Supporting Information

Dithiol-Induced Contraction in Ag_{14} Clusters and Its Manifestation in Electronic Structure

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Table S1. Bader charges for Ag, S and P atoms in $Ag_{14}DT$ cluster

Ag_6 Inner Shell	Bader Charges (e)
Ag_2	0.171
Ag_5	0.179
Ag_7	0.158
Ag_9	0.170
Ag_{12}	0.184
Ag_{14}	0.157
Average	0.170
Ag_8 Outer Shell	
Ag_1	0.303
Ag_3	0.276
Ag_4	0.304
Ag_6	0.307
Ag_8	0.303
Ag_{10}	0.253
Ag_{11}	0.303
Ag_{13}	0.302
Average	0.294
Sulfur atoms	
S_{15}	-0.282
S_{16}	-0.295
S_{17}	-0.280
S_{18}	-0.279
S_{19}	-0.282
S_{20}	-0.298
S_{21}	-0.281
S_{22}	-0.283
S_{23}	-0.289
S_{24}	-0.294
S_{25}	-0.288
S_{26}	-0.295
Average	-0.287
Phosphorus	
P_{27}	1.550
P_{28}	1.563
P_{29}	1.532
P_{30}	1.537
P_{31}	1.523
P_{32}	1.576
P_{33}	1.505
P_{34}	1.555
Average	1.543

Table S2. Crystal data and structure refinement for Ag14-3.

Identification code	AG14-3	
Empirical formula	C198 H159 Ag14 P9 S12	
Formula weight	4711.87	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 23.9695(12) Å	γ= 90°.
	b = 23.9695(12) Å	β= 90°.
	c = 28.297(2) Å	γ = 120°.
Volume	14079.6(18) $Å^3$	
Z	3	
Density (calculated)	1.667 Mg/m^3	
Absorption coefficient	1.685 mm^{-1}	
F(000)	6996	
Crystal size	0.150 x 0.120 x 0.100 mm^3	
Theta range for data collection	3.485 to 18.033°.	
Index ranges	-20<=h<=20, -20<=k<=20, -24<=l<=24	
Reflections collected	46201	
Independent reflections	2151 [R(int) = 0.3070]	
Completeness to theta = 18.033°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.74 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2151 / 493 / 379	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1184	
R indices (all data)	R1 = 0.1234, wR2 = 0.1455	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.595 and -0.426 $e.Å^{-3}$	

Table S3. Results of elemental analysis of Ag_{14}

Sample	$C_{Exp.}$ (content %)	$C_{cal.}$ (content %)	$H_{Exp.}$ (content %)	$H_{Cal.}$ (content %)	$S_{Exp.}$ (content %)	S_{cal} (content %)
Ag_{14}	48.91	48.54	3.52	3.24	9.11	8.64

