Supporting Information

Isomerism in Supramolecular Adducts of Atomically Precise Nanoparticles

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Experimental Details

Instrumentation

The UV-vis spectra were measured using a PerkinElmer Lambda 25 UV-vis spectrophotometer. Mass spectrometric measurements were performed in a Waters Synapt G2-Si high-resolution mass spectrometer. NMR measurements were performed using a Bruker 500 MHz NMR spectrometer.

Chemicals

All the chemicals except the clusters were commercially available and used without further purification. Silver nitrate (AgNO₃, 99.9%) was purchased from Rankem, India. Sodium borohydride (NaBH₄), 1,3-benzene dithiol (1,3-BDT), and cyclodextrins (α , β and γ) were purchased from Sigma-Aldrich. Triphenylphosphine (TPP) was purchased from Spectrochem, India. All the solvents, dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), and dimethylformamide (DMF) were of the HPLC grade and were used without further distillation. Deuterated solvents DMF-d7 used for NMR measurements, was purchased from Sigma-Aldrich.

Synthesis of $[Ag_{29}(BDT)_{12}]^{3-}$ cluster

 $[Ag_{29}(BDT)_{12}]^{3-}$ clusters were synthesized following a reported protocol with slight modifications¹. About 20 mg of AgNO₃ was dissolved in a mixture of 10 mL DCM and 2 mL methanol. To this mixture, about 13.5 µL of the 1,3-BDT ligand was added. The reaction mixture was stirred for about 15 mins. Then, about 10.5 mg of NaBH₄ dissolved in 500 µL of ice-cold water was added. The stirring was continued under dark conditions for about 5 h. Then, the mixture was centrifuged, the precipitate was discarded. The clusters were obtained as the orange supernatant. The solution was evaporated by rotary evaporation, the orange residue was washed with methanol and finally dissolved in DMF. The solution was characterized by UV-vis and ESI MS, which confirmed the formation of $[Ag_{29}(BDT)_{12}]^{3-}$ clusters (Figure S1). However, as the clusters were synthesized without the TPP ligands, they were stable only for a few hours.

Synthesis of $[Ag_{29}(BDT)_{12}(CD)_n]^3$ - complexes

Immediately after the synthesis of $[Ag_{29}(BDT)_{12}]^{3-}$ clusters, CDs (α , β and γ) were added separately to the cluster solution in DMF. The addition of CDs increased the stability of the clusters significantly. The reactivity was monitored using UV-vis and ESI MS studies.

ESI MS and IM MS measurements

All mass spectrometric measurements were conducted using a Waters Synapt G2Si High Definition Mass Spectrometer equipped with electrospray ionization (ESI) and ion mobility (IM) separation. All samples were measured in the negative electrospray ionization mode. The instrument was calibrated using NaI as the calibrant. All samples were measured keeping almost the same conditions with slight modification wherever required. Typical experimental parameters were: desolvation gas temperature 150°C, Source temperature: 100°C, Desolvation gas flow: 400 L/h, capillary voltage, 3 kV; sample cone, 80 V; source offset, 80 V; trap collision energy, 2 V; trap gas flow, 2 mL/min; helium cell gas flow, 90 mL/min; IMS gas flow, 60 mL/min; trap DC bias, 40 V; IMS wave height, 35 V and IMS wave velocity, 400 m/s. The collision voltage in the transfer cell was raised until fragmentations were seen properly (4-60 V).The concentration of the sample was 1 μ g/mL and it was infused at a flow rate of 30 μ L/mins. CCS values of the CD-cluster complexes were calculated by taking the cluster as a calibrant and using the previous literature².

Computational Details:

Molecular docking studies have been carried out using AutoDock 4.2 and AutoDock Tools programs³. The crystal structures of $[Ag_{29}(BDT)_{12}]^{3-1}$ and CDs were used for this study. We used CDs as the "ligand" *i.e.* the movable molecule whose rotational and translational degrees of freedom could be varied during the docking. The 'receptor' molecule was $[Ag_{29}(BDT)_{12}]^{3-}$, and this was the fixed and completely rigid central molecule. We assigned partial charges from DFT for all atoms of $[Ag_{29}(BDT)_{12}]^{3-}$. Receptor grids were generated using $126 \times 126 \times 126$ grid points with a grid spacing of 0.375 Å and map types for all the ligand atoms were created using AutoGrid 4.6. The van der Waals radius σ (Å) and well depth ε (kcal/mol) for Ag of 2.63 Å and 4.560 kcal/mol, respectively, were taken from well-tested sources in literature⁴⁻⁵ and these were

added to the Autodock parameter file which does not contain them by default. The grid parameter file (.gpf) was saved using MGL Tools-1.4.6.50. For docking, the docking parameter files (.dpf) were generated using MGLTools-1.4.6.50 and docking was performed using AutoDock4.2. The results of AutoDock generated an output file (.dlg), and the generated conformers were scored and ranked as per the interaction energy. Ten lowest energy conformers were obtained. The structure showing the lowest binding energy between the interacting molecules was used an initial structure for DFT optimization. The free energies of binding were calculated subtracting the unbound energies from the sum of the intermolecular and intetnal energy terms in the adducts, which is a calculation that is performed within the Autodock program.

