

Electronic supplementary information

Secondary ligand-induced orthogonal self-assembly of silver nanoclusters into superstructures with enhanced NIR emission

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Serial EM and electron tomography reconstruction: The image acquisition was performed using a JEOL JEM-3200FSC field emission TEM operated at 300 kV with an Omega-type zero-loss filter. The tilt series of 2D projections (between $\pm 69^\circ$ angles with 2° increment steps) were recorded using SerialEM software.¹⁻³ The pre-alignment and final alignment were performed using IMOD software.⁴ Finally, the maximum entropy method (MEM),⁵ was used with a custom-made program with a regularization parameter value of $\lambda = 1.0\text{e}^{-3}$ for reconstruction and colored tomograms were prepared using Chimera software.

ESI MS conditions

Sample concentration: 10 $\mu\text{g}/\text{mL}$

Solvent: DCM/TCM/DMF

Flow rate: 30 $\mu\text{L}/\text{min}$

Capillary voltage: 2 kV

Source temperature: 50°C

Sampling cone: 0

Source offset: 0

Desolvation temperature: 65°C

Desolvation gas flow: 400.0 L/h

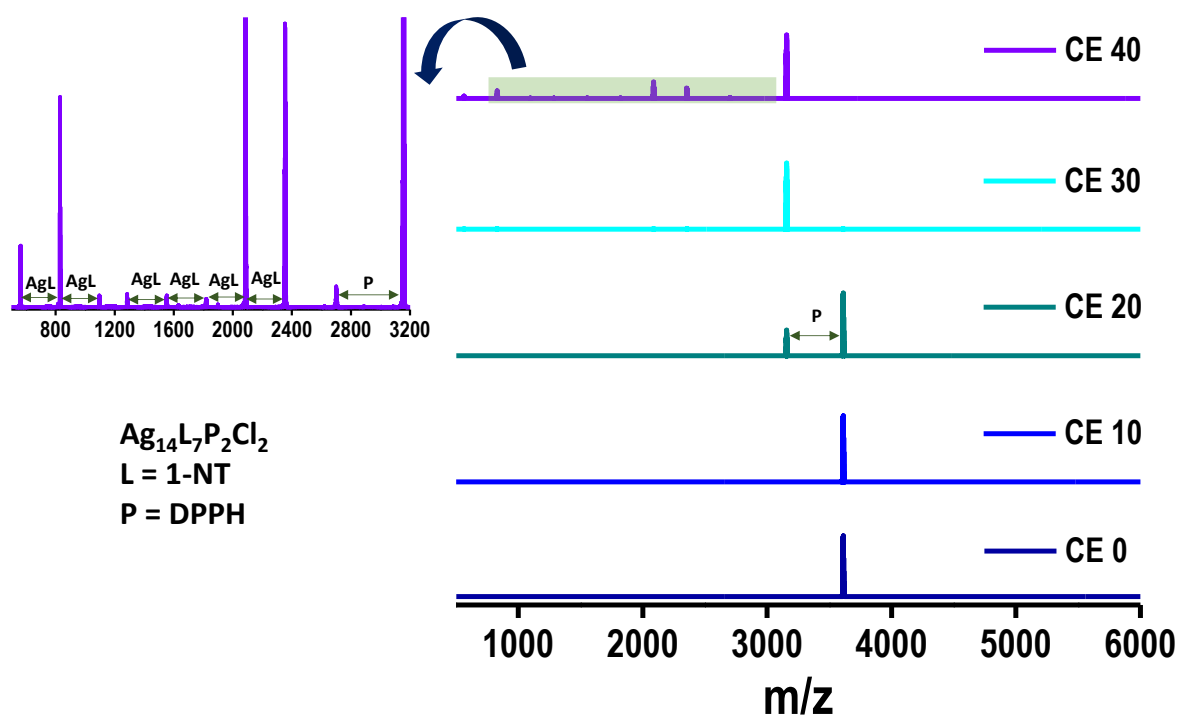


Fig. S1 A) Collision-induced dissociation (CID) mass spectra of the peak which is assigned as $[\text{Ag}_{14}(\text{NT})_7(\text{DPPH})_2\text{Cl}_2]^+$. The systematic loss of two DPPH ligands upon the increase in collision energy was observed along with the loss of some Ag-L.

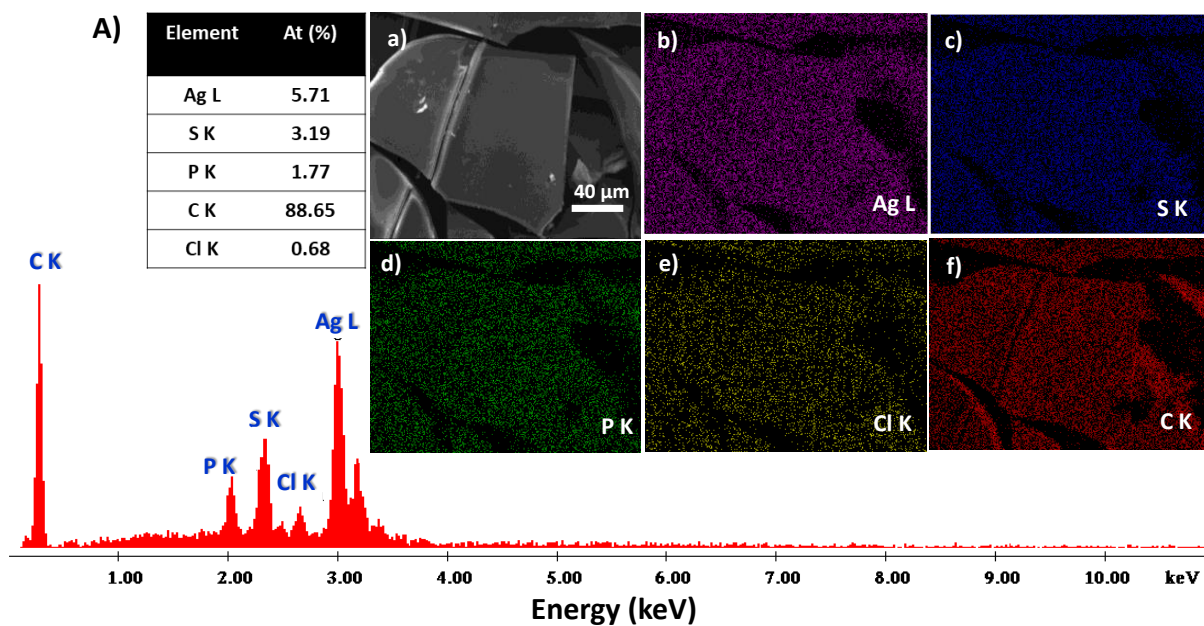


Fig. S2 A) SEM image and EDS mapping of b) Ag L, c) S K, d) P K, e) Cl K, and f) C K.

