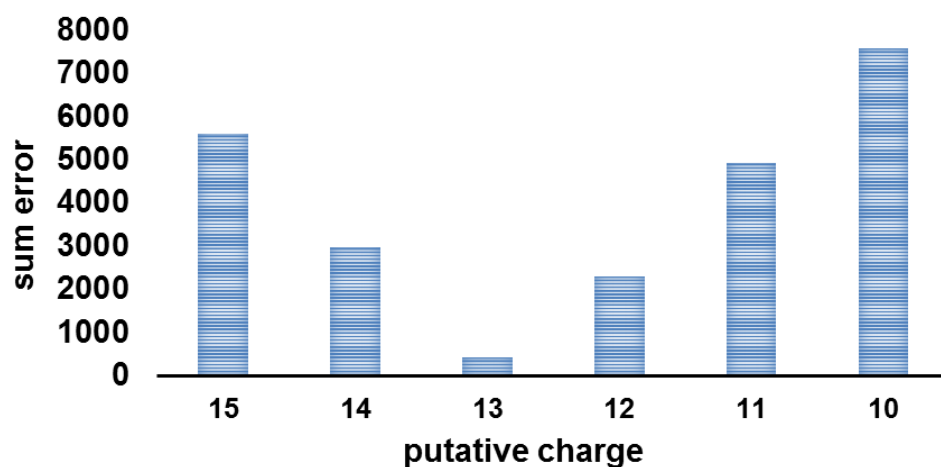


Fig. S27. Charge assignment for the first peak in the compound **E₁** series (=13)

6.4.3 Compound **E₂** charge assignment (**dimeric** series)

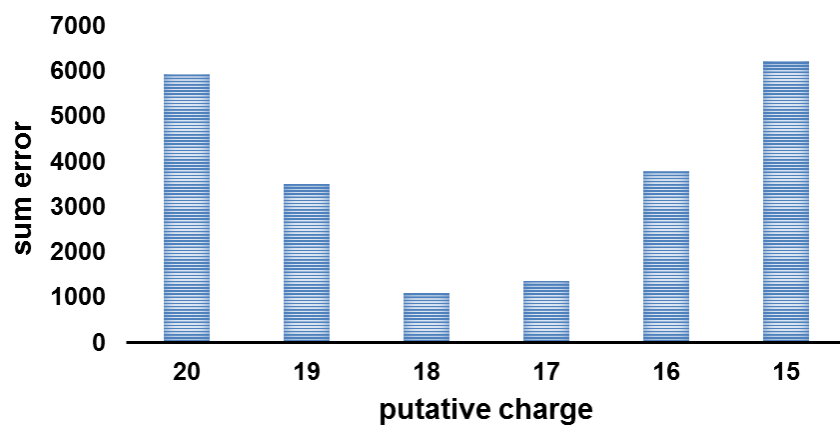


Fig. S28. Charge assignment for the first peak in the compound E₂ series (=18)

