Supporting Information

Crystallization of a Supramolecular Coassembly of an Atomically Precise Nanoparticle with a Crown Ether

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EXPERIMENTAL SECTION

Materials. All the reagents were commercially available and used without further purification. Silver nitrate (AgNO₃, 99.9%) was purchased from Rankem, India. 1,3-Benzene dithiol (BDT), dibenzo-18-crown-6 (DB18C6) and NaBH₄ were purchased from Sigma Aldrich and triphenyl phosphine (TPP) was purchased from Spectrochem, India. The solvents used, MeOH, DCM, DMF, were of the HPLC grade.

Synthesis of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3}$ cluster. $[Ag_{29}(BDT)_{12}(TPP)_4]^{3}$ cluster was synthesized following a reported protocol.¹ About 20 mg of AgNO₃ was dissolved in a mixture of 5 mL methanol and 10 mL DCM. Then, 13.5 µL of BDT ligand was added to this mixture. The color of the solution turned turbid yellow. The mixture was kept under the stirring condition and shortly after this; 200 mg of PPh₃ dissolved in 1 mL of DCM was added. The solution turned colorless indicating the formation of Ag-S-P complex. After about 15 min, 10.5 mg of NaBH₄ in 500 µL of water was added. The color of the solution turned to dark brown. Gradually the color changed to orange, indicating the formation of the nanoclusters. After 3 h of continuous reaction under dark conditions, the reaction mixture was centrifuged, and the supernatant was discarded. The precipitate was washed repeatedly with methanol to remove all the unreacted compounds and the purified cluster was extracted in DMF.

Crystallization of coassemblies of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3}$ **- clusters with DB18C6.** About 10 mg of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3}$ - cluster and 3 mg of DB18C6 was dissolved in 1 ml of DMF and ~ 2.5 mL of MeOH was allowed to vapor diffuse into the solution. Dark red crystals, suitable for SCXRD, were obtained after a week.

INSTRUMENTATION

Optical absorption measurements were performed in a PerkinElmer Lambda 25 UV-vis spectrophotometer.

A Horiba Jobin Yvon Nanolog spectrometer was used for the photoluminescence measurements in solution. The samples were excited at 450 nm. The excitation and the emission band pass was set at 3 nm.

Emission spectra of crystals were collected in a Witec GmbH, Alpha-SNOM alpha300 S confocal Raman instrument using 532 nm laser as the excitation source. For comparing the luminescence from different crystals, all the parameters like laser power, beam spot size, accumulation time and integration time were kept constant in all cases. The maximum emission intensities were considered to compare the enhancement in luminescence of one crystal with respect to the other. By keeping all the parameters same, number of clusters in the illumination volume will be nearly the same in both (parent and crown ether-included crystals) the cases. Inhomogeneity of the crystal surfaces, if any, are averaged out by multiple measurements.

Mass spectrometric measurements were done with a Waters Synapt G2 Si high resolution mass spectrometer. Measurements were done using the following conditions:

Capillary voltage: 3 kV, Cone voltage: 0 V

Source temperature: 50 °C, Desolvation temperature: 80 °C, Desolvation gas flow: 300 L/h

Single crystal X-ray diffraction data were collected using a Bruker D8 VENTURE APEX3 CMOS. Crystal data and refinement conditions are presented in Table S1. The crystal data has been deposited to The Cambridge Structural Database and the CCDC number: 1888965.



Figure S1. A) UV-vis spectrum of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ cluster. Inset shows the structure of the cluster, B) ESI MS of $[Ag_{29}(BDT)_{12}(TPP)_n]^{3-}$ (n=0-4). Inset shows the comparison of the experimental and theoretical isotopic patterns of $[Ag_{29}(BDT)_{12}]^{3-}$.



Figure S2. Optical images of the crystals of the coassemblies of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ cluster with DB18C6 molecules.



Figure S3. Expanded view of the three DB18C6Na⁺ molecules attached on the cluster surface, showing the coordination of H_2O to Na⁺. The O atoms of H_2O are shown in brown color. The H atoms of H_2O were not resolved from the crystal structure.



Figure S4. Structure of II.



Figure S5. Crystallographic packing of A) I and B) Ag₂₉T, viewed from x-axis.



Figure S6. Crystallographic packing of A) I and B) Ag₂₉T, viewed from z-axis.