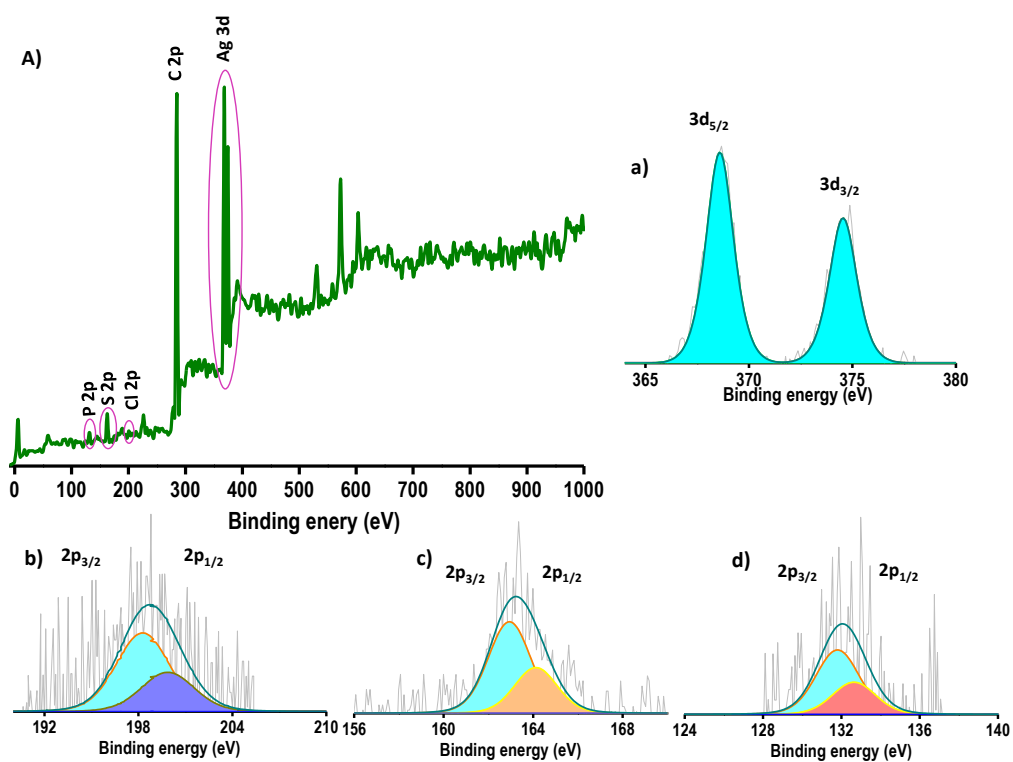


Fig. S3 A) XPS survey spectrum of $[\text{Ag}_{14}(\text{NT})_7(\text{DPPH})_2\text{Cl}_2]^+$. Expanded area of a) Ag 3d, b) Cl 2p, c) S 2p, and d) P 2p.

