Electronic Supplementary Information

Polymorphism of $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$ Cluster: Interactions of Secondary Ligands and Their Effect on Solid State Luminescence

Abhijit Nag[a], Papri Chakraborty[a], Mohammad Bodiuzzaman[a], Tripti Ahuja[a], Sudhadevi Antharjanam[b] and Thalappil Pradeep*[a]

[a] DST Unit of Nanoscience and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India, *Email: pradeep@iitm.ac.in

[b] Sophisticated Analytical Instruments Facility (SAIF), Indian Institute of Technology Madras

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Materials and methods

Chemicals

All chemicals including silver nitrate ($AgNO_3$, 99%), benzene-1,3-dithiol (BDT, 99%), sodium borohydride ($NaBH_4$, 99.99% metals basis), and triphenylphosphine (TPP, 97%) were purchased from Sigma-Aldrich and used without further purification. Solvents including methanol, dichloromethane and DMF were used from Sigma Aldrich as received.

Synthesis of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ cluster: $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ clusters were synthesized following a reported protocol[1] with slight modifications. About 20 mg of $AgNO_3$ was dissolved in a mixture of 2 mL methanol and 10 mL DCM. To this reaction mixture, about 13.5 µL of the 1,3-BDT ligand was added. The mixture was stirred for about 15 mins and then about 10.5 mg of $NaBH_4$ dissolved in 500 µL of ice-cold water was added. The stirring was continued under dark conditions for about 5 h. Then, the reaction mixture was centrifuged, the precipitate was discarded, and 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 $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ clusters (Figure S1).

Crystallization of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ by drop cast method: This was performed following the reported method[1]. The thoroughly dried powder was dispersed in 400 µL of DMF, vortexed for at least 1 min, and then filtered using a syringe filter with a pore size 220 nm. The filtered sample was then spotted on microscope glass plates and left to evaporate slowly at room temperature under air in a dark box placed in a ventilated fume hood. After approximately 2

days, several square dark orange crystals were harvested. We used the reported cubic unit cell throughout the paper.

Crystallization of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ by vapour diffusion method: $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ (10 mg) was dissolved in DMF (1 mL). The solution was filtered and MeOH (ca. 3 mL) was allowed to vapour diffuse into the solution. After 3 months, red orange crystals suitable for X-ray crystallographic analysis were obtained.

Instrumentation

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

Emission spectra were collected in a Witec GmbH, Alpha-SNOM alpha300 S confocal Raman instrument equipped with 532 nm laser as the excitation source.

X-ray Crystallography

Single crystal data were measured using a Bruker D8 VENTURE APEX3 CMOS diffractometer using Cu*K*α (λ = 1.54178 Å). Indexing was performed using APEX3. Data integration and reduction were performed using SaintV8.37A. Absorption correction was performed by multi-scan method implemented in SADABS. Space group was determined using XPREP implemented in APEX3. Structure was solved using Direct Methods (SHELXT-2014) and refined using SHELXL-2014 (full-matrix least-squares on *F*2) contained in WinGX v1.80.05. Crystal data and refinement conditions are shown in Table S1. The crystal data has been deposited to the Cambridge Structural Database and the CCDC number: 1812439.

