

Supporting Information

Dissociation of Gas Phase Ions of Atomically Precise Silver Clusters Reflects Their Solution Phase Stability

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Table of Content

Description	Page Number
Synthesis of $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}][\text{PPh}_4]_4$	3

List of Figures	Description	Page Number
S1	UV-vis and ESI MS characterization of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]$ cluster	3
S2	UV-vis and ESI MS characterization of $[\text{Ag}_{44}(\text{FTP})_{30}]$ cluster	4
S3	UV-vis and ESI MS characterization of $[\text{Ag}_{25}(\text{DMBT})_{18}]$ cluster	5
S4	MS/MS spectra of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ ion	6
S5	Experimental and calculated patterns are shown for $[\text{Ag}_{24}(\text{BDT})_9]^{2-}$, $[\text{Ag}_{19}(\text{BDT})_6]^-$ and $[\text{Ag}_{26}(\text{BDT})_{10}]^{2-}$	7
S6	MS/MS spectra of $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$	8
S7	MS/MS spectra of $[\text{Ag}_{44}(\text{FTP})_{30}]^{3-}$	9
S8	Experimental and calculated isotopic patterns are shown for	10

	$[\text{Ag}_{43}(\text{FTP})_{28}]^{3-}$, $[\text{Ag}_{42}(\text{FTP})_{27}]^{3-}$, $[\text{Ag}_{43}(\text{FTP})_{28}]^{2-}$ and $[\text{Ag}_{42}(\text{FTP})_{27}]^{2-}$	
S9	ESI MS of $[\text{Ag}_{44}(\text{DCBT})_{30}]$ cluster and collision energy resolved fragmentation curves	11
S10	MS/MS at higher collision energies for $[\text{Ag}_{19}(\text{DMBT})_{12}]^{-}$	12
S 11	Fitting parameters for the sigmoidal fit of survival yield curves	13
S 12	Solution phase stability comparison of $[\text{Ag}_{29}(\text{BDT})]_{12}$, $[\text{Ag}_{25}(\text{DMBT})_{18}]$ and $[\text{Ag}_{44}(\text{FTP})_{30}]$	14
S 13	Pressure dependence of collision energies	15
S 14	Collision energy resolved fragmentation curves of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ ion in presence of Ar and CO gas	16

Synthesis of $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}][\text{PPh}_4]_4$. Approximately 20 mg of AgNO_3 was dissolved in 5 mL methanol and 9 mL DCM. To this reaction mixture, 48 μL of 2,4-DCBT (in 0.5 mL DCM) and 12 mg PPh_4Br (in 0.5 mL DCM) were added at 5 min time interval. After about 20 min, NaBH_4 (23 mg in 2 mL ice cold water) was added under stirring condition. The reaction was continued for 11-12 h in an ice bath. The reddish brown colored solution was taken in a round bottomed flask and the solvent was evaporated completely. Then the precipitate was washed with methanol and the cluster was collected by dissolving the precipitate in DCM.

Supporting Information 1

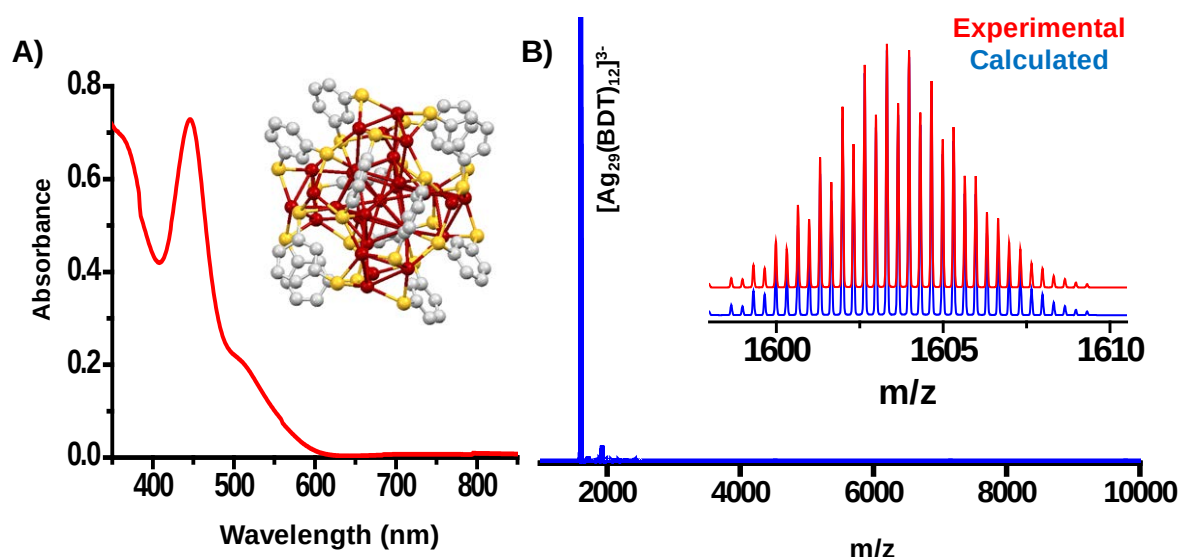


Figure S1: A) UV-vis and **B)** ESI MS characterization of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]$ cluster. Structure[†] of the cluster is shown in the inset of **A)**. Inset of **B)** shows the matching of experimental and calculated patterns of the peak for $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ (m/z 1604).

[†]Structure has been modelled assuming the co-ordinates from the crystal structure. Color codes: red=silver, yellow=sulphur, grey=carbon, hydrogen atoms are not shown for clarity.