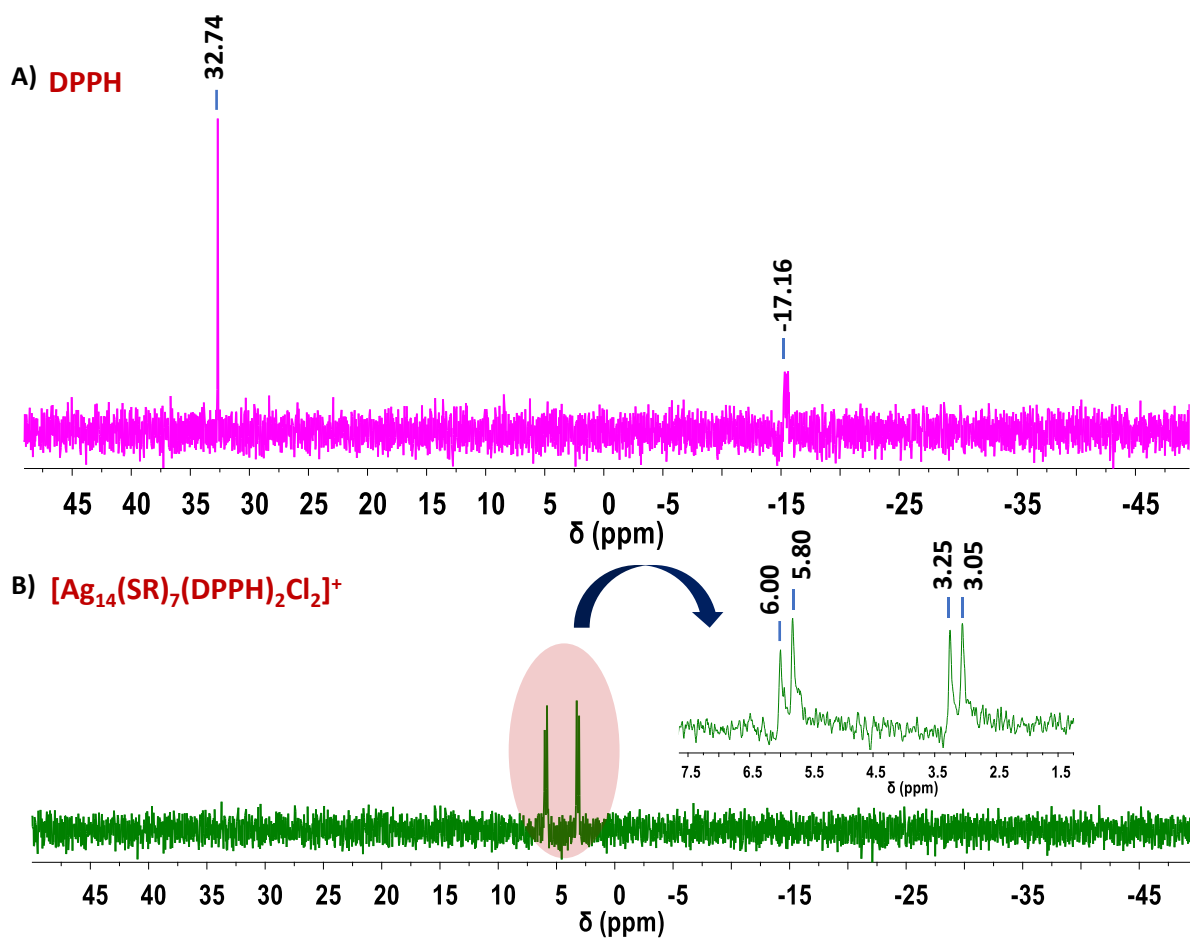


Fig. S4 The ^{31}P NMR spectra of A) DPPH and B) $[\text{Ag}_{14}(\text{NT})_7(\text{DPPH})_2\text{Cl}_2]^+$ NCs confirm the formation of Ag-P bonds.

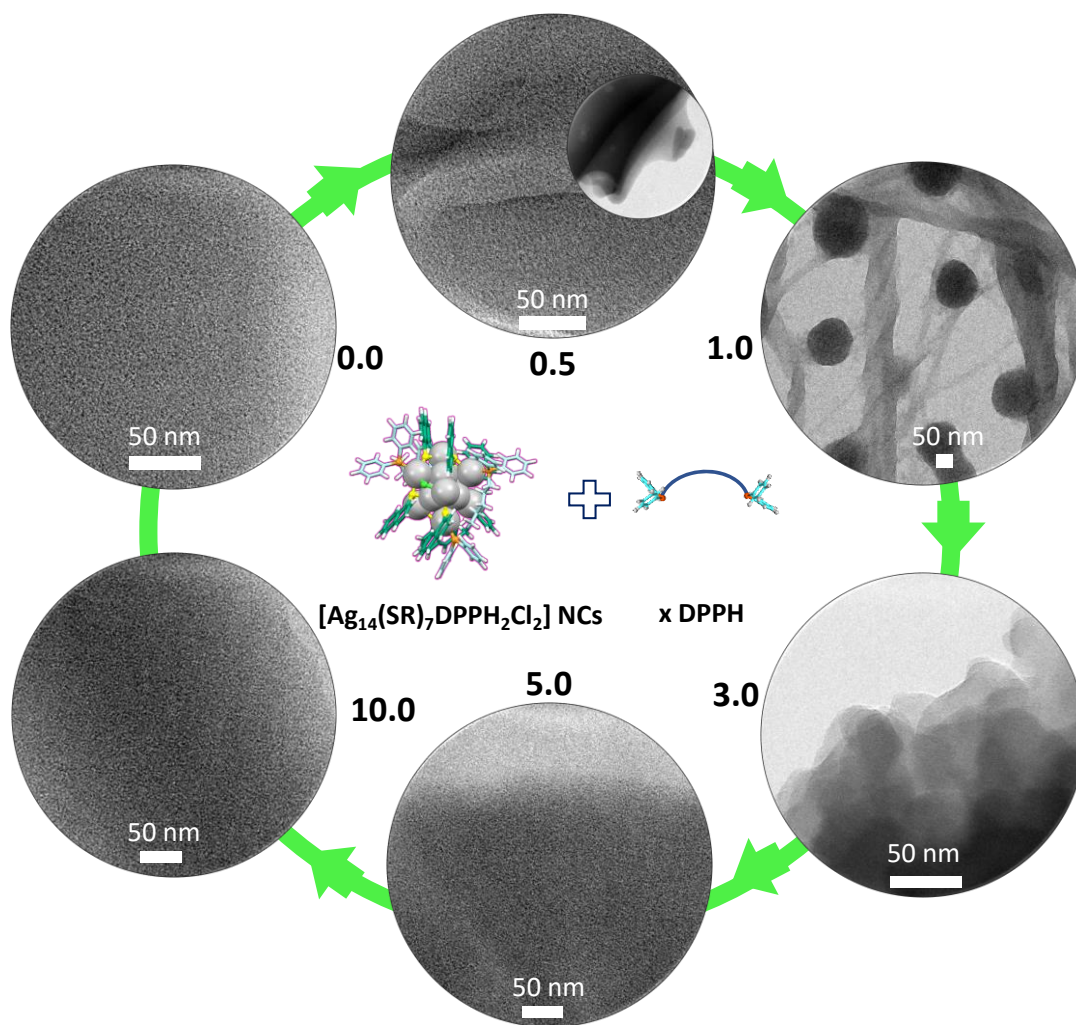


Fig. S5 TEM images showing the structural evolution of $[\text{Ag}_{14}(\text{NT})_7(\text{DPPH})_2\text{Cl}_2]^+$ NCs with the addition of different molar ratios of DPPH ligand.