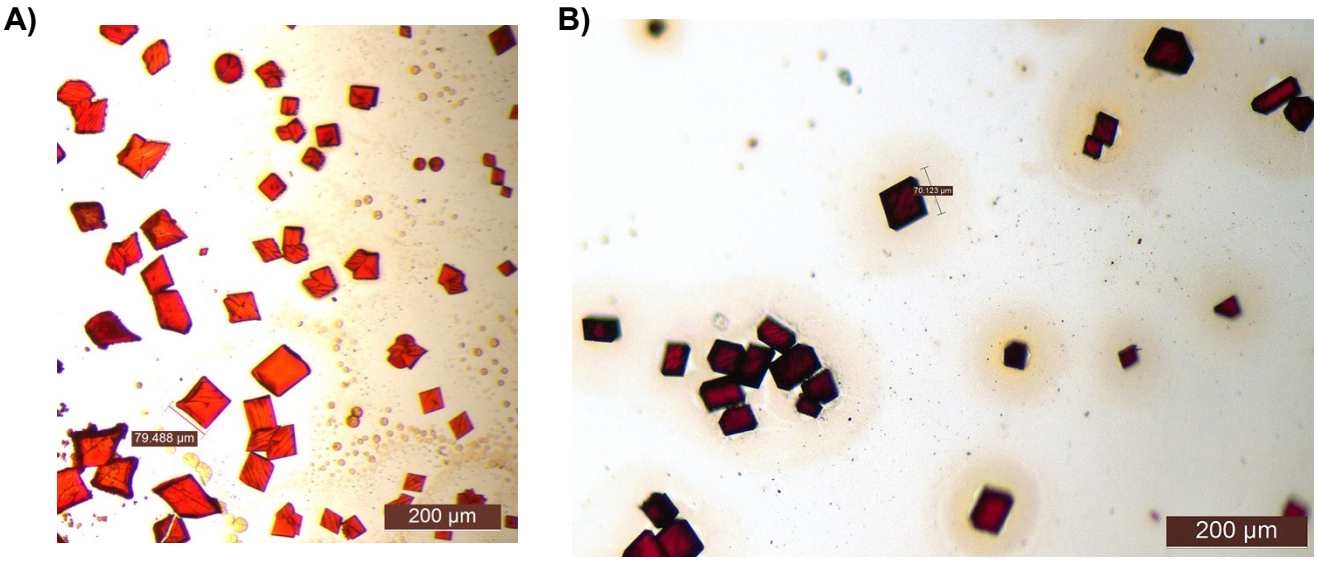

Fig. S1. Optical images of the crystals **A)** Cubic and **B)** Trigonal unit cells. Note that from optical images, crystal systems could be distinguished.

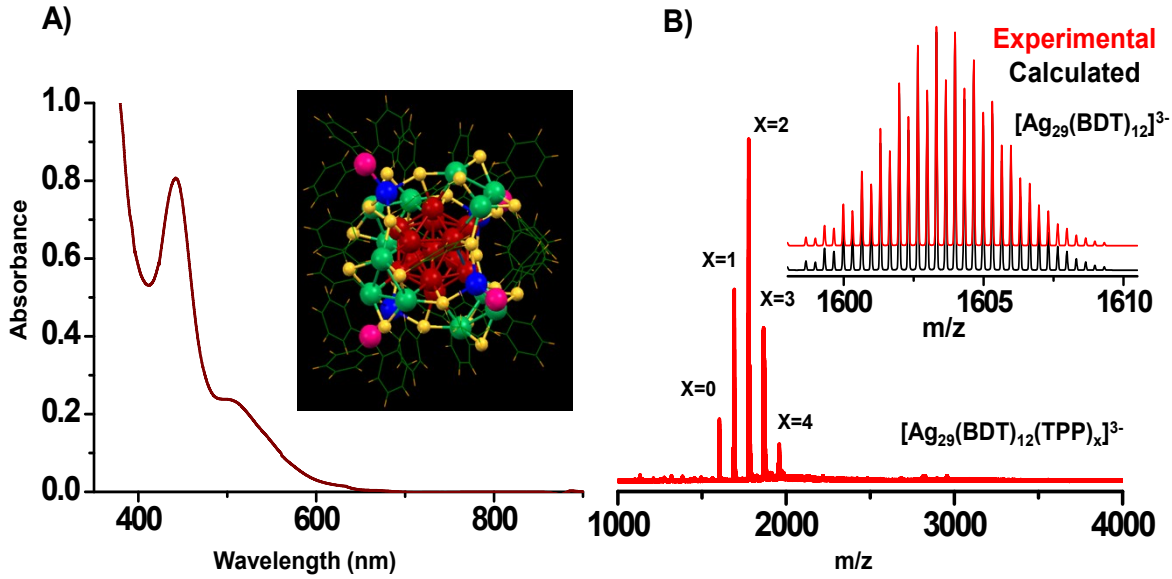

Fig. S2. A) UV-vis and **B)** ESI MS of $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$. Inset of **A)** shows the DFT optimized structure of cluster and inset of **B)** shows the experimental and calculated isotope patterns of $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$. MS measurement results in the sequential loss of TPP during ionization, marked as X = 0 to 4.