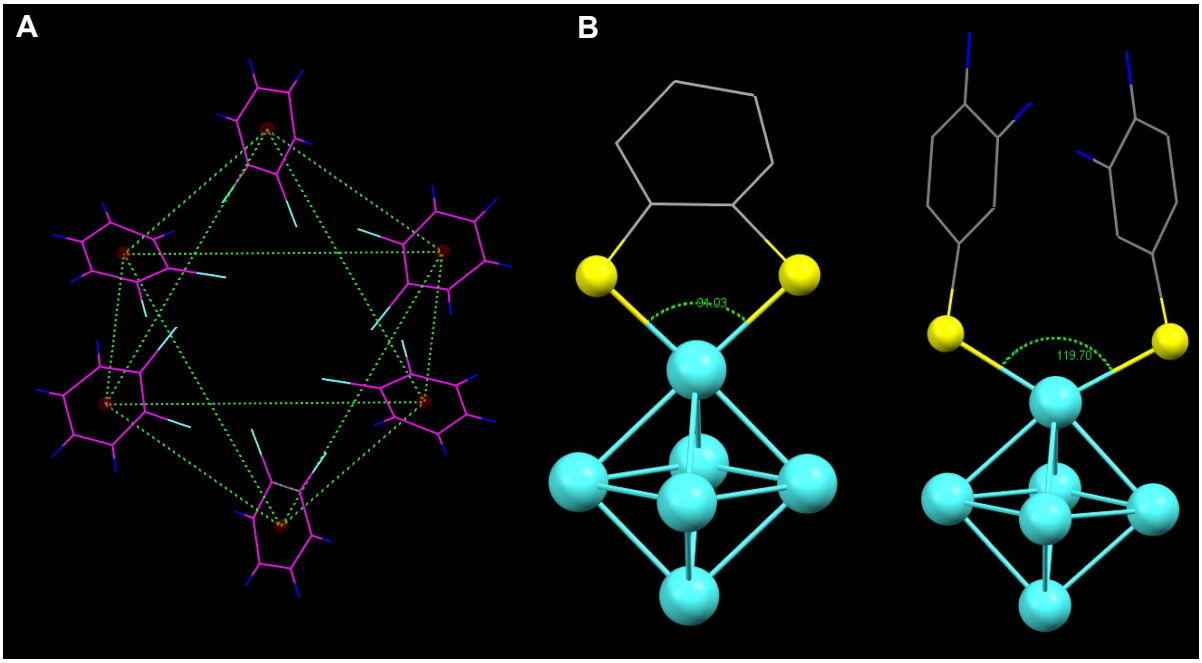

Figure S1 (A) The orientation of the primary ligands in a cluster. Centroids of the six benzenedithiol ligands form an octahedron. Green dotted lines are drawn to show the octahedron. (B) The comparison of the S-Ag-S bond angles in $Ag_{14}DT$ and $Ag_{14}MT$.

