

## Supporting information

### Synthesis

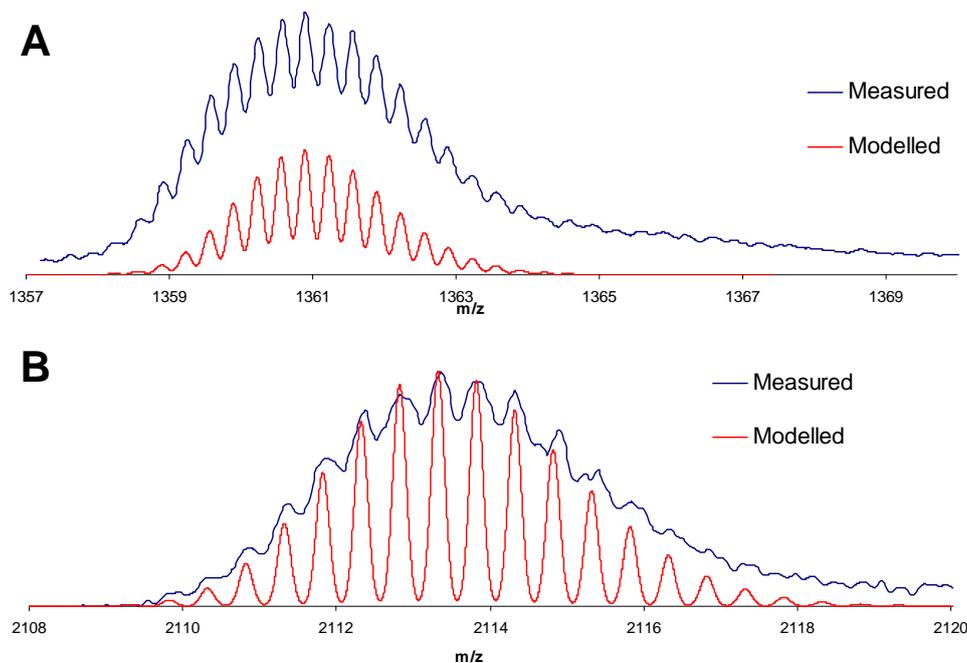
The cages were synthesized according to protocols outlined by Lusby et al.<sup>[1]</sup>

### MS Sample Preparation

~0.5 mL solutions were prepared at a concentration of 200  $\mu\text{M}$  in either Nitromethane or TCE (1,1,2,2-Tetrachloroethane). In order to help dissolution the dispersions were ultra-sonicated for 10 seconds. Samples were diluted further to give 100  $\mu\text{M}$  cage solutions, filtered through 45  $\mu\text{m}$  syringe filter and analysed within 5 hours of preparation.

### High Resolution MS

High resolution mass spectrometry was performed on a Q-ToF Ultima (Micromass Ltd, Manchester UK) fitted with nano-ESI source and using Argon as the collision gas. Nano-ESI source charged sample solutions (100  $\mu\text{M}$ ) via platinum wire inserted into capillary tip. Capillary voltages were adjusted between 1 and 1.5 kV to optimize spray quality, while the cone voltage was typically set to 20 V. Source temperature was set at 80°C. Energy of collision with inert gas was set to 3.5z eV (where z is the charge state of ion). Peaks were assigned on the basis of their isotopic distribution and compared with simulated isotopic distribution. The isotopic distribution modelling of the selected m/z was performed using the Molecular Weight Calculator v6.48 Software by Matthew Monroe (<http://ncrr.pnl.gov/software/>). Example of peak assignment procedure has been presented in Figure S1.



**Figure S1. CNC Cage. Experimental vs Modelled Isotopic Distribution of +3(3PF<sub>6</sub><sup>-</sup>) peak 1361 m/z (A) and for +2(4PF<sub>6</sub><sup>-</sup>) peak 2113 m/z (B) (Q-ToF Ultima, 100  $\mu\text{M}$  of Cage in Nitromethane).**

As in the Figure S1, broad shape and “tail” were common features of experimental isotopic distributions. This may suggest the presence of the higher order oligomers under this peak. For example the presence of a dimer at charge state +4 with would occur at the same  $m/z$  as the +2 monomer. An attempt to find other peaks originating from such species (ie odd numbered oligomer charge states) was made, but no such signals were detected. Therefore, an assumption was made that the above appearance is an experimental artefact.