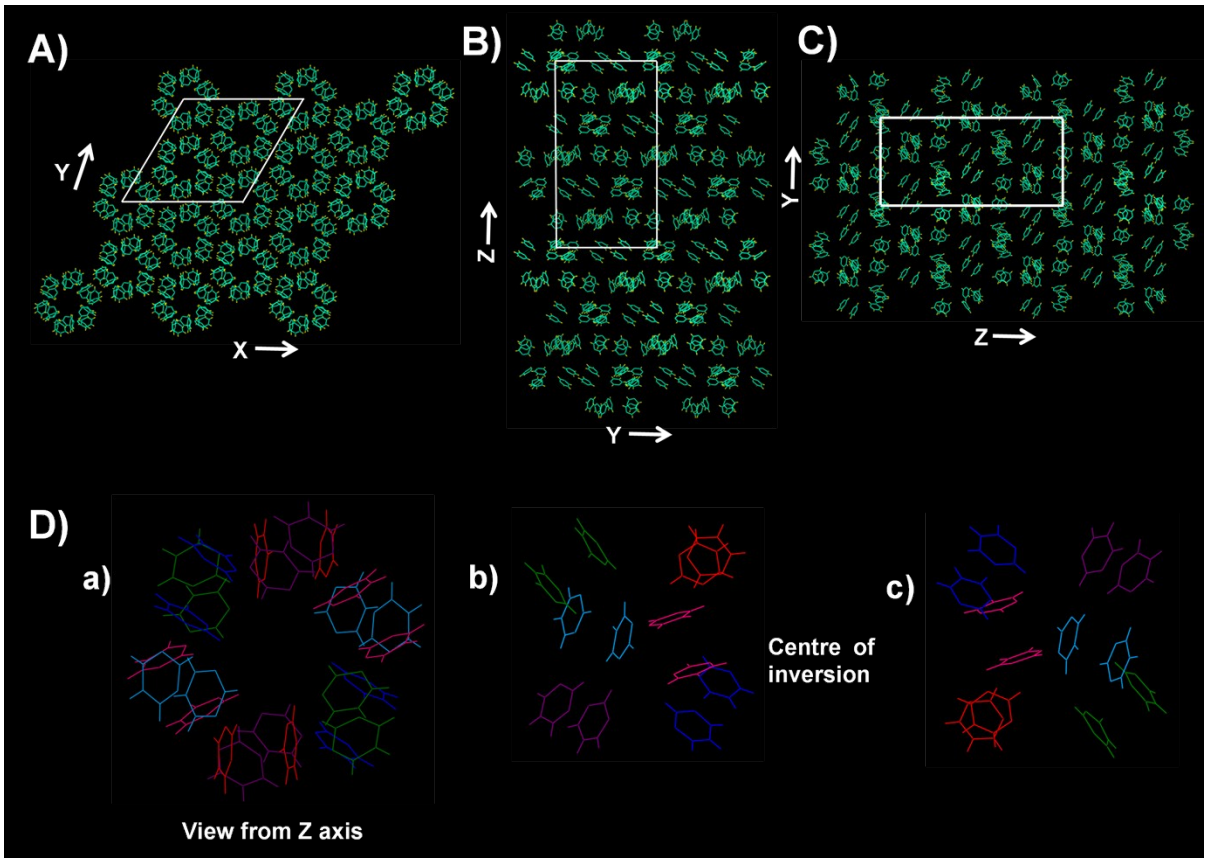

Fig. S3. Packing of the BDT ligands, viewed from, **A)** Z-axis, **B)** Y-axis and **C)** X-axis. **D) a)** View of the cluster packing from Z-axis. Two NCs formed two different (001) and (00-1) layered planes. **b)** and **c)** are the BDT ligands of the two different clusters of **a)**. They have a center of inversion.