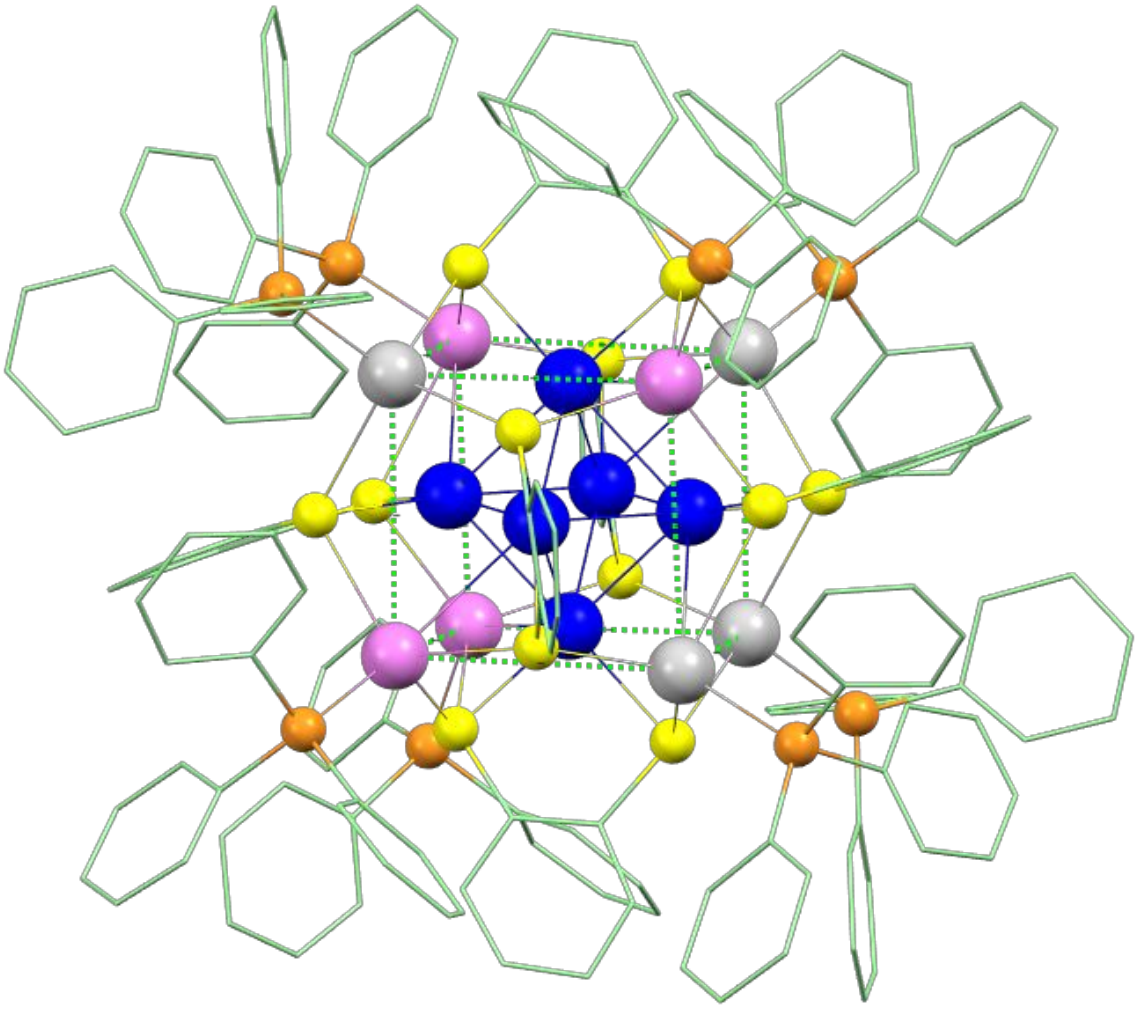

Figure S2 Different environments of silver in Ag_{14} are noted in different colors. Blue shows the inner shell atoms and in outer shell, there are two types of silver atoms as shown in violet and grey.

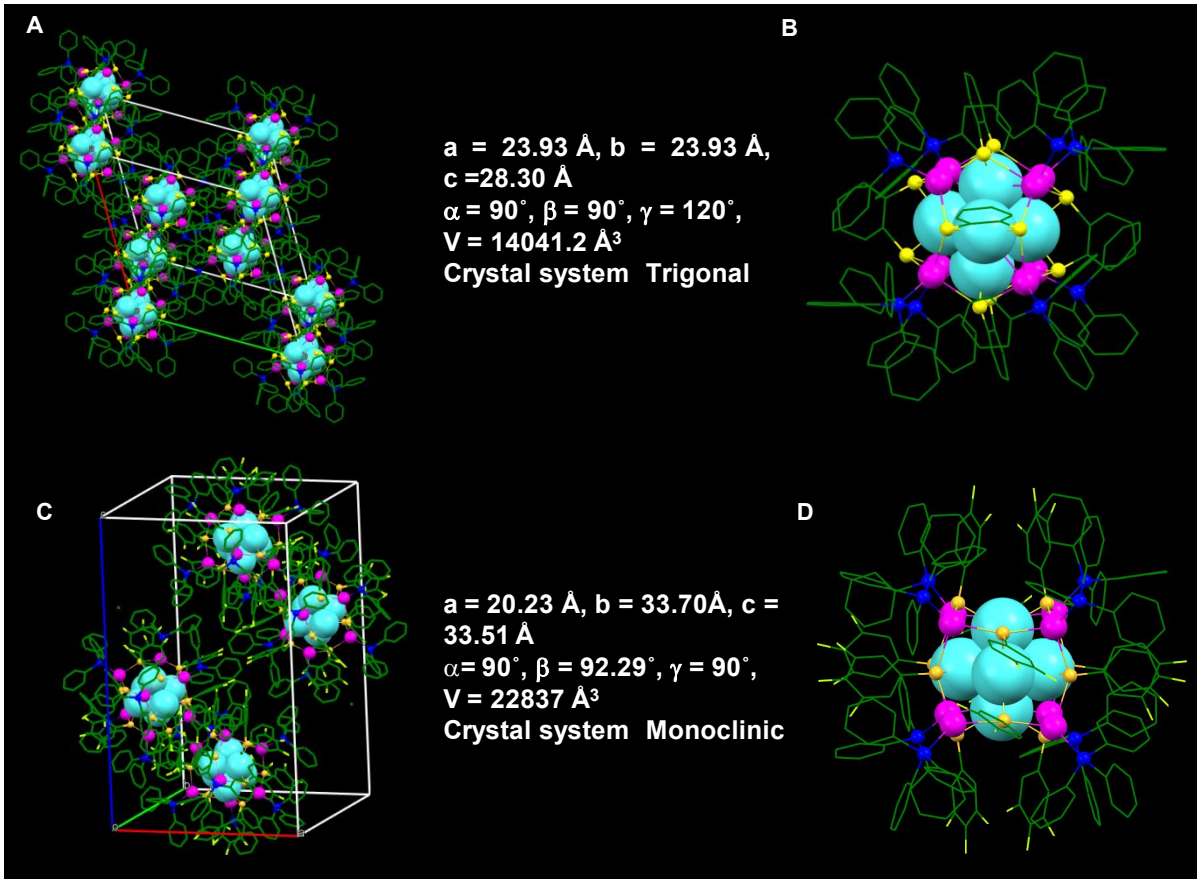

Figure S3 Comparison of crystal structures of Ag_{14} clusters. (A) and (C) Unit cell representations of both the clusters. The number of molecules in a unit cell is not same as evident from the packing. (B) and (D) Full structures of $[Ag_{14}(BDT)_6(PPh_3)_8]$ and $[Ag_{14}(SPhF_2)_6(PPh_3)_8]$, respectively. The octahedral core is shown in space filling and carbon atoms in wireframe model. Hydrogen atoms are omitted for clarity.