The PAW set-up was $Ag(4d^{10}5s^1)$, $S(3s^23p^4)$, $C(2s^22p^2)$ and $H(1s^1)$ with scalar-relativistic effects included for Ag. The initial structure of $[Ag_{29}(BDT)_{12}]^{3-}$ was optimized by taking the crystal structure of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$, as reported by Bakr et al. and removing its TPP ligands¹. The geometric optimizations of the supramolecular complexes were mainly carried out using the PBE exchange functional⁶ and a double zeta polarization (DZP) basis set, with a grid spacing of 0.2 Å in LCAO mode⁷, with the convergence criteria as 0.05 eV/Å for the residual forces acting on atoms without any symmetry constraints. Further, the calculated ground state geometry and energy of the complexes were compared with the vdW-DF2 functional⁸. The strength of the interaction between the cyclodextrins and $[Ag_{29}(BDT)_{12}]^{3-}$ cluster was studied by calculating their binding energies by subtracting the sum of energies of isolated $[Ag_{29}(BDT)_{12}]^{3-}$ cluster and CDs from the total energy of the adducts, $[Ag_{29}(BDT)_{12}(CD)_n]^{3-}$. All structures were built up using the Avogadro software package⁹.



Figure S1. A) UV-vis and **B)** ESI MS of $[Ag_{29}(BDT)_{12}]^{3^{-}}$. Inset of **A)** shows the DFT optimized structure of the cluster and inset of **B)** shows the experimental and calculated isotope patterns of $[Ag_{29}(BDT)_{12}]^{3^{-}}$.



Figure S2. A) ESI MS of $[X \cap (CD)_n]^{3-}$ (n = 1 to 4) supramolecular complexes when ratio of X : CD in DMF was 1:4, where X and CD represent $Ag_{29}(BDT)_{12}$ and β -cyclodextrin.



Figure S3. A) ESI MS of $[X \cap (CD)_n]^{3-}$ (n = 1 to 4) supramolecular complexes when the ratio of X : CD in DMF was 1:4, where X and CD represent $Ag_{29}(BDT)_{12}$ and α -cyclodextrin.



Figure S4. A) ESI MS of $[X \cap (CD)_n]^{3-}$ (n = 1 to 4) supramolecular complexes when the ratio of X : CD in DMF was 1:4, where X and CD represent Ag₂₉(BDT)₁₂ and γ -cyclodextrin.



Figure S5. A) ESI MS of $[X \cap (CD)_n]^{3-}$ (n = 1 to 6) supramolecular complexes when the ratio of X : CD in DMF was 1:6, where X and CD represent Ag₂₉(BDT)₁₂ and α -cyclodextrin.



Figure S6. A) ESI MS of $[X \cap (CD)_n]^{3-}$ (n = 1 to 6) supramolecular complexes when the ratio of X : CD in DMF was 1:6, where X and CD represent Ag₂₉(BDT)₁₂ and γ -cyclodextrin.



Figure S7. Collision induced dissociation (CID) of $[X \cap (CD)_4]^{3^-}$, where CD is β -cyclodextrin. With the increase of collision of energy (CE), CD lost from the complex. CE is controlled by applied potential (in V).



Figure S8. Collision induced dissociation (CID) of $[X \cap (CD)_3]^{3-}$, where CD is β -cyclodextrin. With the increase of collision of energy (CE), CD was lost from the complex. CE is controlled by applied potential (in V).



Figure S9. Collision induced dissociation (CID) of $[X \cap (CD)_2]^{3-}$, where CD is β -cyclodextrin. With the increase of collision of energy (CE), CD was lost from the complex. CE is controlled by applied potential (in V).



Figure S10. Collision induced dissociation (CID) of $[X \cap (CD)_1]^{3-}$, where CD is β -cyclodextrin. With the increase of collision of energy (CE), CD was lost from the complex. CE is controlled by applied potential (in V).



Figure S11. Comparison of energy resolved fragmentation of $[X \cap (CD)_1]^{3-}$ complex with different CDs, where CD stands for α , β , & γ -cyclodextrin. With the increase of cavity size, the interaction energy increases.