Collision Induced Dissociation (CID) experiments were performed on Q-ToF Ultima with MS/MS setting. CID experiments involved selection of the ions with  $m/z$  of interest at the quadrupole analyser. Isolated ions were then accelerated to higher kinetic energies and collided with the argon molecules in the hexapole collision cell. Increased collision energies (0-30z eV above nominal collision energy of 3.5z eV) induced dissociation of the isolated ions. Identification of so called fragmentation pathways provided insight into the stability of the structure and also the strength of particular non-covalent interactions.

### **Ion Mobility MS**

Ion mobility mass spectrometry measurements were performed on the MoQ-ToF, an in-house modified<sup>[2][1]</sup> Q-ToF 1 (Micromass UK Ltd) fitted with nano-ESI source. Capillary voltages were adjusted between 1 and 1.5 kV to optimize spray quality, while the cone voltage was set to 38V. Source temperature was set at 80°C. The energy of injection into the drift cell was set at 36V.

Modification of instrument involved the insertion of a 5.1 cm long copper drift cell and supplementary ion optics situated post source optics and before the quadrupole analyzer.<sup>[1]</sup> A potential difference can be applied across the drift cell, thus when ions are pulsed into the drift cell (which is filled with helium at pressure of ~3.5 Torr, room temperature) and drift through under the influence of this field, they are hindered by collisions with the intervening buffer gas molecules. Thus the time taken for ions to traverse the cell, in conjunction with the strength of the electric field applied across the drift cell, is due to the charge they carry and their mobility ( $K$ ).  $K$  is inversely related to the rotationally averaged CCS of the ion. The ions then pass through the quadrupole and time of flight analyzers and are detected by microchannel plates. The time from when ions are pulsed into the drift cell to when they are detected is therefore a combination of the time the ions spend in the drift cell (drift time) and that outside it (dead time). This is obtained from the measured mass selected arrival time distribution (ATD), and can be deconvoluted into ATDs of each individual ion.

For a given mass/charge the drift time will vary depending on its CCS but the dead time will be invariant. The ions ATD distributions are measured to at least 6 different values of the electric field applied to the drift cell (15-60V). If the arrival times are plotted against  $P/V$  the intercept will be the dead time and the gradient  $1/K$ . After normalising for the experimental temperature and pressure inside the drift cell  $K$  can be converted into reduced mobility  $K_0$  and this to ascertain a value for  $\Omega$  using the Mason-Schamp equation below.<sup>[3]</sup>

$$K_0 = \frac{3ze}{16N_0} \left( \frac{2\pi}{\mu k_B T} \right)^{\frac{1}{2}} \frac{1}{\Omega}$$

where  $z$  is ion charge,  $e$  is electron charge,  $N_0$  is the buffer gas number density,  $\mu$  is the reduced mass of the buffer gas and ion,  $k_B$  is the Boltzmann constant,  $T$  is the effective temperature and  $\Omega$  is the momentum transfer collision integral.

Prior analysis both mass spectrometers were calibrated using a solution (2 mg/mL) of sodium iodide in 50:50 water:isopropanol. NanoESI tips were manufactured from glass capillaries (World Precision Instruments, Sarasota, USA) using a micropipette puller (Fleming/Brown p-97 Sutter Instruments, Novato, USA). Both instruments were operated using Mass Lynx 4.1 Software (Micromass Ltd, Manchester UK).