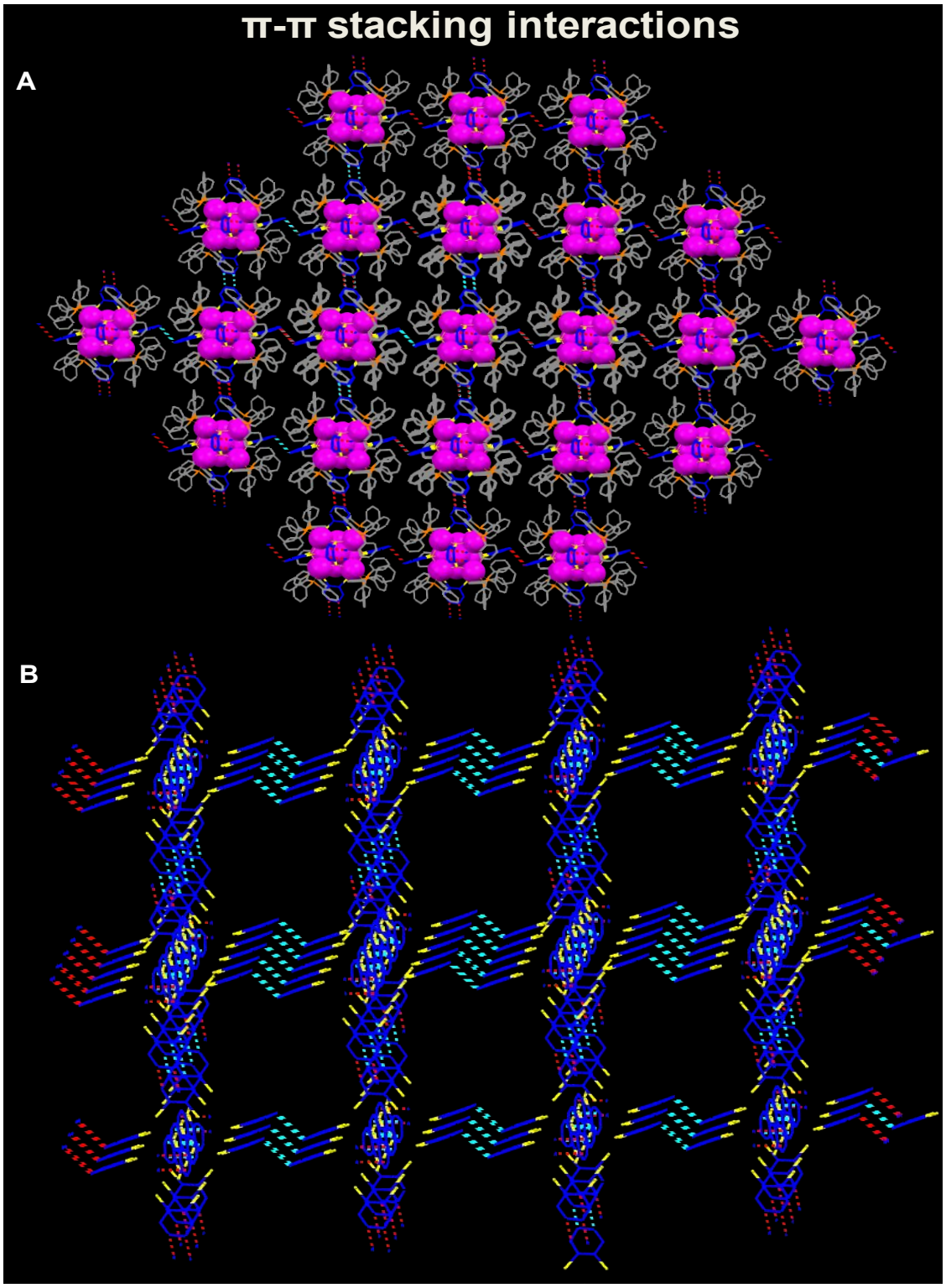

Figure S4 (A) π...π interactions between the benzene rings. BDT are shown in blue. (B) π...π interactions result in the zigzag structure.