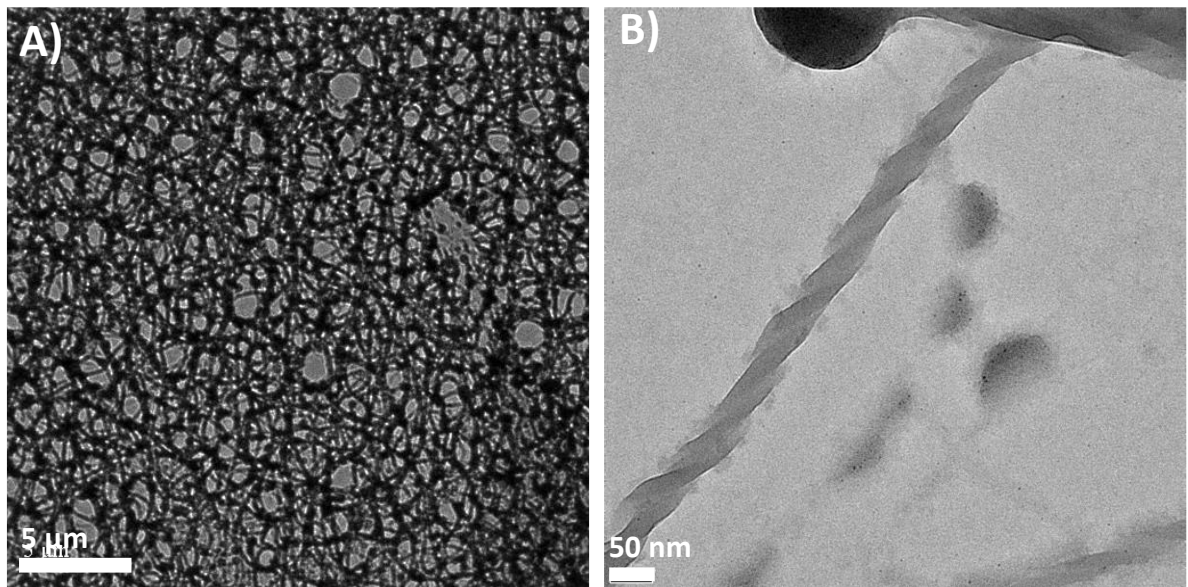


Fig. S6 A) Large area TEM images of NCA-1.0. B) Expanded view of super helical structures.

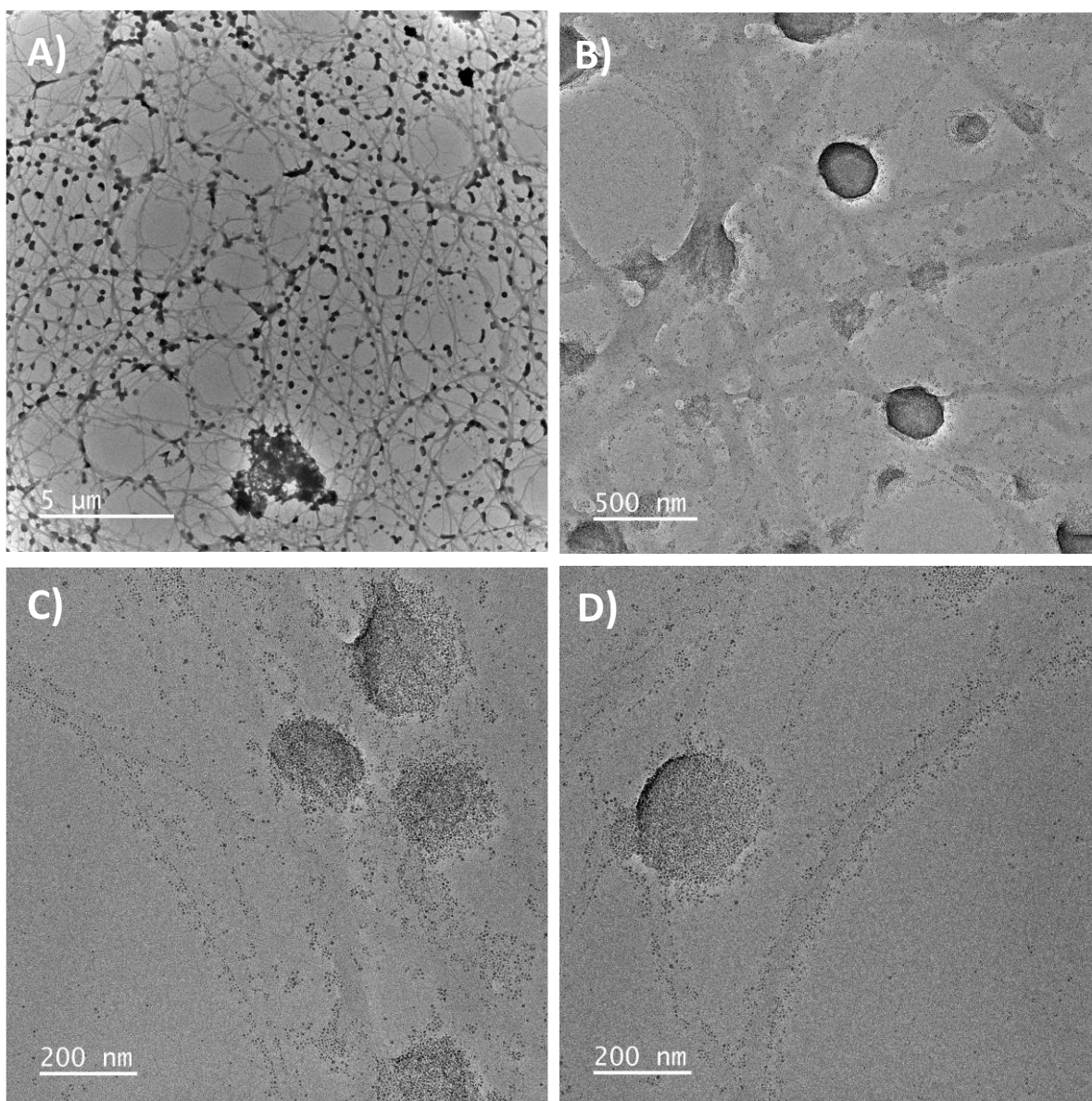


Fig. S7 A) Large area HRTEM images of NCA-1.0. B), C), and D) are the expanded view which confirms the presence of nanoclusters in the helical and spherical structures.