Supporting Information 2

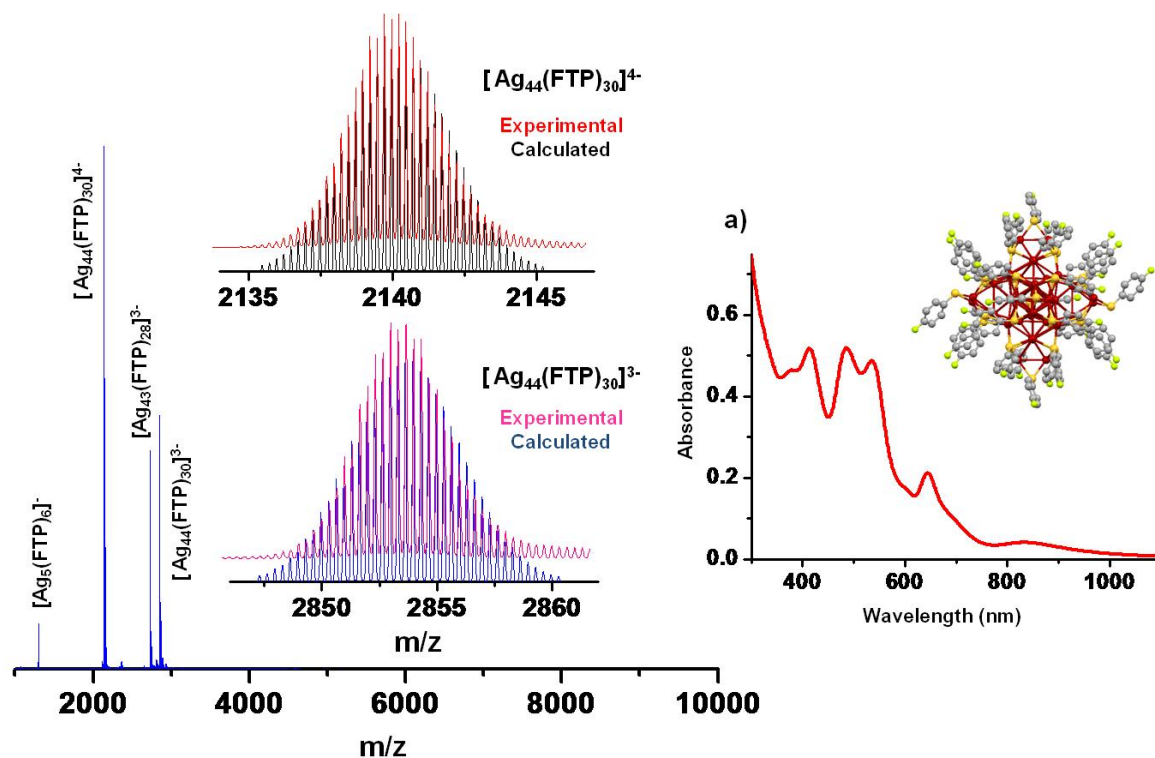


Figure S2: Full range ESI MS of $[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$ cluster. Experimental and calculated isotopic distributions for $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ and $[\text{Ag}_{44}(\text{FTP})_{30}]^{3-}$ are also shown. Inset **a)** shows the UV-vis absorption features of the cluster. Structure[†] of the cluster is also shown.

[†] Structure has been modelled assuming the co-ordinates from the crystal structure. Color codes: red=silver, yellow=sulphur, grey=carbon, yellowish green=fluorine, hydrogen atoms are not shown for clarity.

Supporting Information 3

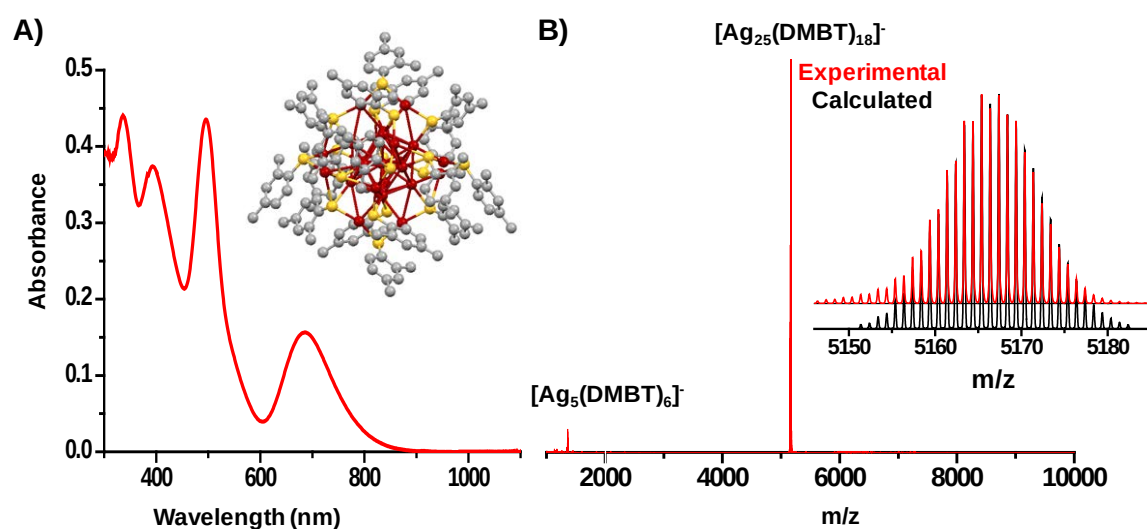


Figure S3: A) UV-vis and **B)** Full range ESI MS of $[\text{Ag}_{25}(\text{DMBT})_{18}]^-$ cluster. Structure[†] of the cluster is represented in the inset of **A)** and inset of **B)** shows the experimental and calculated patterns of the peak for $[\text{Ag}_{25}(\text{DMBT})_{18}]^-$ (m/z 5166).