7. Calibration Curves

7.1 Calibration curve – calibrants (compounds 1-4) and POWs (compounds A-C)

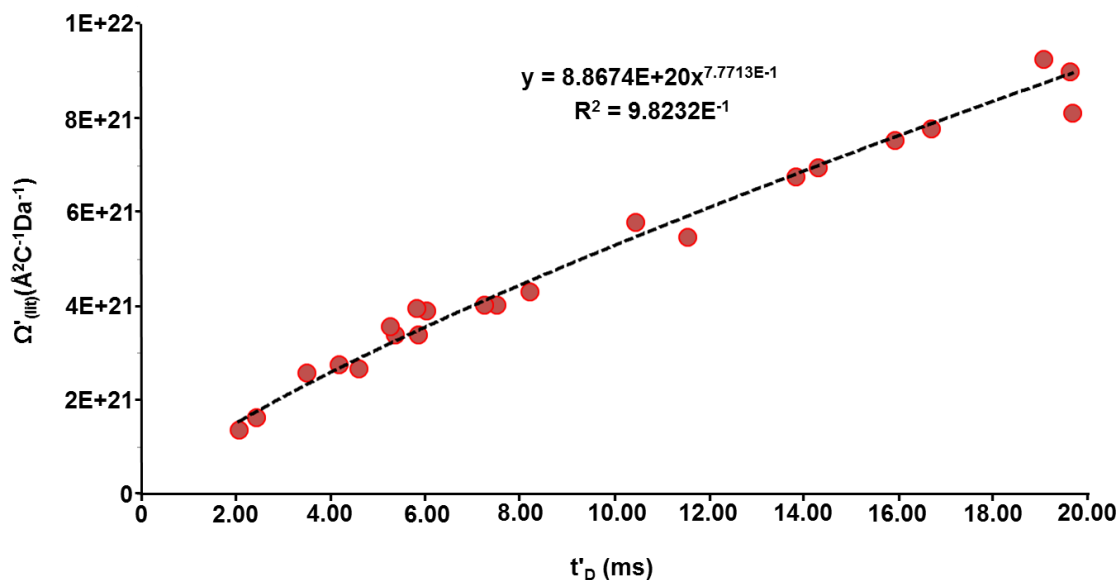


Fig. S29. TW-IM-MS calibration curve generated from compounds 1-4 run under the conditions used to assess compounds A-C; equation corresponds to the fitted power trend-line.

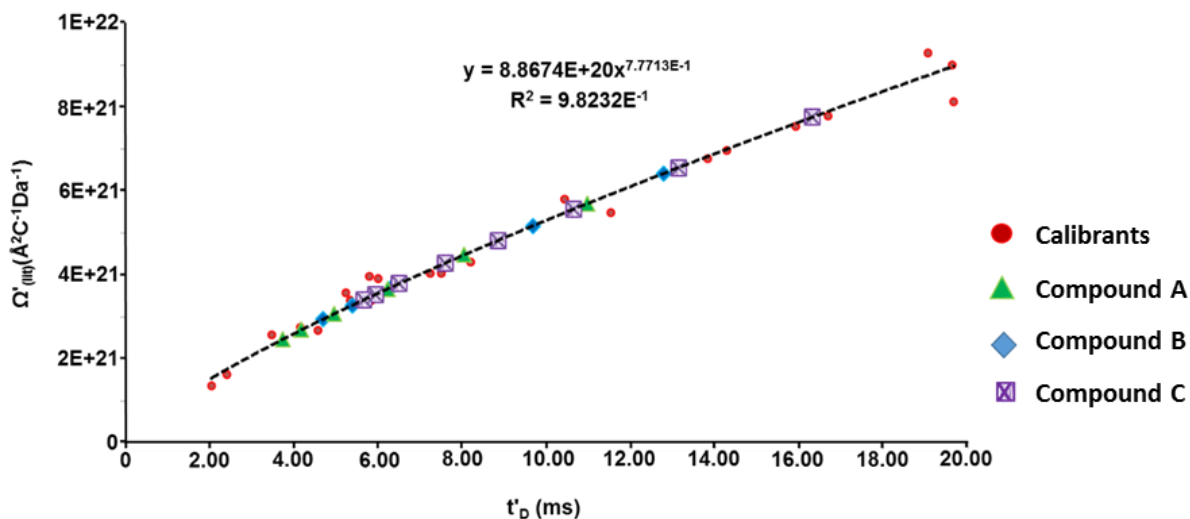


Fig. S30. Same calibration as above, but with the additional analyte species derived from compounds A-C included, CCS values for these points were calculated from the fitted trend-line. Note: all of the analyte species (derived from compounds A-C) can be assessed using this calibration curve without extrapolation beyond the range covered by the calibrant set (red dots).