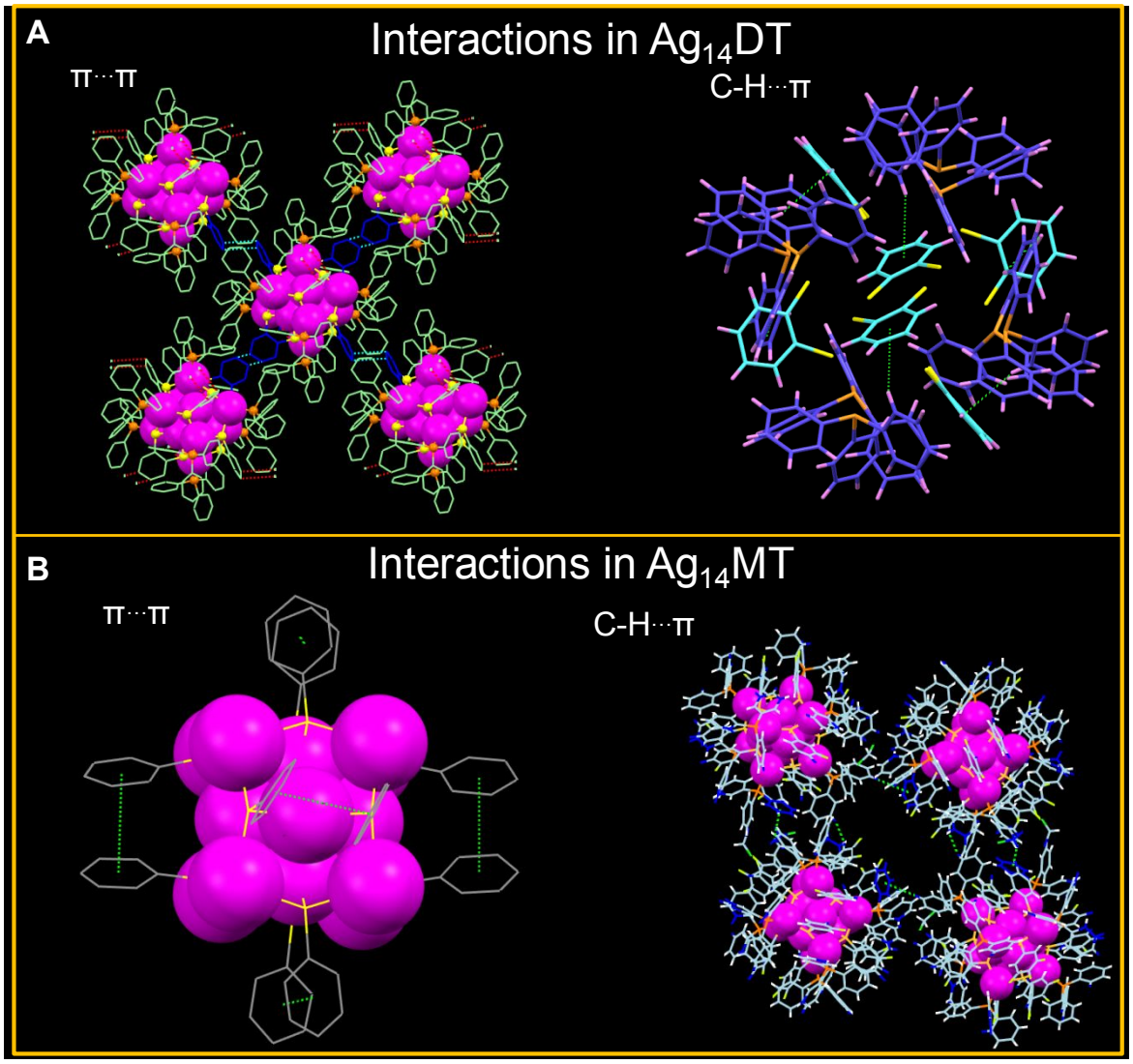

Figure S5 (A) Supramolecular interactions between the clusters. Interactions between the electrons of benzene rings are shown in blue. Intracluster interactions in $Ag_{14}DT$ where C-H…π interactions are shown by green dotted lines. (B) Intercluster interactions in $Ag_{14}MT$. H…H vdw forces and C-H...π interactions are shown by green dotted lines. In $Ag_{14}MT$ π…π interactions are observed in the cluster. The nature of surface structure dictates the supramolecular interactions.

