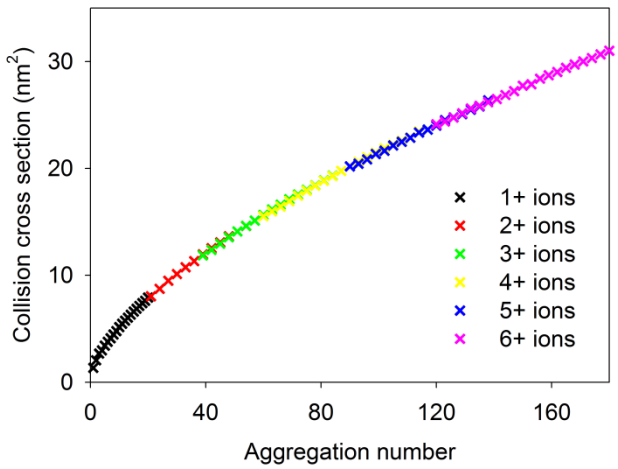
Supplementary information

Absence of charge dependency in the cluster collision cross sections

The collision cross sections in figures 3 and 4a (main text) represent mean values that were also averaged when different charge states overlapped the same aggregation number. This averaging process could hide interesting charge-dependent details in the cluster collision cross sections. However, no charge effects were observed in the collision cross sections of the clusters as shown for the 1+ to 6+ ions of 6TAB that are given without averaging (Figure S1).

Figure S1



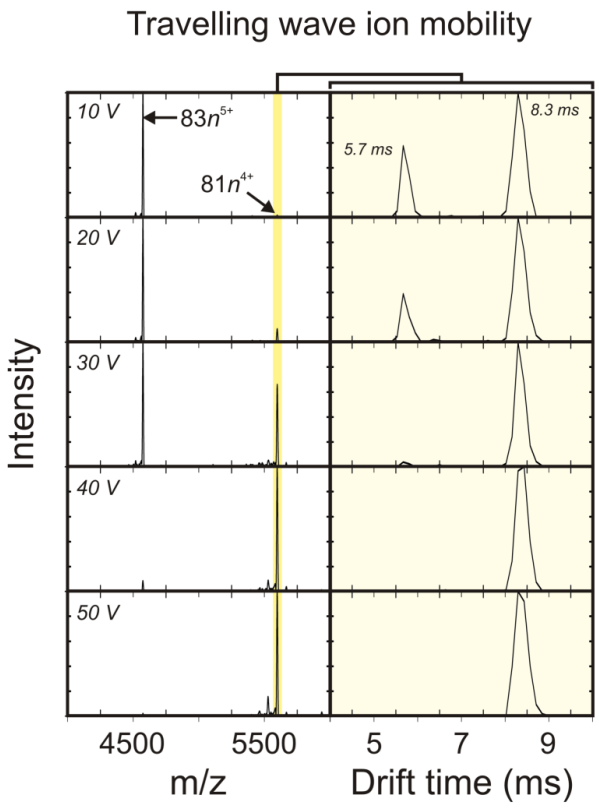
Characterisation of possible cluster dissociation during ion mobility separation

Cluster dissociation during IMS separation was characterised for both the G2-TWIMS and LFIMS devices used in the present work. This characterisation was important since many of the clusters dissociate rapidly in the experimental time frame. Thus, the possible dissociation of clusters during IMS had to be characterised to discount and possible coupling between the ion drift times and the degree of cluster dissociation. Theoretical calculations based on TWIMS have also suggested that this technique can result in significant heating. [1]

However, more recent work has shown that TWIMS can be operated under conditions where thermal heating of the ions does not take place. [2]

To characterise the G2-TWIMS under the current experimental conditions, drift times were recorded for the $83n^{5+}$ clusters of 10TAB as a function of the collision voltage. Five different ATDs were obtained between 10 V and 50 V over which range the $81n^{4+}$ product ion populations varied from ~ 0% (10 V) to ~100% (50 V). The MSMS spectra and associated ATDs of the $81n^{4+}$ product ions are shown in Figure S2. Note these cluster were selected as they neatly spanned the full range of dissociation rates over these voltages.

Figure S2



Between 10 V and 20 V collision energy the ATD of the product ion is composed of two peaks, with drift times of 5.7 ms and 8.3 ms. The 5.7 ms drift time is equivalent to the drift time of the precursor ion indicating that these ions have remained intact during ion

mobility but dissociate in the transfer region. The 8.3 ms drift time is equivalent to the drift time of $81n^{4+}$ clusters (interrogated by MSMS at 10 V on a separate acquisition). Thus, these species are formed from the dissociation of clusters in the trap region, prior to ion mobility. At collision voltages ≥ 30 V, where increased fission occurs, the ATD of the product ion is characterised by a single peak with a drift time of 8.3 ms. Thus, at higher collision voltages dissociation occurs exclusively in the trap region. Crucially, peaks with intermediate drift times or significantly broadened ATDs across the different range of collision voltages are not observed. Thus, regardless of the applied collision voltage and rate of cluster fission the dissociation of these clusters occurs exclusively in the trap and transfer regions and not during mobility separation under these conditions.