7.2 Calibration curve – calibrants (compounds 1-4) and literature standards

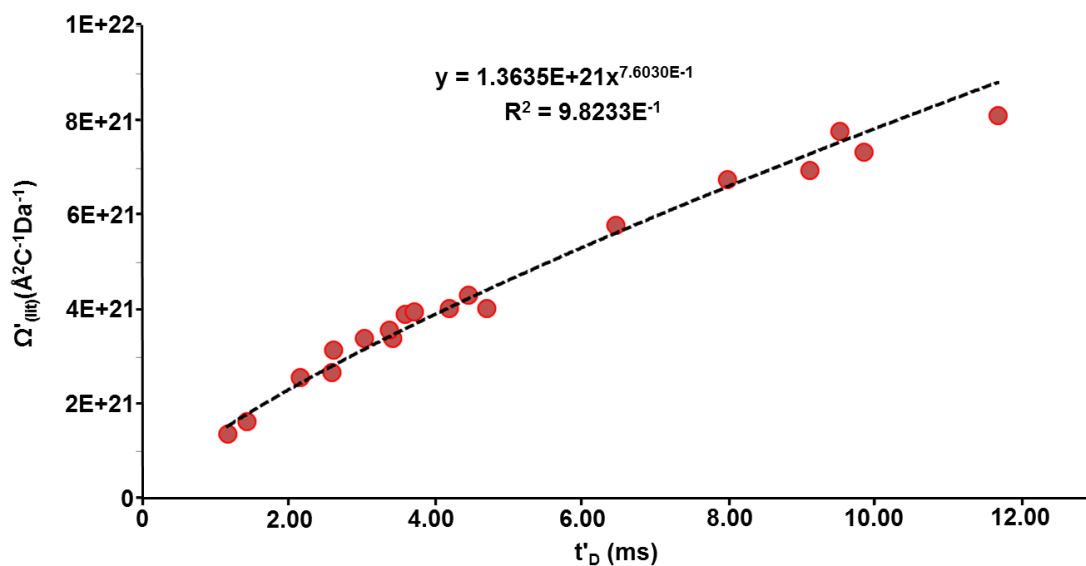


Fig. S31. TW-IM-MS calibration curve generated from compounds 1-4 run under the conditions used to assess T_{10} and **CytC**; equation corresponds to the fitted power trend-line.

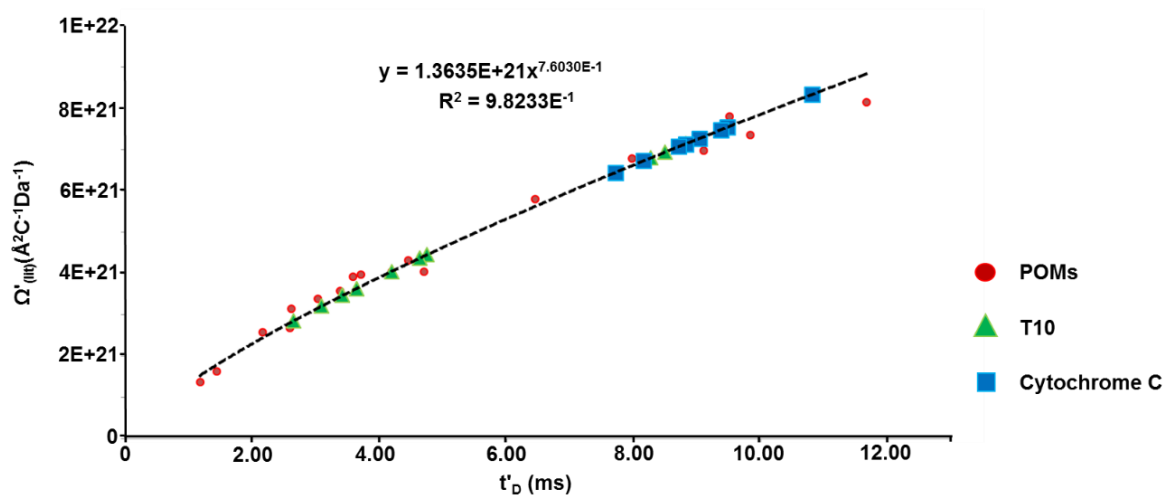


Fig. S32. Same calibration as above, but with the additional analyte species derived from T_{10} and **CytC** included, CCS values for these points were calculated from the fitted trend-line. Note: all of the analyte species (derived from T_{10} and **CytC**) can be assessed using this calibration curve without extrapolation beyond the range covered by the calibrant set (red dots).