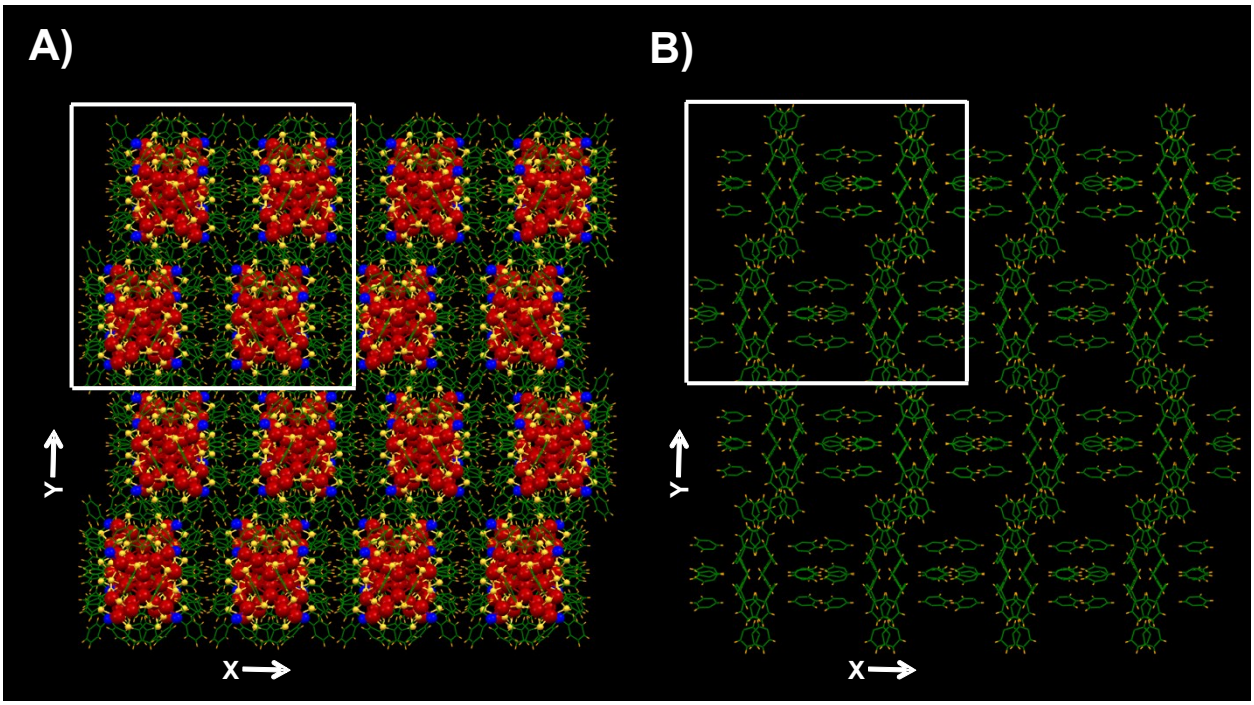

Fig. S4. Packing of the A) cluster and B) BDT ligands, viewed from Z-axis of the cubic unit cell.