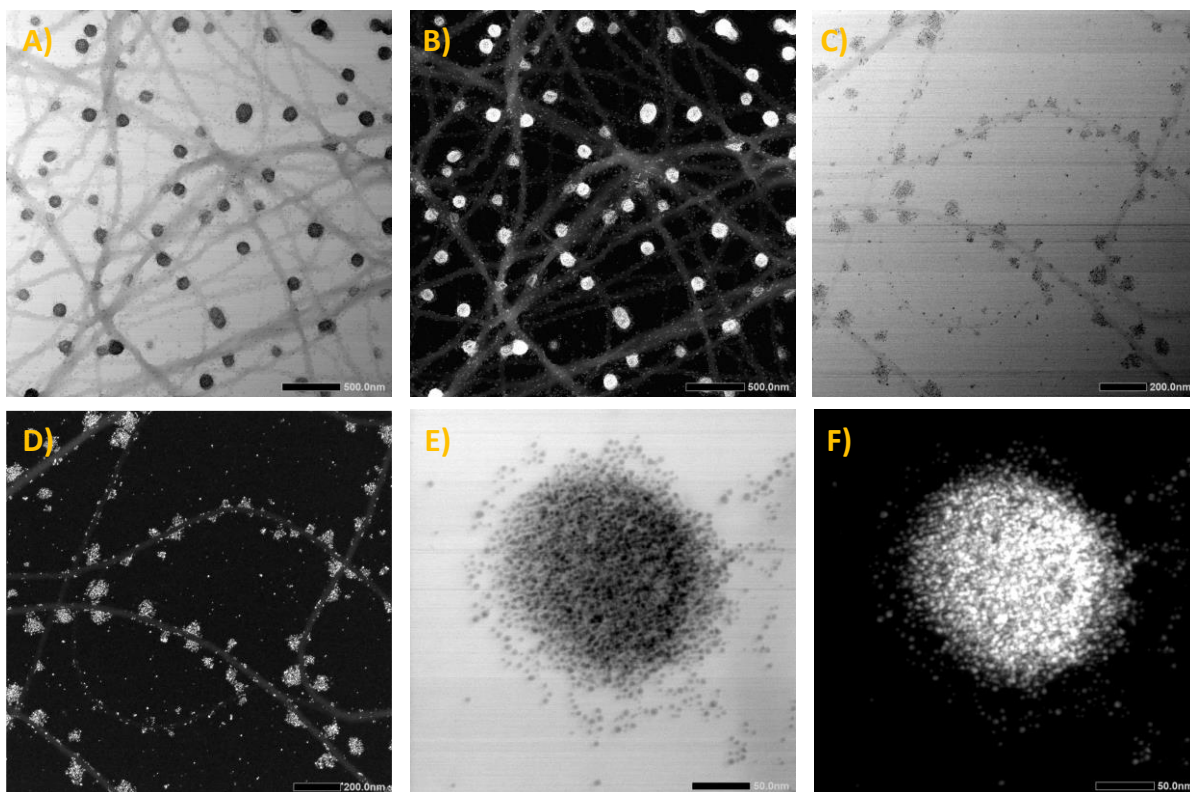


Fig. S8 Bright field (BF) and dark field (DF) STEM images of different regions of the NCA-1.0 sample.

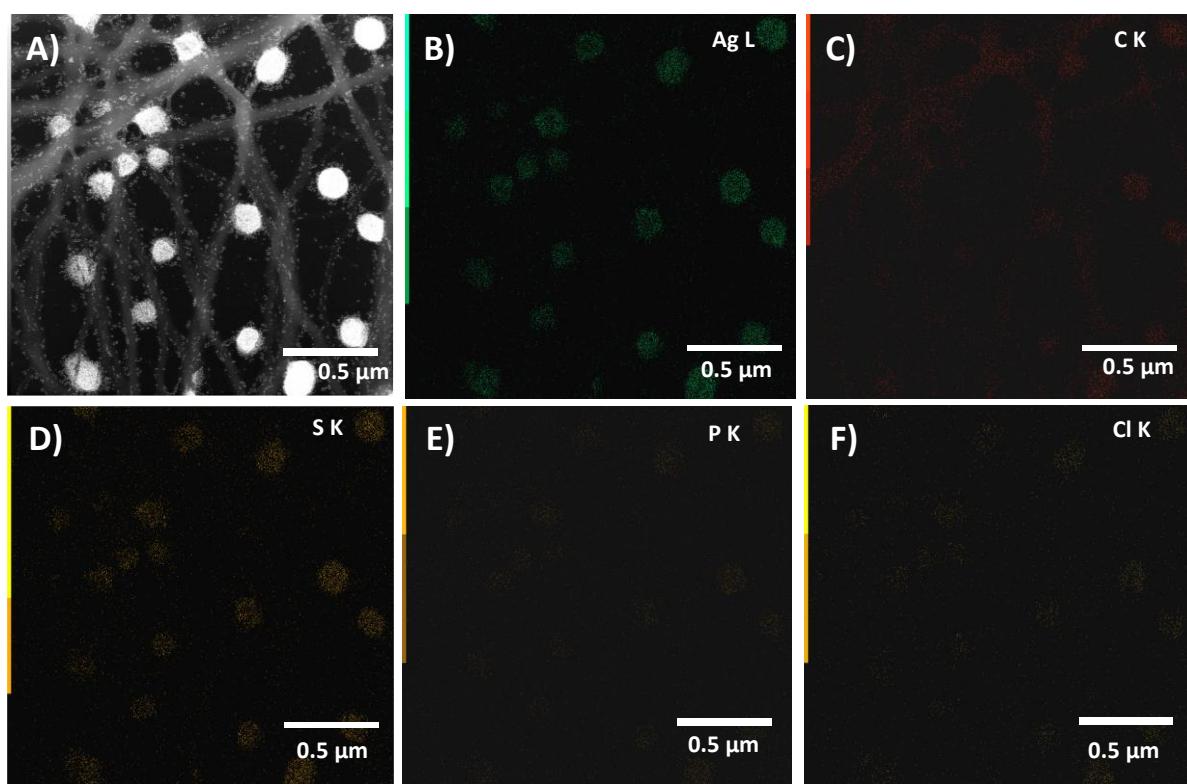


Fig. S9 STEM-EDS mapping of Ag, C, S, P, and Cl of NCA-1.0.