[†]Structure has been modelled assuming the co-ordinates from crystal structure. Color codes: red=silver, yellow=sulphur, grey=carbon, hydrogen atoms are not shown for clarity.

Supporting Information 4

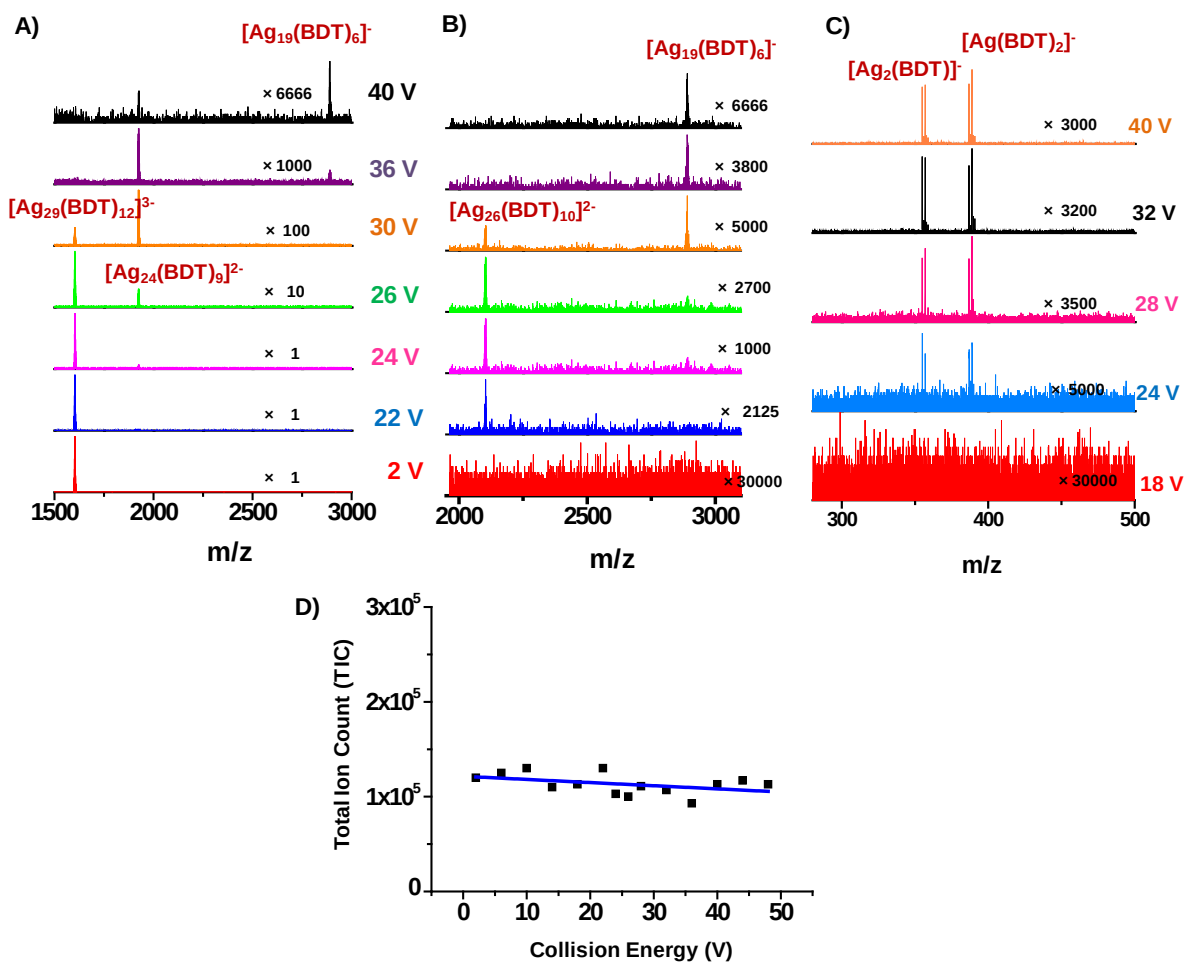


Figure S4: MS/MS spectra of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ ion with increasing collision energy. **A)** the region between m/z 1500 to 3000, **B)** an expanded view of the region between m/z 2000 to 3000 and **C)** expanded view of lower mass region from m/z 300 to 500. Each spectrum is normalized with respect to the most intense peak, and the actual multiplication factor of the intensities as compared to the original full range mass spectrum is indicated in each case. **D)** shows a plot of TIC vs collision energy (V).

Supporting Information 5

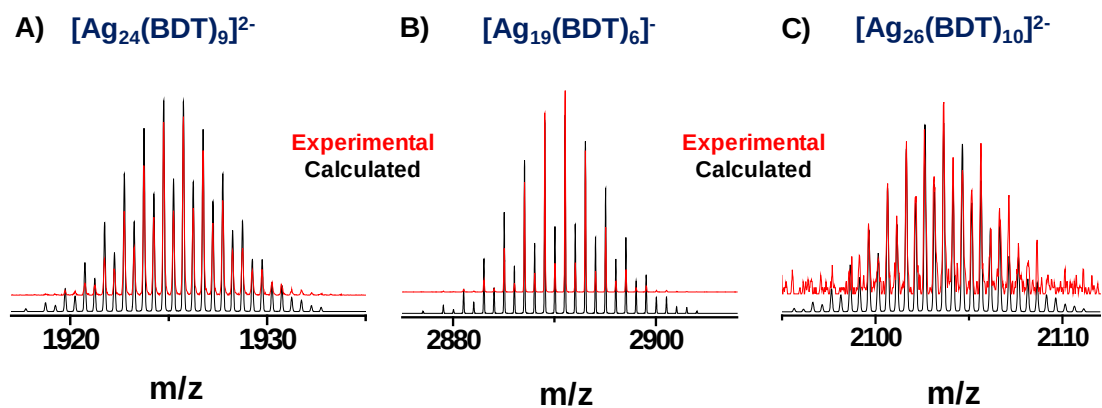


Figure S5: Experimental and calculated mass spectral distributions are shown for **A)** $[\text{Ag}_{24}(\text{BDT})_9]^{2-}$, **B)** $[\text{Ag}_{19}(\text{BDT})_6]^-$ and **C)** $[\text{Ag}_{26}(\text{BDT})_{10}]^{2-}$.