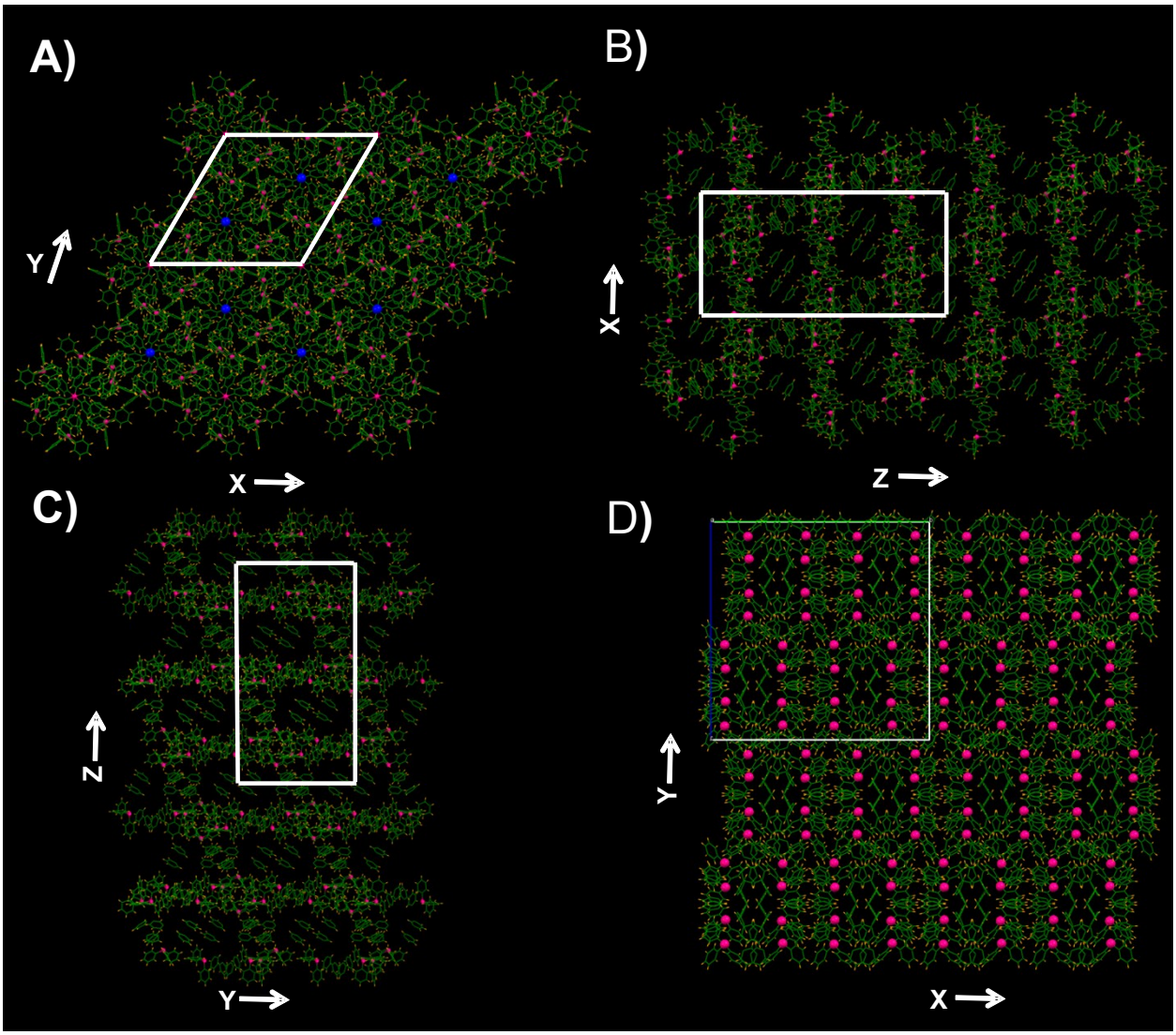

Fig. S5. Packing of the BDT and TPP ligands viewed from, **A)** Z-axis, **B)** Y-axis and **C)** X-axis of the trigonal unit cell. **D)** Packing of the BDT and TPP ligands viewed from the Z-axis of the cubic system.