We next characterised the LFIMS to determine if cluster fission was occurring during ion mobility on this device. This instrument required a different characterisation approach to the G2-TWIMS. This was due to poor ion transmission at the quadrupole resolution required to ensure the unique selection of individual cluster populations making MSMS unfeasible. To characterise the linear field instrument the drift times of a range of different 2+ clusters of 6TAB ($25n^{2+}$, $35n^{2+}$, $45n^{2+}$) were determined as a function of collision voltage (10 V to 200 V). At higher collision voltages the 2+ clusters represent the breakdown products and residual ions from clusters with significantly higher charge states that have ejected multiple charges during MS (see Figures 7 and 8 in the main section). The drift times of these clusters should then depend significantly on the applied collision voltage, if charge was lost during ion mobility. The 6TAB clusters were chosen to characterise the LFIMS as these cluster span the widest range of different aggregation states for their 2+ ions at the higher collision voltages.

The drift times of the various clusters were obtained in nitrogen between the collision voltages of 10 V and 200 V. From a plot of drift time against collision voltage it is clear that

no coupling of these processes takes place (Figure S3a). Furthermore, no significant peak broadening is observed in the ATD of the clusters with increasing collision voltage (Figure S3b). We suggest the broader peaks at low collision voltage are due to some space charging effects. This is consistent with the observation of a reduction in peak width on signal attenuation for these ATDs. This did not change the centroid drift times (data not shown). Thus, as with the commercial travelling wave device, we can conclude that cluster dissociation does not occur during mobility separation on the LFIMS under the current conditions.

Figure S3

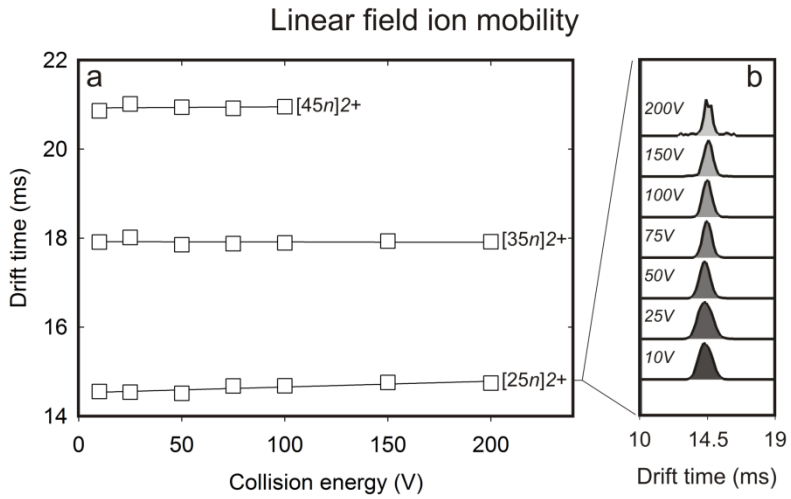


Figure legends

Figure S1

Collision cross sections for the 1+ to 6+ clusters of 6TAB colour coordinated as shown for the different charge states. The collision cross sections report values obtained from a single acquisition, three of which were averaged to produce the projection shown in figure 3. The plot demonstrates the lack of charge dependency in the cluster collision cross sections. Collision cross sections were obtained in nitrogen using LFIMS.

Figure S2

Left panel shows the MSMS spectra of the $83n^{5+}$ ions of decyltrimethylammonium bromide (10TAB) detergent cluster at different collision voltages, the collision voltage is shown in italics. The respective peaks for the precursor ion ($83n^{5+}$) and major product ion ($81n^{4+}$) are on the left and right hand sides of the MSMS spectra. Right hand panel shows the arrival time distributions (ATD) for the $81n^{4+}$ product ions with increasing collision voltage. The ATD show only two peaks with drift times corresponding to the precursor (5.7 ms) and product ions (8.3 ms). The clusters were selected for these experiments since they spanned the full range of fissioning rates between these voltages. Furthermore at 50 V no significant detergent evaporation was observed in these clusters which could have complicated interpretation. Drift times were obtained in nitrogen on a G2-TWIMS device.

Figure S3

In panel (a) the dependence of the collision voltage on the observed drift times the $25n^{2+}$, $35n^{2+}$ and $45n^{2+}$ clusters of 6TAB. In panel (b) the extracted arrival time distributions for the $25n^{2+}$ cluster of 6TAB at each collision voltage, given in italics. 6TAB cluster were selected for these experiments as these clusters spanned the widest range of aggregation numbers at 200 V and thus assisted instrument characterisation. Drift times were obtained in nitrogen on a LFIMS device.

1. A. A. Shvartsburg and R. D. Smith, *Anal. Chem.*, 2008, **80**, 9689-9699.
2. S. I. Merenbloom, T. G. Flick and E. R. Williams, *J. Am. Soc. Mass Spectrom.*, 2012, **23**, 553-562.