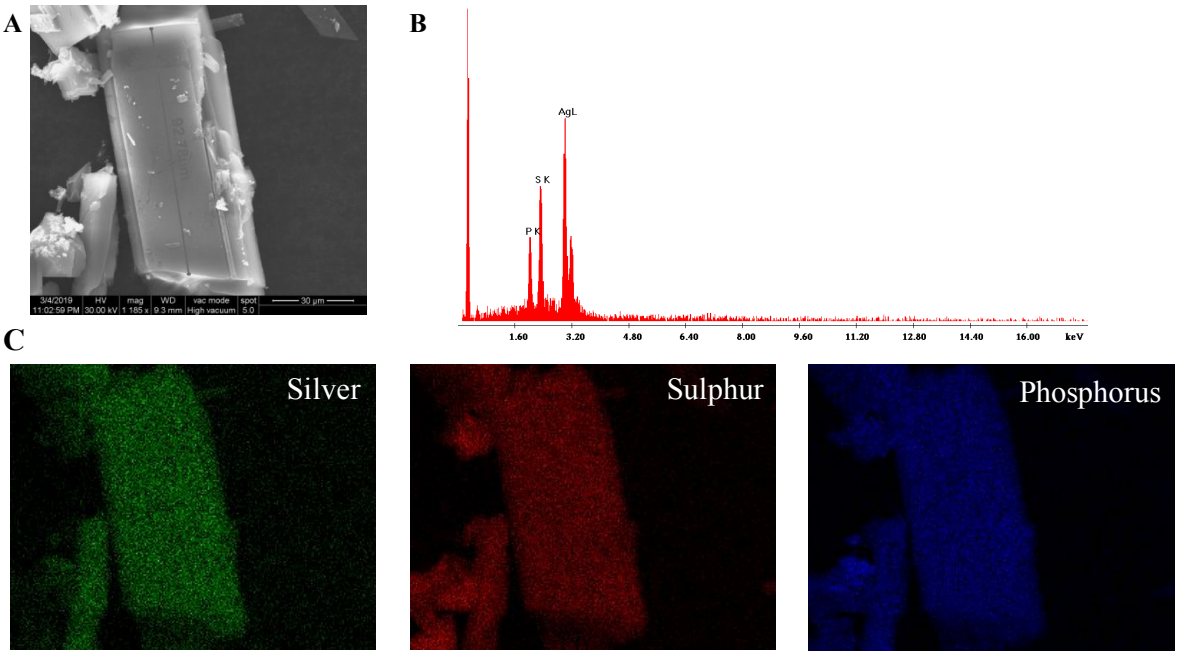

Figure S6 (A) SEM image of the single crystal. (B) SEM EDS shows the presence of Ag, S, and P as major elements. (C) Elemental mapping of the crystal which shows the uniformity of the elements in the crystal.