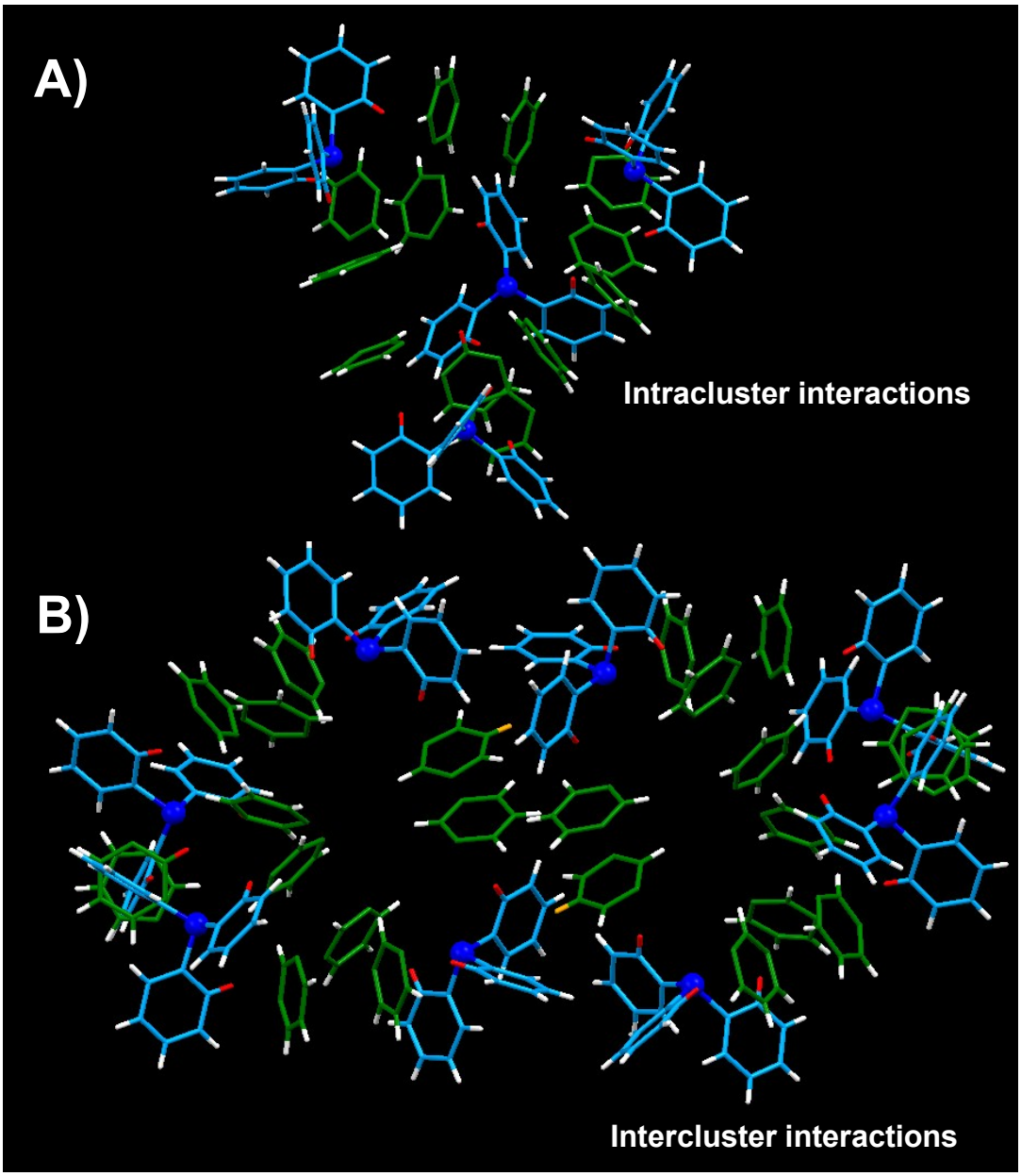

Fig. S6. A) Intracluster and **B)** Intercluster C-H···π interactions between the BDT and TPP ligands for both the systems. The red and orange colored hydrogens represent the intracluster and intercluster interactions, respectively with the nearest benzene ring.