Supporting Information 6

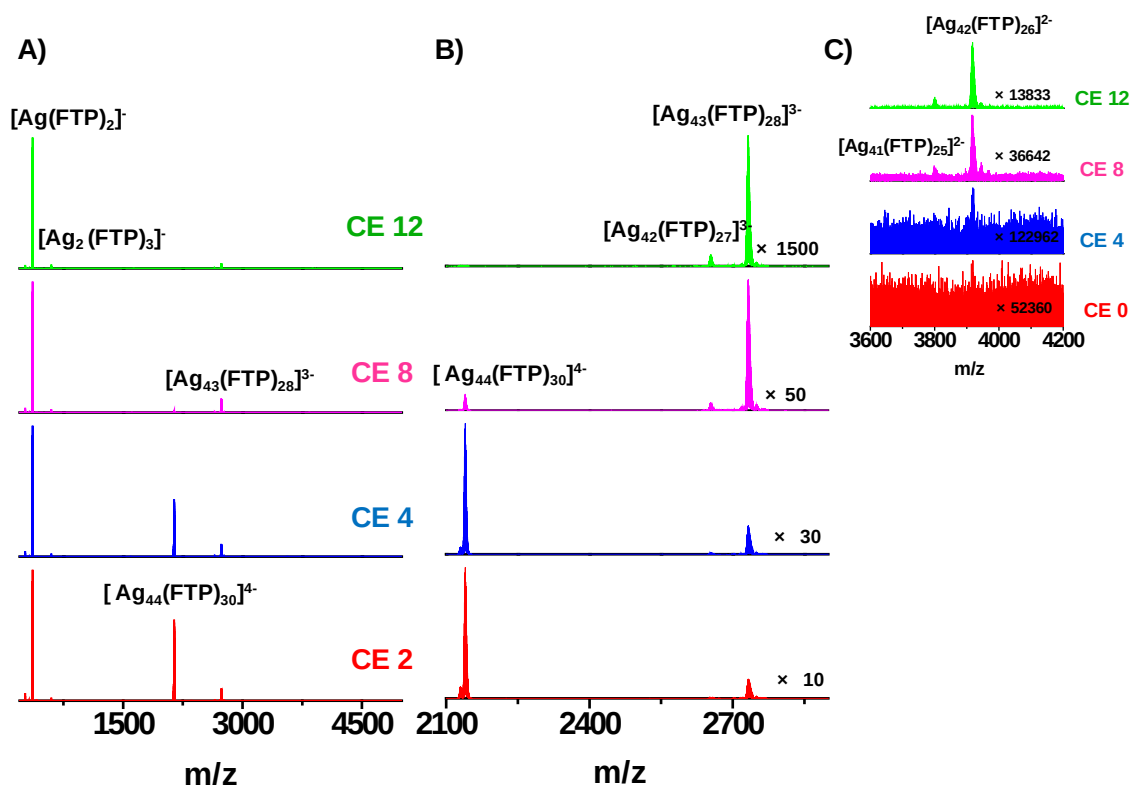


Figure S6: A) MS/MS spectra of $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$, B) an expanded view of the higher mass region between m/z 2100 and 2900, C) species $[\text{Ag}_{42}(\text{FTP})_{26}]^{2-}$ and $[\text{Ag}_{41}(\text{FTP})_{25}]^{2-}$ are detected, although, they are at very low intensities. Each spectrum is normalized with respect to the most intense peak, and the actual multiplication factor of the intensities as compared to the original full range spectrum is also indicated.