7.3 Calibration curve – calibrants (compounds 1-4) and unknown POWs (compounds D and E)

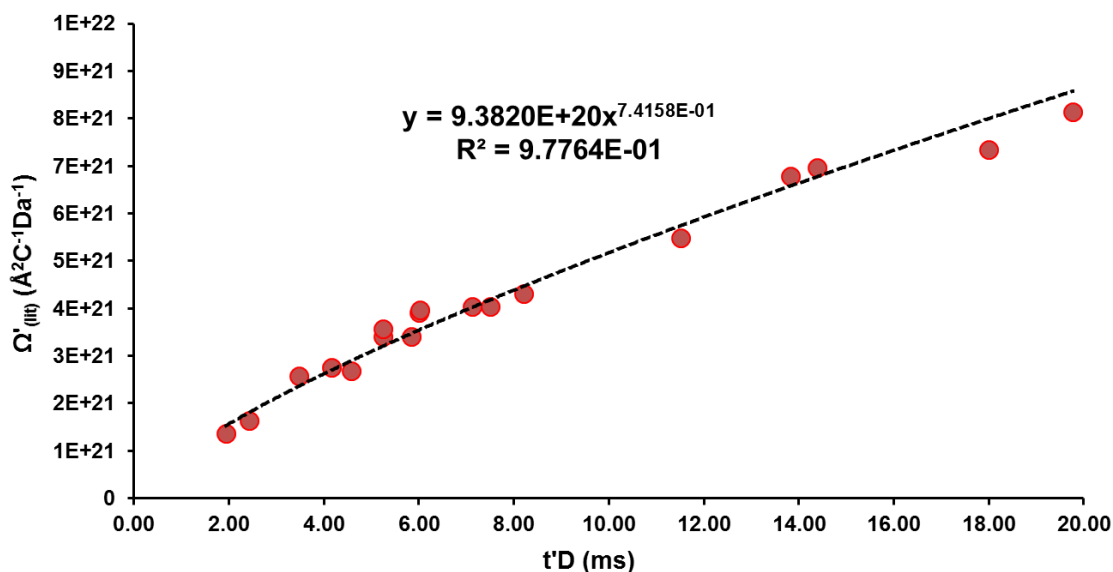


Fig S33. TW-IM-MS calibration curve generated from compounds 1-4 run under the conditions used to assess compounds D and E; equation corresponds to the fitted power trend-line.