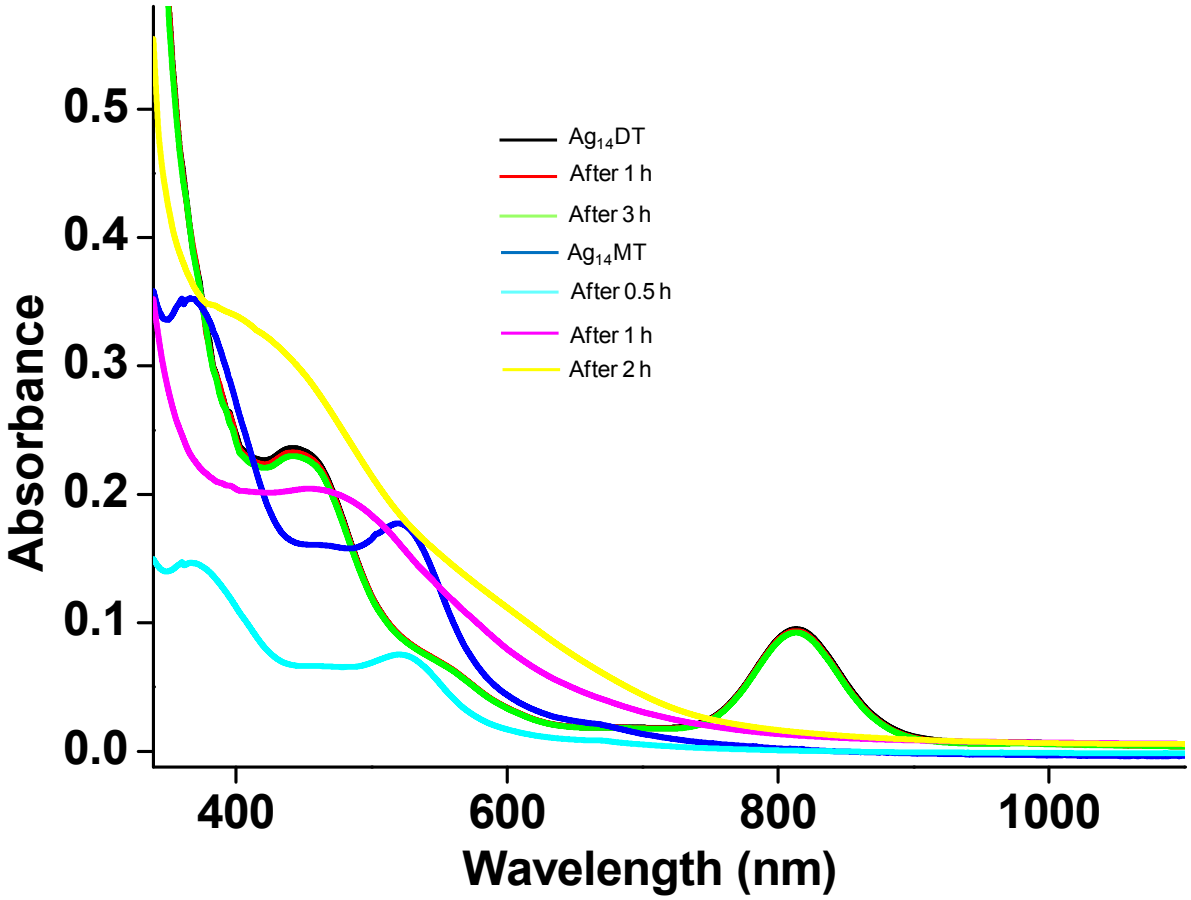

Figure S7 Comparison of thermal stability of $Ag_{14}DT$ and $Ag_{14}MT$ by time-dependent UV/Vis spectroscopy.