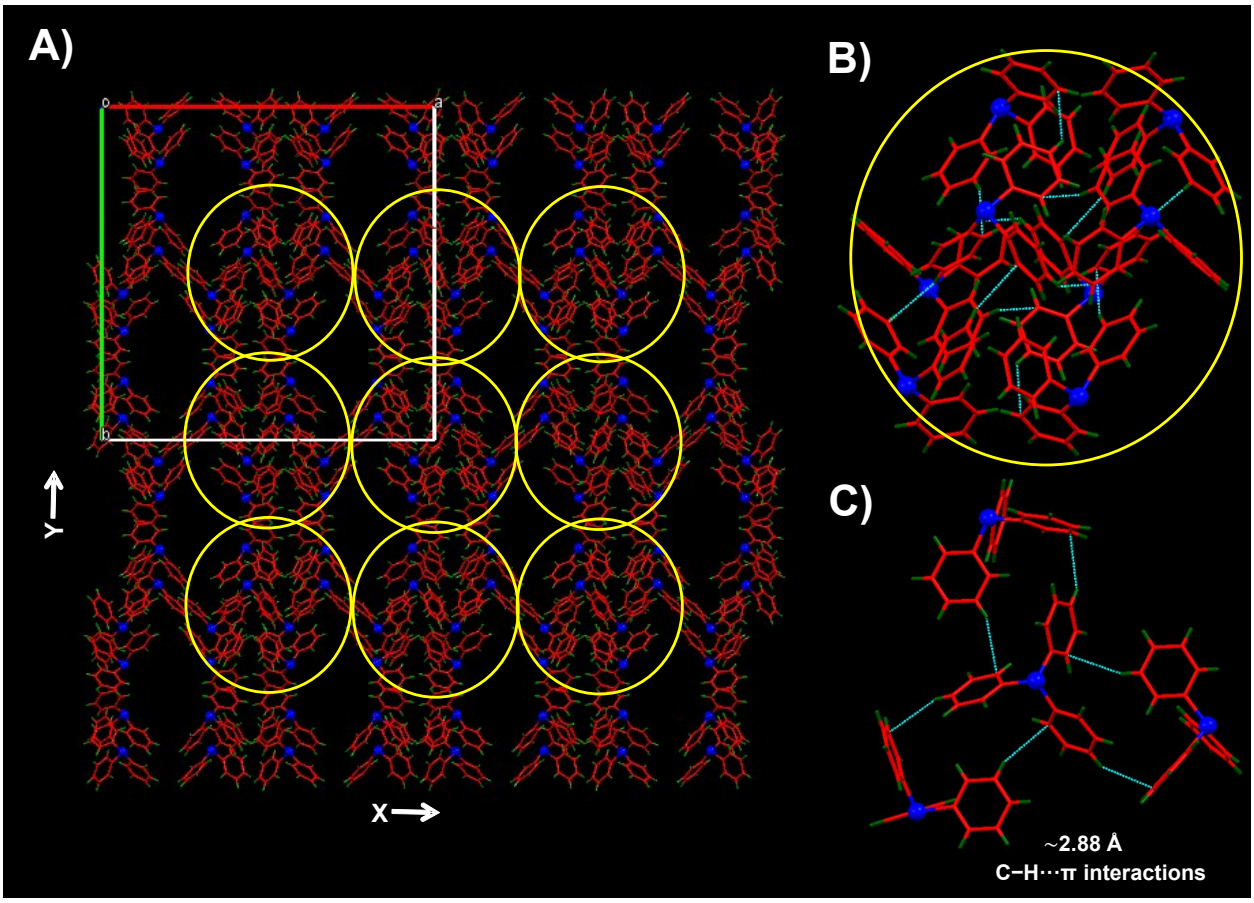

Fig. S7. A) Packing of the TPP ligands viewed from, Z-axis. **B)** An expanded view of the yellow circle. **C)** C-H···π interactions between the TPP ligands.