Supporting Information 7

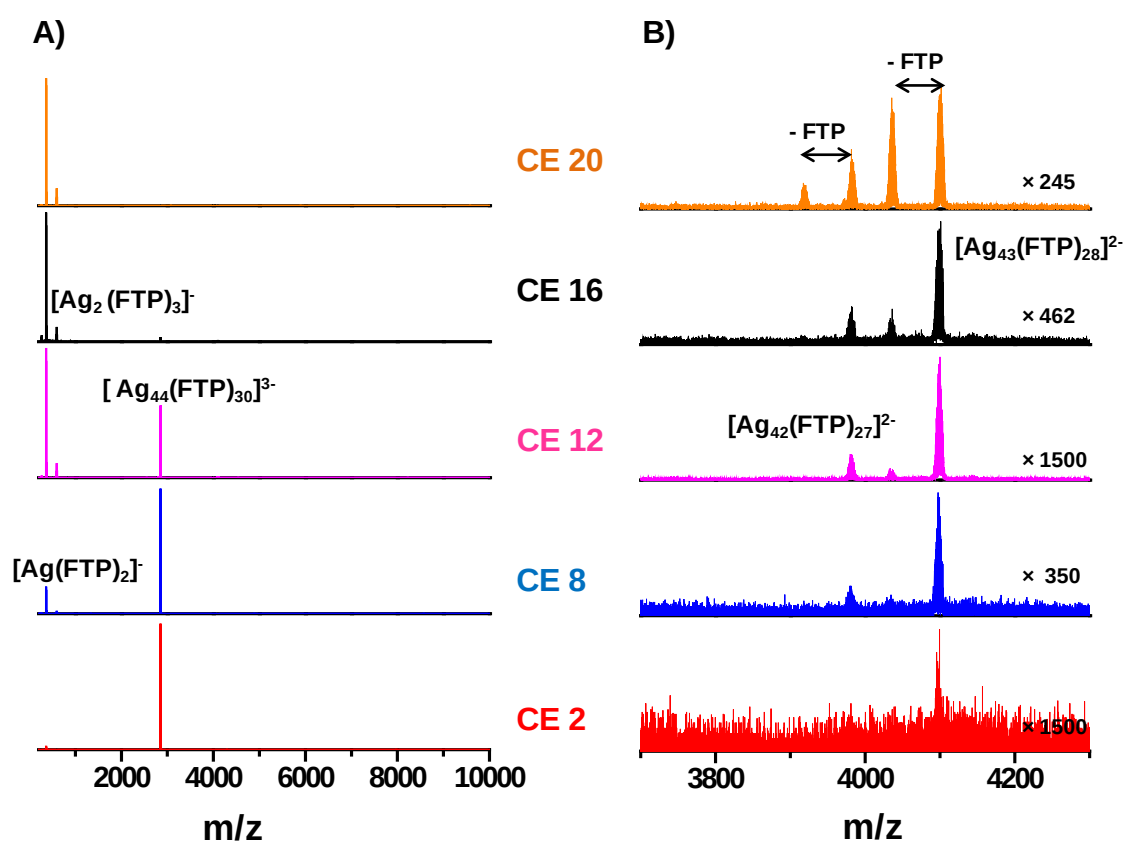


Figure S7: **A)** MS/MS spectra of $[Ag_{44}(FTP)_{30}]^{3-}$ with increasing collision energy and **B)** an expanded view of the region between m/z 3700 and 4300 (multiplication factor of intensities is also indicated).

Supporting Information 8

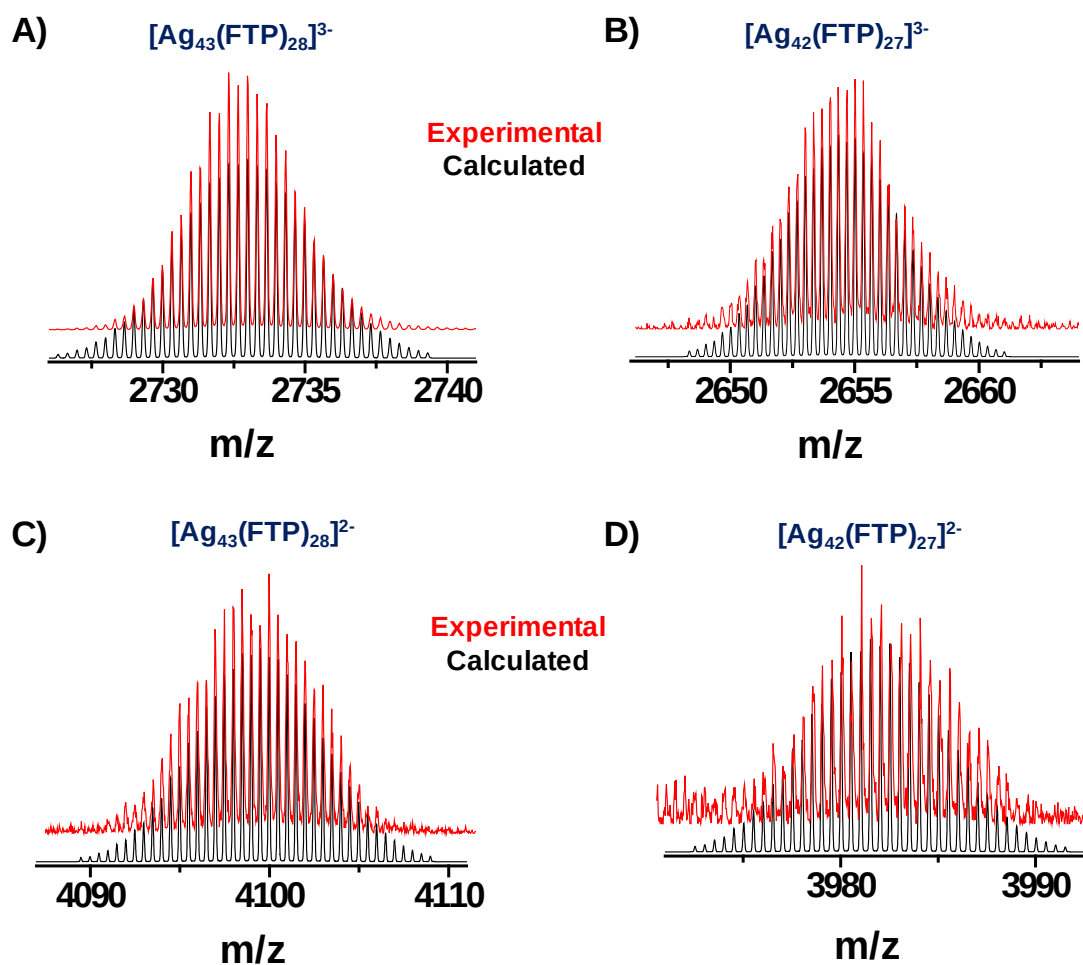


Figure S8: Experimental and calculated isotopic patterns for **A)** $[\text{Ag}_{43}(\text{FTP})_{28}]^{3-}$, **B)** $[\text{Ag}_{42}(\text{FTP})_{27}]^{3-}$, **C)** $[\text{Ag}_{43}(\text{FTP})_{28}]^{2-}$ and **D)** $[\text{Ag}_{42}(\text{FTP})_{27}]^{2-}$.