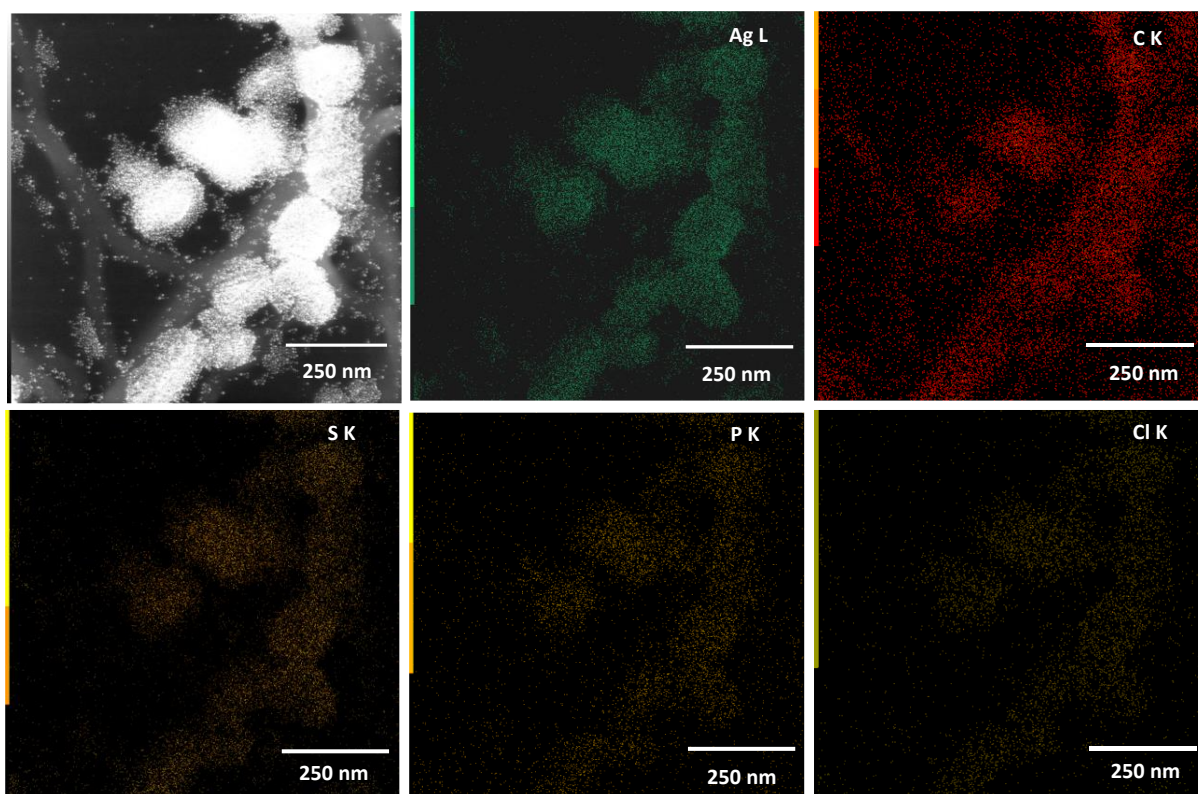


Fig. S10 STEM-EDS mapping of Ag, C, S, P, and Cl in spherical structures of NCA-1.0.

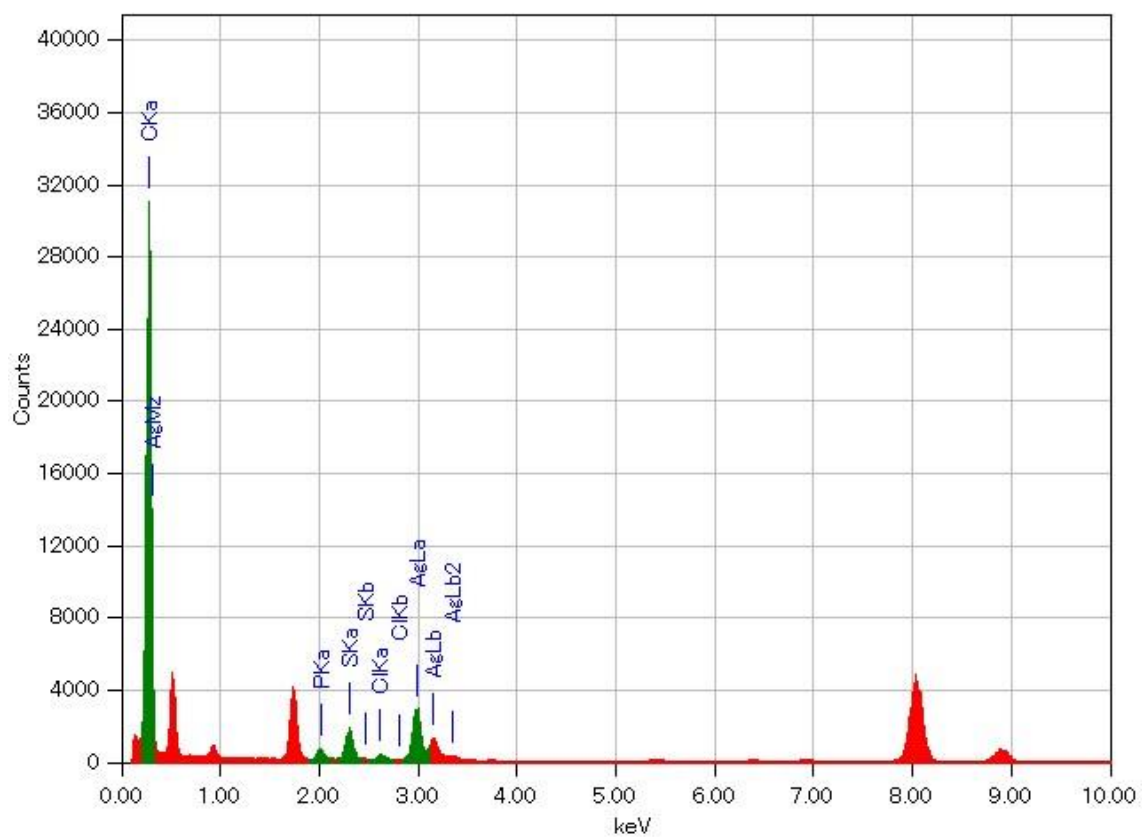


Fig. S11 EDX spectrum of NCA-1.0.