Figure S7. Trapping of water molecules inside the crown ether cages. The H_2O molecules are coordinated to Na⁺. The O atoms of H_2O are shown in brown color. The H atoms of H_2O were not resolved from the crystal structure.



Figure S8. Emission from Ag₂₉-DB18C6, Ag₂₉T and Ag₂₉C crystals, excited at 532 nm.



Figure S9. A) Solution-phase emission spectra of Ag_{29} clusters and Ag_{29} -DB18C6 crystals dissolved in DMF, excited at 450 nm. B) Optical absorption spectra of Ag_{29} clusters and Ag_{29} -DB18C6 crystals dissolved in DMF.



Figure S10. Positive mode ESI MS showing the detection of DB18C6Na⁺. The comparison of the theoretical and experimental isotopic distribution patterns of DB18C6Na⁺ is shown in the inset.

Table S1. Crystal structure data

Identification code	Ag29DB18C6	
Empirical formula	C192.63 H181.27 Ag29 Na3 O22.50 P3.29 S24	
Formula weight	6924.53	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 27.424(5) Å	a= 90°
	b = 27.424(5) Å	b= 90°
	c = 57.155(10) Å	$g = 120^{\circ}$
Volume	37225(14) Å ³	
Ζ	6	
Density (calculated)	1.853 Mg/m ³	
Absorption coefficient	2.507 mm ⁻¹	
F(000)	20078	
Crystal size	0.150 x 0.100 x 0.050 mm	1 ³
Theta range for data collection	2.971 to 26.061°	
Theta Tange for data concetion		
Index ranges	-33<=h<=33, -33<=k<=33	3, -70<=l<=66
Index ranges Reflections collected	-33<=h<=33, -33<=k<=33	3, -70<=l<=66
Index ranges Reflections collected Independent reflections	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891]	3, -70<=l<=66
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242°	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 %	3, -70<=l<=66
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi	3, -70<=l<=66 valents
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55	3, -70<=l<=66 valents
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares of	3, -70<=l<=66 valents on F ²
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares of 16328 / 1264 / 893	3, -70<=1<=66 valents on F ²
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F ²	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares o 16328 / 1264 / 893 1.412	3, -70<=1<=66 valents on F ²
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)]	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares of 16328 / 1264 / 893 1.412 R1 = 0.1136, wR2 = 0.320	3, -70<=l<=66 valents on F ²
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data)	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares of 16328 / 1264 / 893 1.412 R1 = 0.1136, wR2 = 0.320 R1 = 0.1834, wR2 = 0.398	3, -70<=1<=66 valents on F ² 61 89
Index ranges Reflections collected Independent reflections Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data) Extinction coefficient	-33<=h<=33, -33<=k<=33 139409 16328 [R(int) = 0.0891] 99.8 % Semi-empirical from equi 0.78 and 0.55 Full-matrix least-squares of 16328 / 1264 / 893 1.412 R1 = 0.1136, wR2 = 0.320 R1 = 0.1834, wR2 = 0.398 n/a	3, -70<=1<=66 valents on F ² 51 89

Details on refinement of crystal structure. From X-ray diffraction two molecules were found in the crystal lattice: $[Ag_{29}(BDT)_{12}(TPP)_4][(DB18C6Na)_3]$ (I) and $[Ag_{29}(BDT)_{12}(TPP)][(DB18C6Na)_3]$ (II). During the initial stages of structure determination itself, when atom Ag1 was omitted from structure, the Fourier map clearly showed two peak positions which could not be refined as a single atom. The refinement results showed two disordered positions for the Ag atom, each showing different connectivity. The structure was carefully explored to find out whether any meaningful disorder or inexplicable connectivity

existed at any other part of the structure. But none could be found, indicating that no other molecule/fragment existed in the lattice.

The quality of diffraction was not sufficient to justify refinement of hydrogen atoms of H_2O molecules. Minor absorption errors coupled with Fourier series termination effects could have resulted in the positive electron densities near the heavy atom positions. Since all the heavy atoms are assigned full occupancy of the site, any minor Fourier electron density at heavy atom sites may be thought as due to small errors in the data.

References

1. AbdulHalim, L. G.; Bootharaju, M. S.; Tang, Q.; Del Gobbo, S.; AbdulHalim, R. G.; Eddaoudi, M.; Jiang, D.-e.; Bakr, O. M., Ag₂₉(BDT)₁₂(TPP)₄: A Tetravalent Nanocluster. *J. Am. Chem. Soc.* **2015**, 137, 11970-11975.