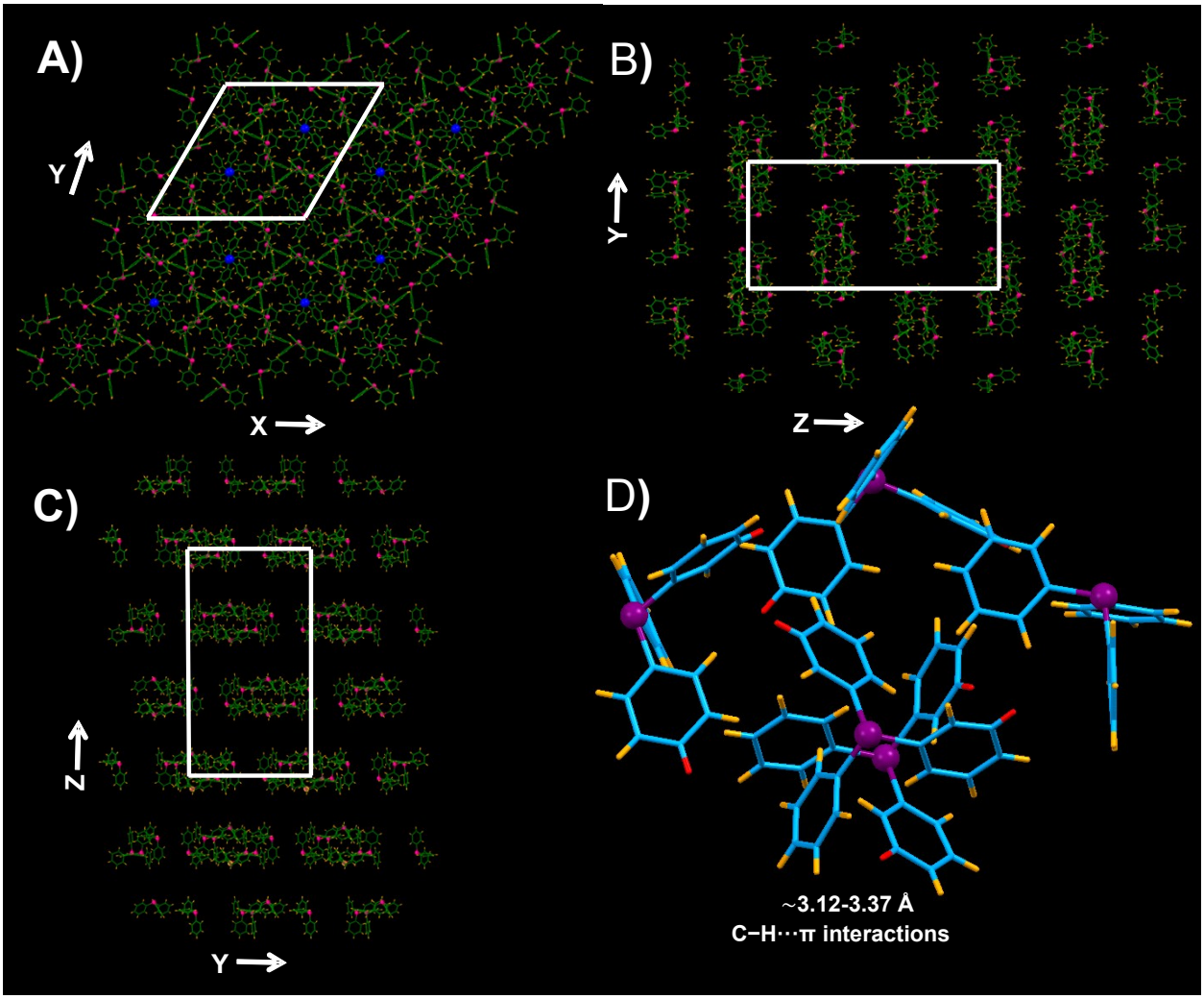

Fig. S8. Packing of the TPP ligands viewed from, **A)** Z-axis, **B)** Y-axis and **C)** X-axis of the trigonal unit cell. **D)** C-H···π interactions between the TPP ligands. The red color hydrogens represent the interactions with the nearest benzene ring.

Table S1. Crystal data and structure refinement

Identification code	AG29R3
Empirical formula	C159 H108 Ag29 N3 O10 P4 S24
Formula weight	6242.03
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system	Trigonal
Space group	R-3
Unit cell dimensions	a = 27.4634(6) Å α = 90°. b = 27.4634(6) Å β = 90°. c = 46.6552(16) Å γ = 120°.
Volume	30474.7(17) $Å^3$
Z	6
Density (calculated)	2.041 Mg/m^3
Absorption coefficient	24.818 mm^{-1}
F(000)	17820
Crystal size	0.150 x 0.100 x 0.100 mm^3
Theta range for data collection	3.218 to 46.668°.
Index ranges	-25<=h<=25, -25<=k<=25, -43<=l<=43
Reflections collected	173079
Independent reflections	5939 [R(int) = 0.3629]
Completeness to theta = 46.668°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7451 and 0.3859
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5939 / 210 / 662
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0768, wR2 = 0.1520
R indices (all data)	R1 = 0.1609, wR2 = 0.1907
Extinction coefficient	n/a
Largest diff. peak and hole	0.910 and -0.686 $e.Å^{-3}$

References

[1] L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D.-e. Jiang, O. M. Bakr, *J. Am. Chem. Soc.* **2015**, *137*, 11970-11975.