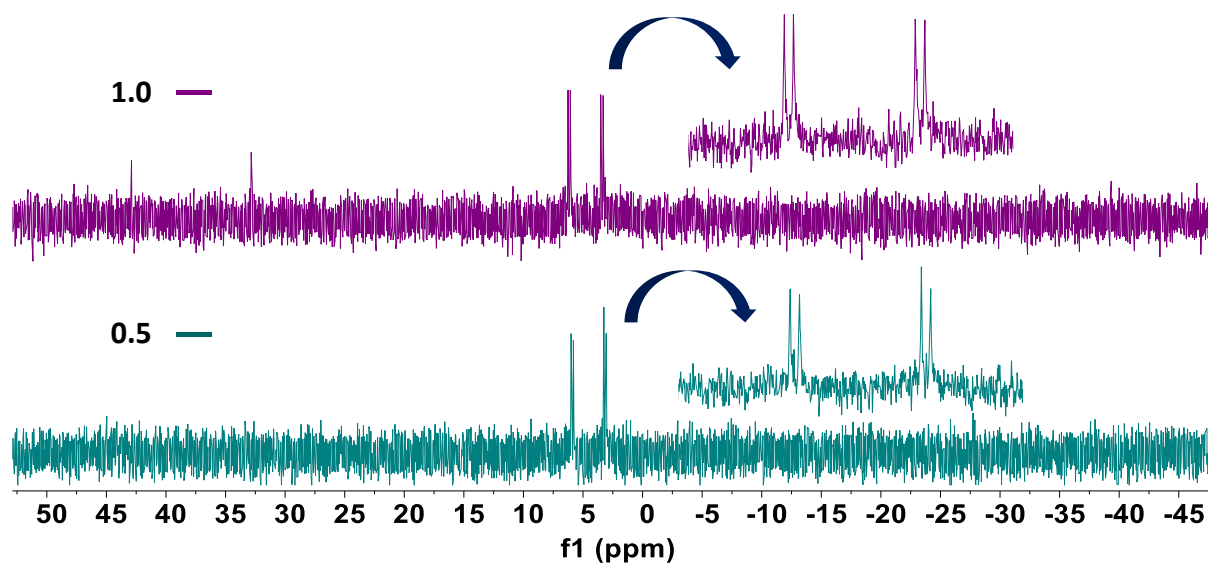


Fig. S12 The ^{31}P NMR spectra of NCA 0.5 and NCA 1.0.

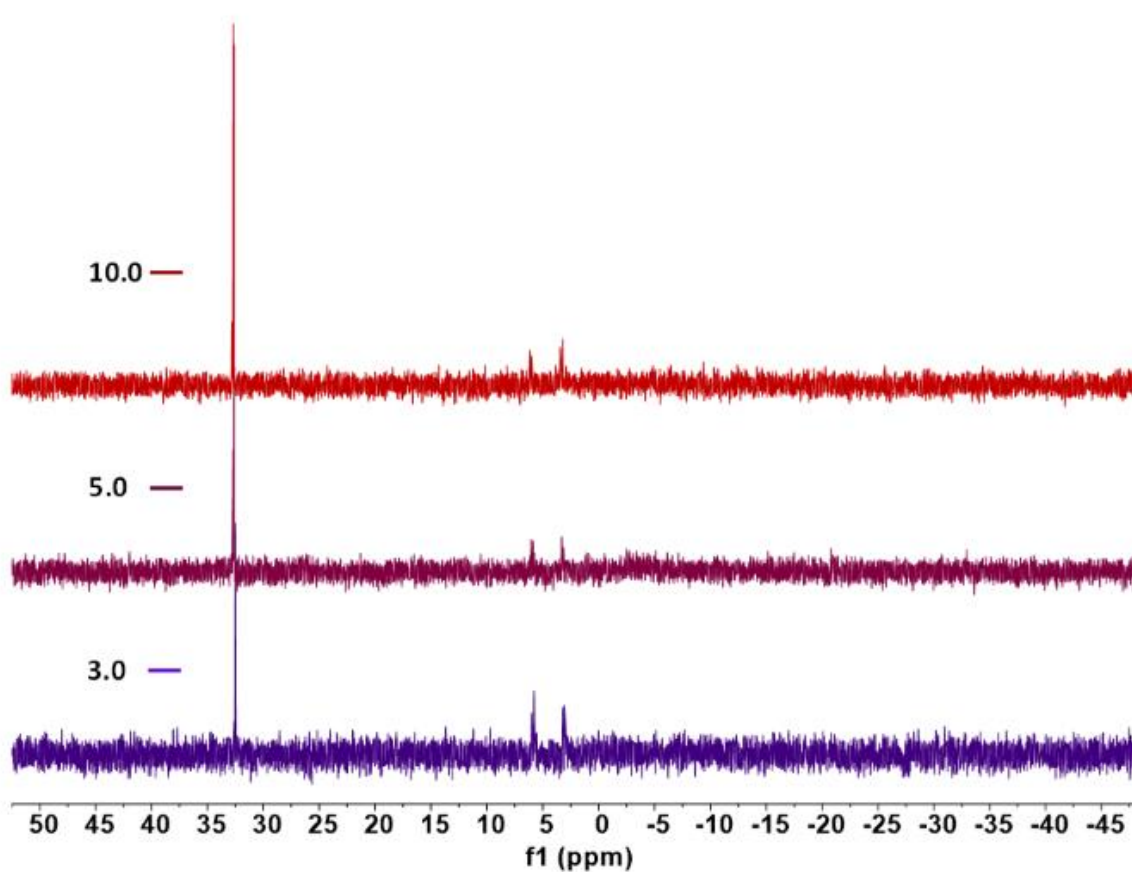


Fig. S13 The ^{31}P NMR spectra of NCA 3.0, NCA 5.0, and NCA 10.0.