Figure S12. UV-vis spectra showing slight changes upon addition of β -CD to the Ag₂₉(BDT)₁₂³⁻ indicating that electronic structure of the cluster is almost unaffected by CD complexation. The concentration of the cluster:CD was varied from 1:1 to 1:4 in room temperature.



Figure S13. 1H NMR spectra (500 MHz, 298 K, DMF- d_7) of **a**) only β -CD and **b**) β -CD in the presence of Ag₂₉(BDT)₁₂³⁻.1H NMR spectra showed changes in the resonances for the inner-cavity H-5 and H-3 protons. The peaks with the * marked are also due to H3 and H5 proton and they were showing some changes. The ratio of the concentration of cluster:CD was 1:6. Cyclodextrins are highly symmetric. But when they are encapsulated in a pair of BDT ligands, the symmetry was lost and they were distorted slightly. This will lead to anisotropy in the structure. Because of this anisotropy, H-1 proton could change significantly in NMR after the addition of the cluster.



Figure S14. Structural isomers of octahedral complexes. A) MA_5B does not show any structural isomerism. B) MA_4B_2 shows *cis-trans* isomerism and C) MA_3B_3 shows *fac-mer* isomers.



Figure S15. Drift time of $[X \cap (\beta - CD)_2]^{3-}$ showing the presence of two isomeric structures. The isotopic distributions of the isomers are matching with the calculated spectrum. The CCS values are shown.



Figure S16. Drift time of $[X \cap (\beta - CD)_3]^{3-}$ showing the presence of two isomeric structures. The isotopic distributions of the isomers are matching with the calculated spectrum. The CCS values are shown.



Figure S17. Drift time of $[X \cap (\beta - CD)_4]^{3-}$ showing the presence of two isomeric structures. The isotopic distributions of the isomers are matching with the calculated spectrum. The CCS values are shown.



Figure S18. a) to **c)** Molecular docking lowest energy structures of $[X \cap (CD)_1]^{3-}$ complexes where CD stands for α , β , and γ - CD, respectively.



Figure S19. DFT optimized structure of $[X \cap (\beta - CD)_1]^{3-}$ with binding energy, where CD encapsulates the cluster from the tail side.



Figure S20. A) a), b) and d), f) DFT optimised structures of C/T isomers of $[X \cap (CD)_n]^{3-}$ for n = 2 and 4, respectively and their corresponding CCS values and binding energies are given below. c) and d) The DFT optimized *fac-mer* isomers with binding energies and CCS values.



Figure S21. A) DFT optimized structure of $[X \cap (\beta - CD)_n]^{3-}$ where n = 5 **a**) and 6 **b**) with CCS values and binding energies.

Table S1. Binding energy values

Systems	(PBE) BE (kcal/mol)	(vdw-DF2) BE (kcal/mol)
$[X \cap (\alpha - CD)_1]^{3-}$	- 33.46	- 71.74
$[X \cap (\beta - CD)_1]^{3-}$	- 65.15	- 99.28
$[X \cap (\gamma - CD)_1]^{3-}$	- 69.01	- 145.82
C -[X \cap (β -CD) ₂] ³⁻	- 68.24	- 143.31
T -[X \cap (β -CD) ₂] ³⁻	- 46.78	- 101.48
$fac-[X\cap(\beta-CD)_3]^{3-}$	- 76.31	- 147.01
$mer-[X\cap(\beta-CD)_3]^{3-}$	- 68.42	- 119.02
C -[X \cap (β -CD) ₄] ³⁻	- 76.43	- 100.68
T -[X \cap (β -CD) ₄] ³⁻	- 66.23	- 86.43
$[X \cap (\beta - CD)_5]^{3-}$	- 72.09	- 98.23
$[X \cap (\beta - CD)_6]^{3-}$	- 69.88	- 96.11
Tail-[X∩(β-CD)₁] ³⁻	- 27.21	- 63.65

Table S2. Experimental and theoretical CCS valu	les
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Possible structures	Exp. CCS ($Å^2$)	Calculated CCS by PA ($Å^2$)
$[X \cap (\beta - CD)_1]^{3-}$	438.0	421.0
C - $[X \cap (\beta$ -CD) ₂] ³⁻	526.0	511.0
T -[X \cap (β -CD) ₂] ³⁻	540.0	526.0
fac - $[X \cap (\beta$ -CD) ₃] ³⁻	613.0	586.0
<i>mer</i> -[X \cap (β -CD) ₃] ³⁻	628.0	601.0
C -[X \cap (β -CD) ₄] ³⁻	695.0	660.0
T -[X \cap (β -CD) ₄] ³⁻	724.0	693.0
$[X \cap (\beta - CD)_5]^{3-}$	790.0	744.0
$[X \cap (\beta - CD)_6]^{3-}$	860.0	820.0

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