Supporting Information 9

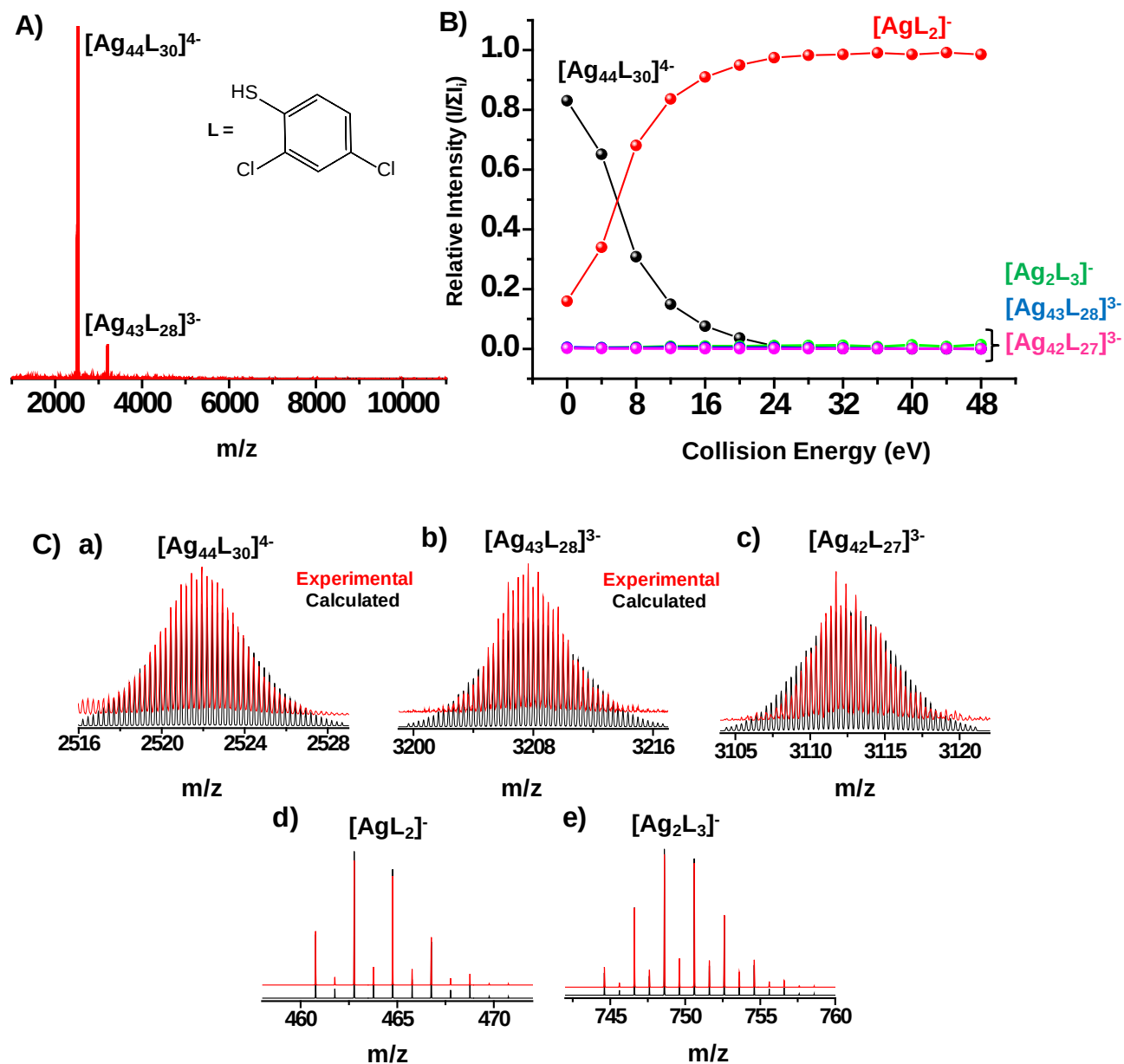


Figure S9: **A)** Full range ESI MS of $[\text{Ag}_{44}(\text{DCBT})_{30}]$ cluster, **B)** Collision energy resolved fragmentation curves of $[\text{Ag}_{44}\text{L}_{30}]^{4-}$ ion. **C)** Experimental and calculated isotopic distributions of **a)** $[\text{Ag}_{44}\text{L}_{30}]^{4-}$, **b)** $[\text{Ag}_{43}\text{L}_{28}]^{3-}$, **c)** $[\text{Ag}_{42}\text{L}_{27}]^{3-}$, **d)** $[\text{AgL}_2]^-$ and **e)** $[\text{Ag}_2\text{L}_3]^-$. (L=2,4-DCBT).