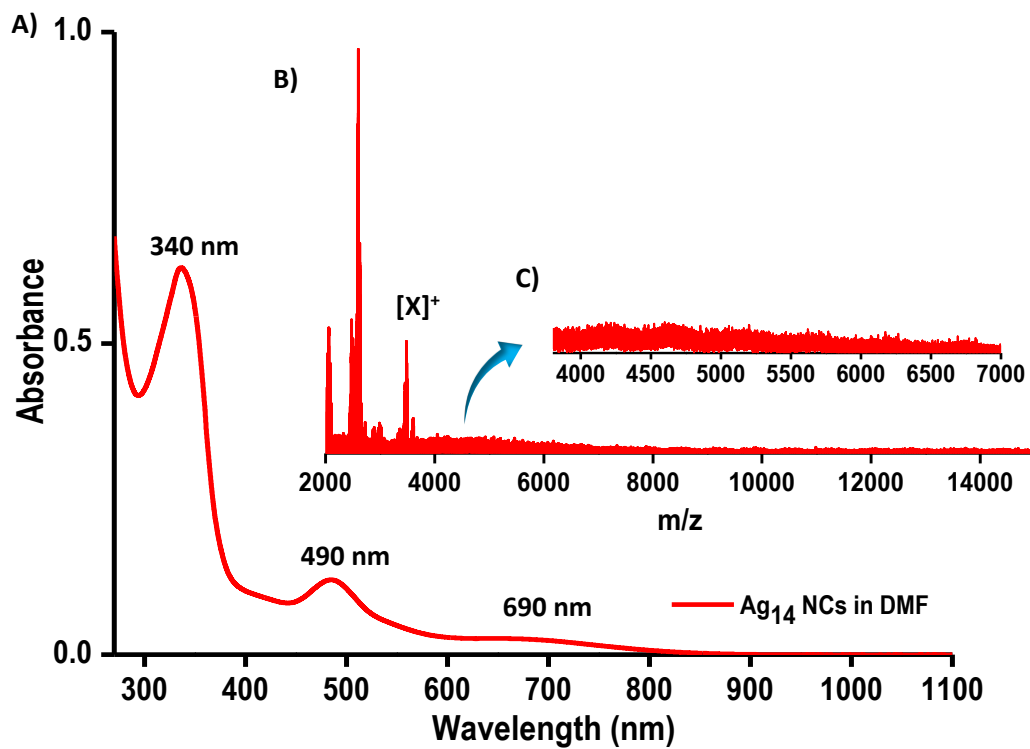


Fig. S14 A) UV-vis spectrum of NCA-1.0 redispersed in DMF. B) The corresponding ESI MS. C) Enlarged view.

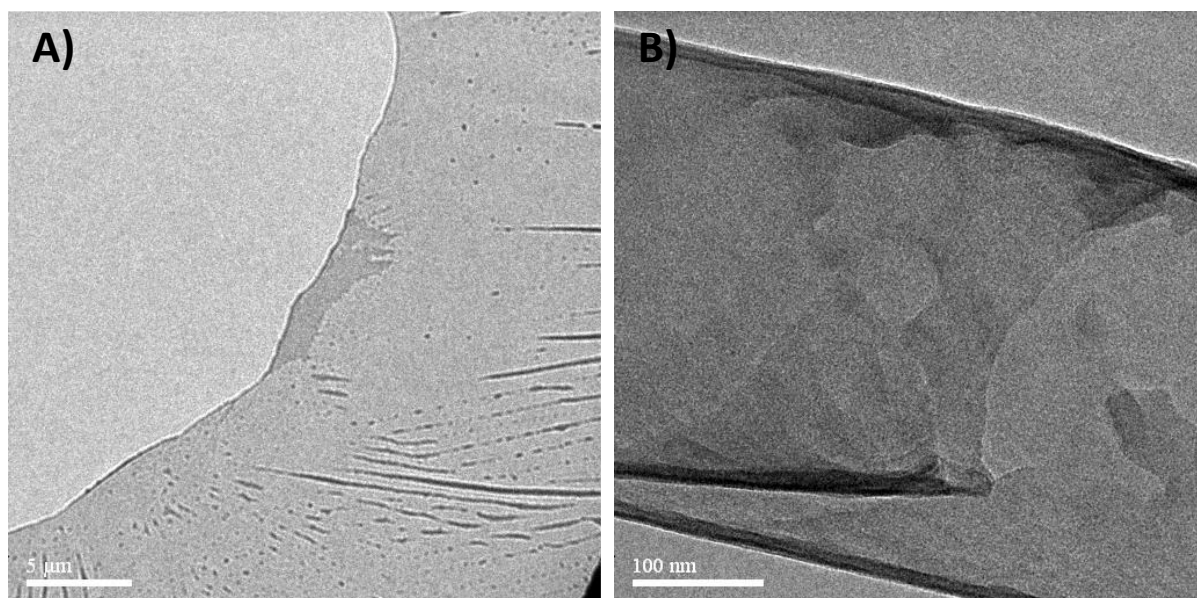


Fig. S15 A) and B) is the TEM images of the DPPH-NT mixture.

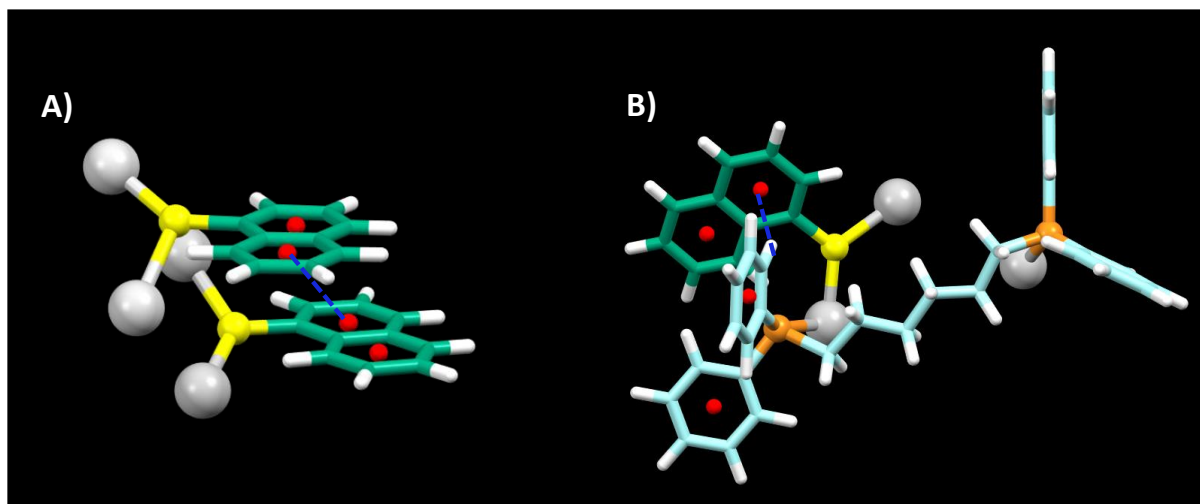


Fig. S16 Schematic illustration of possible supramolecular interactions in Ag₁₄ NC assemblies. A) $\pi \dots \pi$ interactions between NT ligands. B) CH... π interactions between NT and DPPH ligands.

References

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