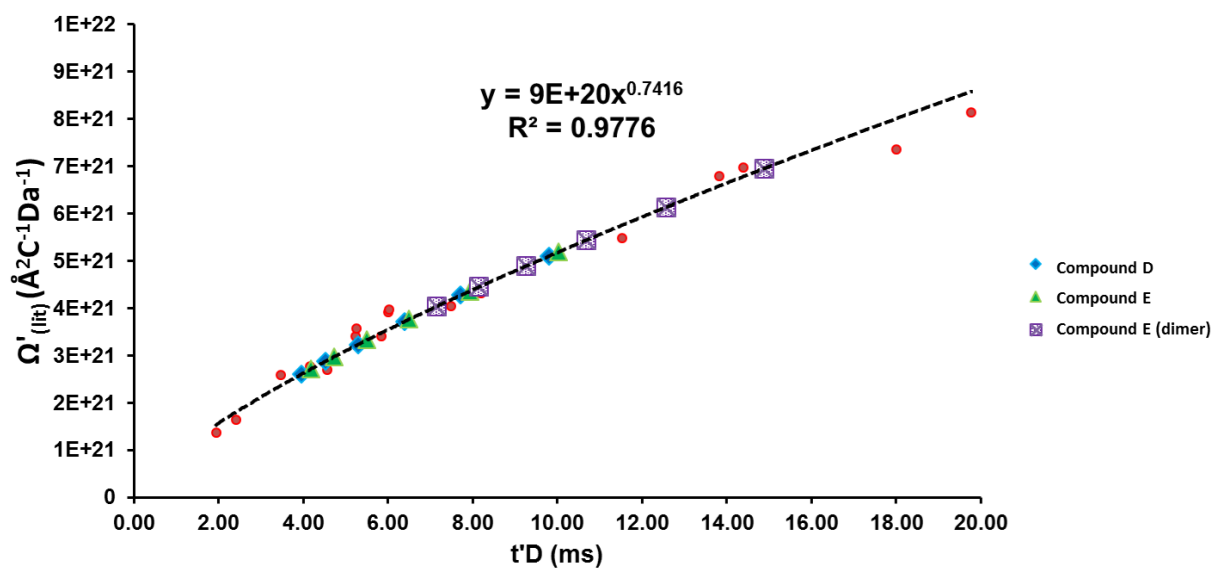


Fig. S34. Same calibration as above, but with the additional analyte species derived from compounds D and E included, CCS values for these points were calculated from the fitted trend-line. Note: all of the analyte species (derived from compounds D and E) can be assessed using this calibration curve without extrapolation beyond the range covered by the calibrant set (red dots).

8. Comparison of CCS values – known vs. unknown POWs

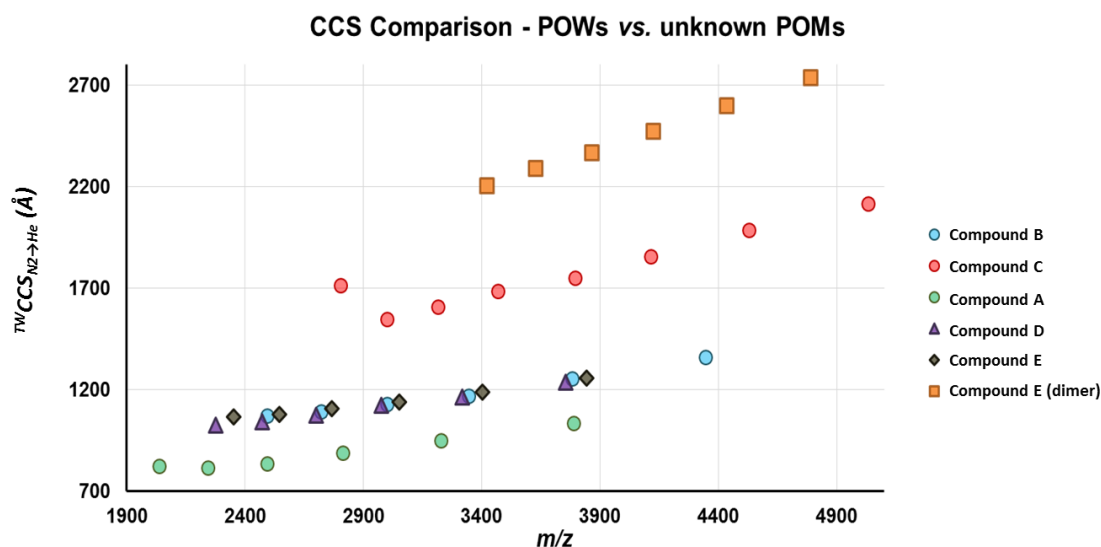


Fig. S35. Plot depicting the $^{TW}CCS_{N_2 \rightarrow He}$ value for each POW m/z species – known and unknown – serves to highlight the tight correlation between both of the compounds **D** and **E**₁ (unknown monomeric series) with compound **B** (the known POW tetramer).

9. References

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