Supporting Information 10

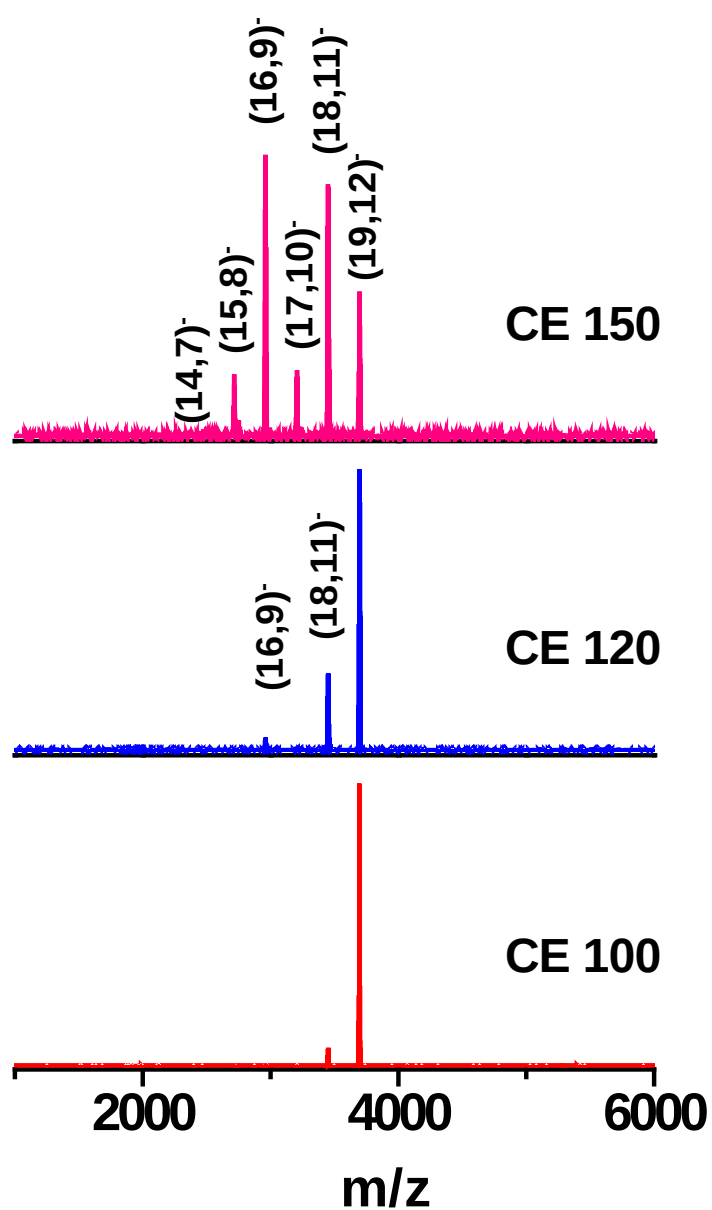


Figure S10: MS/MS at higher collision energies showing fragmentation from $[\text{Ag}_{19}(\text{DMBT})_{12}]^-$. The peaks are labelled as $(x,y)^-$ where 'x' represents the number of Ag atoms and 'y' represents the number of DMBT ligands.

Supporting Information 11

$$\text{Equation : } y = (a-b)/(1 + \exp((x-x_{50})/dx)) + b$$

A) [Ag₂₉(BDT)₁₂]³⁻	Adj. R-Square	0.99867	
		Value	Standard Error
	a	0.99946	0.00704
	b	-9.58389E-4	0.00693
	x ₅₀	71.57234	0.15176
	dx	3.14822	0.13754
B) [Ag₂₅(DMBT)₁₈]⁻	Adj. R-Square	1	
		Value	Standard Error
	a	0.99969	1.95137E-4
	b	3.24014E-4	1.7949E-4
	x ₅₀	53.87215	0.00479
	dx	1.09123	0.00416
C) [Ag₄₄(FTP)₃₀]³⁻	Adj. R-Square	0.99963	
		Value	Standard Error
	a	0.96353	0.00607
	b	-0.00656	0.00417
	x ₅₀	10.8473	0.05218
	dx	1.74467	0.04673

Figure S11: Fitting parameters for the sigmoidal fit of survival yield curves of **A)** [Ag₂₉(BDT)₁₂]³⁻, **B)** [Ag₂₅(DMBT)₁₈]⁻ and **C)** [Ag₄₄(FTP)₃₀]³⁻.

Supporting Information 12

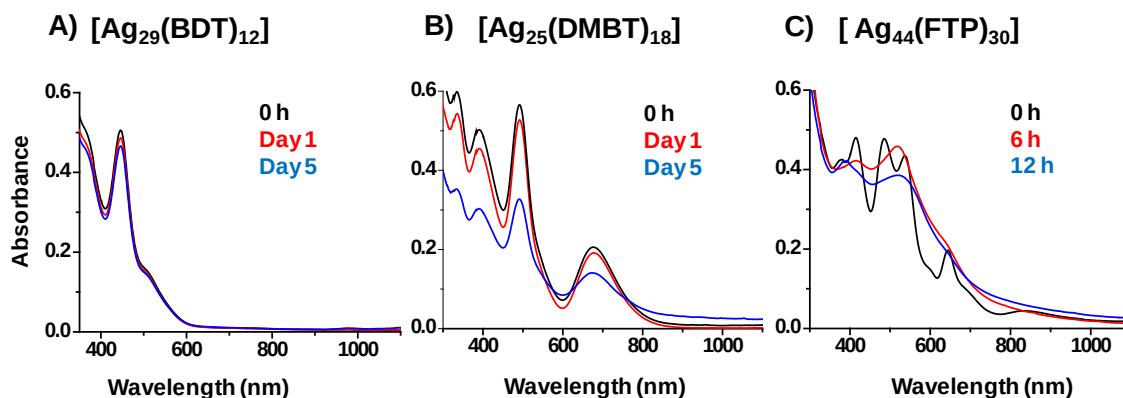


Figure S12: Time dependent UV-vis absorption features of **A)** $[\text{Ag}_{29}(\text{BDT})_{12}]$, **B)** $[\text{Ag}_{25}(\text{DMBT})_{18}]$ and **C)** $[\text{Ag}_{44}(\text{FTP})_{30}]$. The less stability of $[\text{Ag}_{44}(\text{FTP})_{30}]$ is reflected in its absorption features, the characteristic features are lost after about 6 h. Under ambient conditions $[\text{Ag}_{25}(\text{DMBT})_{18}]$ is also less stable compared to $[\text{Ag}_{29}(\text{BDT})_{12}]$, as its absorbance decreases significantly (stability is shown upto 5days).