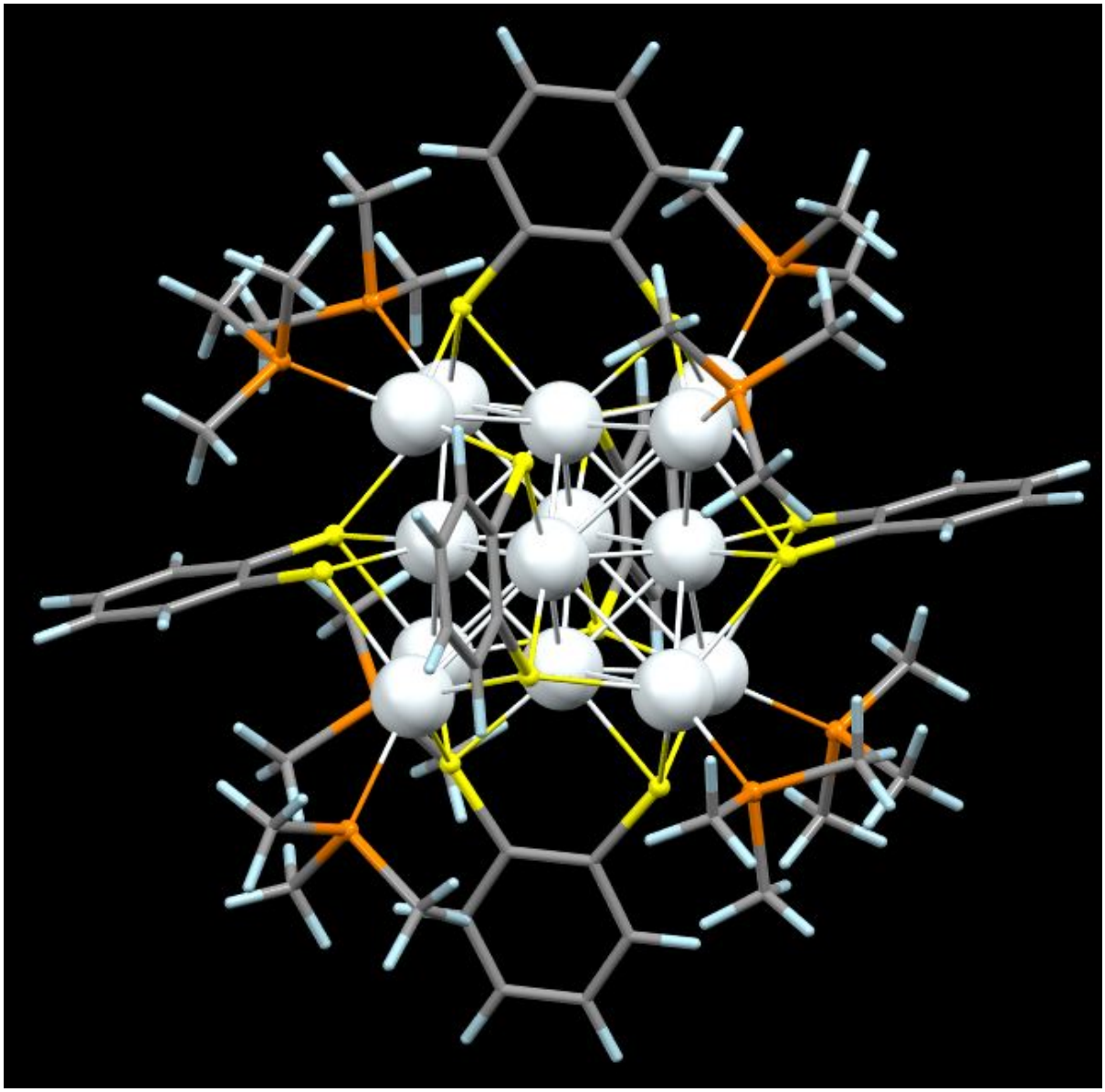

Figure S8 Optimized structure of $Ag_{14}DT$ in reduced ligands. Phenyl rings of the PPh_3 were reduced to $P(CH_3)_3$.

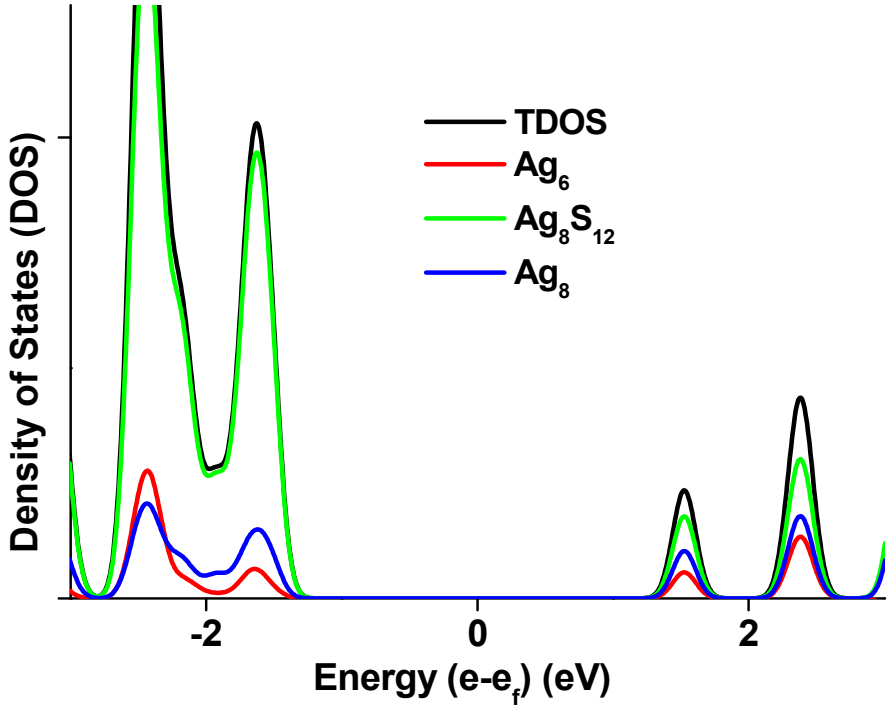

Figure S9 Density of states of inner core and outer shell of Ag_{14} cluster.