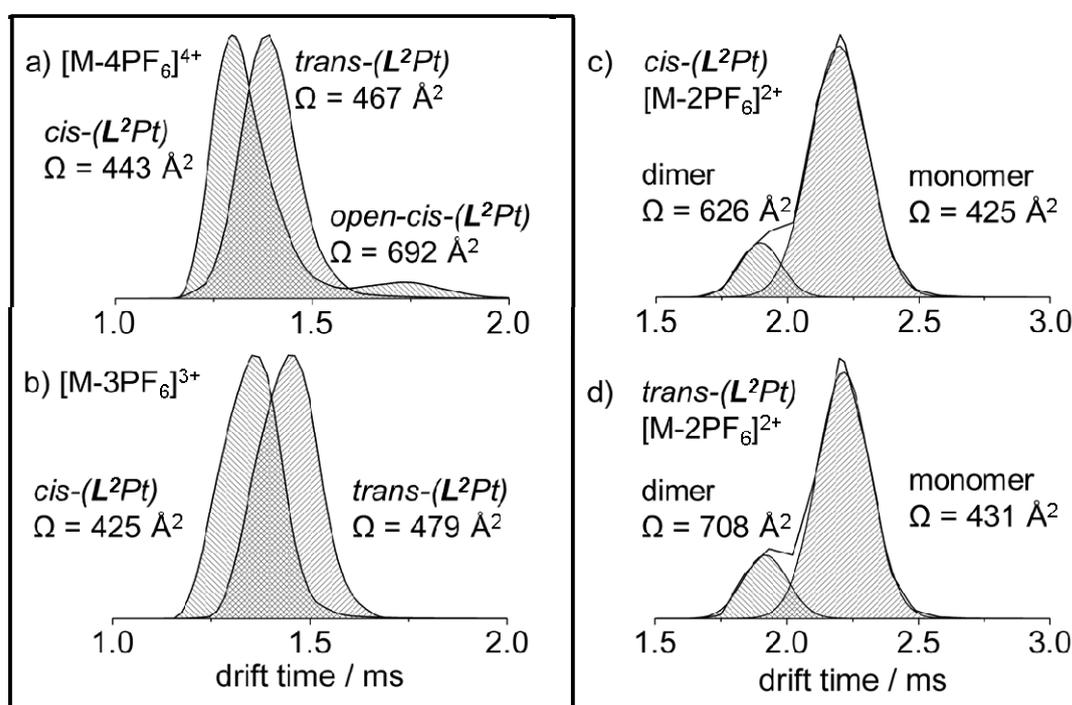


Figure S2. ATDs for the (L<sup>2</sup>Pt) cages: a) ATDs for *trans* and *cis* isomers for the peak due to [M-4PF<sub>6</sub>]<sup>4+</sup> at 869 m/z; b) ATDs for *trans* and *cis* isomers for the peak due to [M-3PF<sub>6</sub>]<sup>3+</sup> at 1208 m/z; b) and c) presents ATDs for the *cis* and *trans* isomers respectively, for the peak attributed to [M-2PF<sub>6</sub>]<sup>2+</sup> at 1886 m/z. Samples were sprayed at a concentration of 100 μM from TCE.

Fragment	m/z	Charge State	Precursor Species	CCS / Å <sup>2</sup>	± / Å <sup>2</sup>
	503	2	<i>cis</i> -(L <sup>1</sup> Pt) <i>cage</i>	195	2
	505	1	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	104	1
	505	1	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	103	1
	581	1	<i>cis</i> -(L <sup>1</sup> Pt) <i>cage</i>	141	1
	581	2	<i>trans</i> -(L <sup>1</sup> Pt) <i>cage</i>	251	4
	661	1	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	162/124	*
	661	1	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	129	*
	898	3	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	379	16
	909	2	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	298	8
	992	3	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	450	12
	992	3	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	447	2
	1020	3	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	466	*
	1065	3	<i>trans</i> -(L <sup>1</sup> Pt) <i>cage</i>	466	*
	1093	2	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	352	11
	1101	2	<i>cis</i> -(L <sup>1</sup> Pt) <i>cage</i>	475	*
	1114	3	<i>trans</i> -(L <sup>2</sup> Pt) <i>cage</i>	467	*
	1118	3	<i>trans</i> -(L <sup>1</sup> Pt) <i>cage</i>	524	*
	1151	1	<i>cis</i> -(L <sup>1</sup> Pt) <i>cage</i>	216	6
	1166	3	<i>cis</i> -(L <sup>2</sup> Pt) <i>cage</i>	475	10
	1308	2	<i>cis</i> -(L <sup>1</sup> Pt) <i>cage</i>	370	*

**Table S1. Common fragments observed in IMMS with corresponding a average collision cross sections accompanied by value of statistical uncertainty from a set of triplicate measurements. \*  
species were not resolved on all three occasions, therefore no error value is provided.**

## References

- [1] P. J. Lusby, P. Muller, S. J. Pike, A. M. Z. Slawin, *Journal of the American Chemical Society* **2009**, *131*, 16398.
- [2] B. J. McCullough, J. Kalapothakis, H. Eastwood, P. Kemper, D. MacMillan, K. Taylor, J. Dorin, P. E. Barran, *Anal Chem* **2008**, *80*, 6336.
- [3] E. A. Mason, E. W. McDaniel, *Transport properties of ions in gases*, Wiley, New York, **1988**.