Supporting Information 13

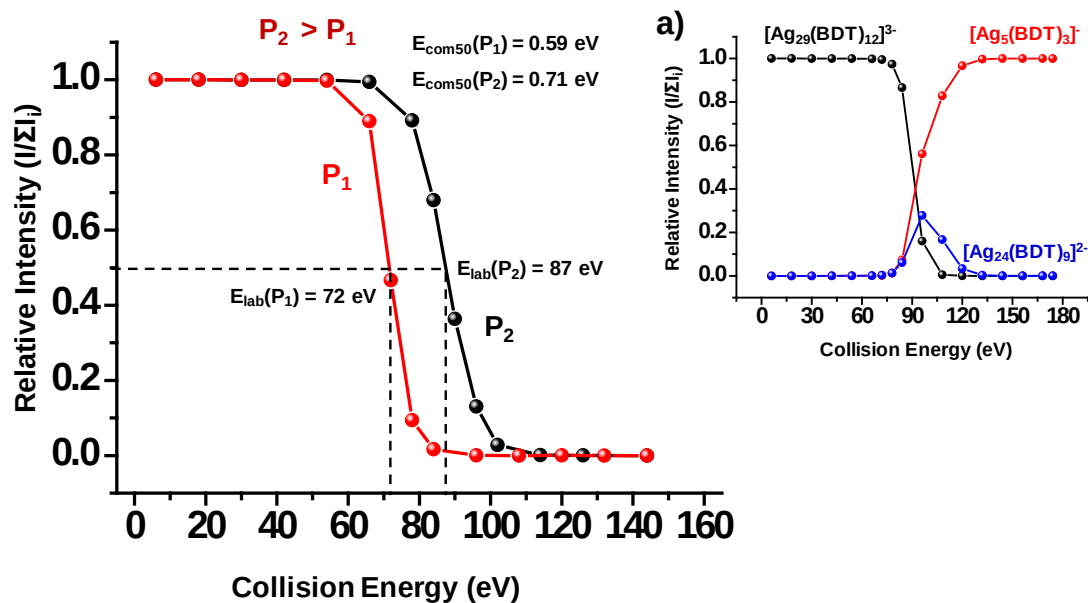


Figure S13: Collision energy resolved fragmentation curves of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster ion at two different pressures. Pressure P_1 is the normal trap pressure (trap gas flow of 2 mL/min) and P_2 is the pressure corresponding to a trap gas flow of 10 mL/min. E_{com50} increases with increase of pressure. There is a slight change in the branching ratios of the fragment ions at higher pressure (trap gas flow of 10 ml/min) as shown in the fragmentation curves in the inset a).

Supporting Information 14

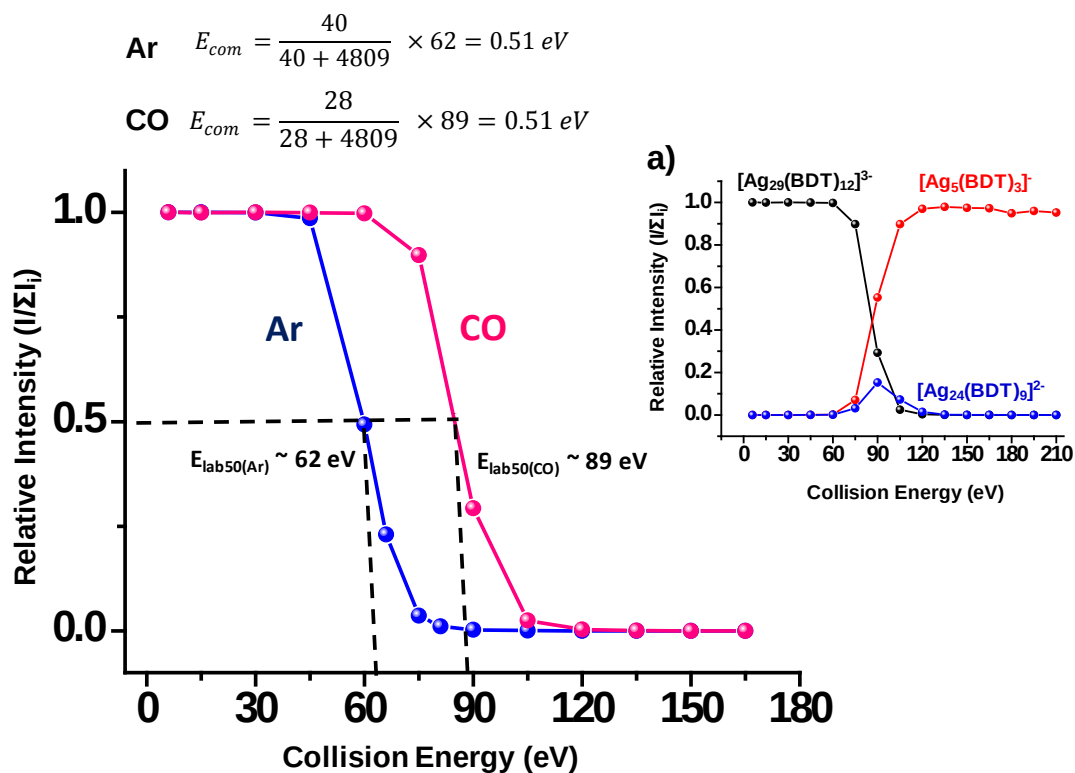


Figure S14: Collision energy resolved fragmentation curves of $[Ag_{29}(BDT)_{12}]^{3-}$ ion in presence of Ar and CO. Higher energy (in laboratory scale) is required for the dissociation in presence of CO but the calculated true energy in the center-of-mass frame is exactly the same for the two gases (conditions were kept as: capillary voltage 3 kV, cone voltage 50 V and trap gas flow 10 mL/min). Collision energy resolved fragmentation curves for the parent as well the fragment ions in presence of CO gas is also shown in inset a).