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Hierarchical assembly of Ag_{40} nanowheel ranging from building blocks to diverse superstructure regulation

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Thomas C. W. Mak

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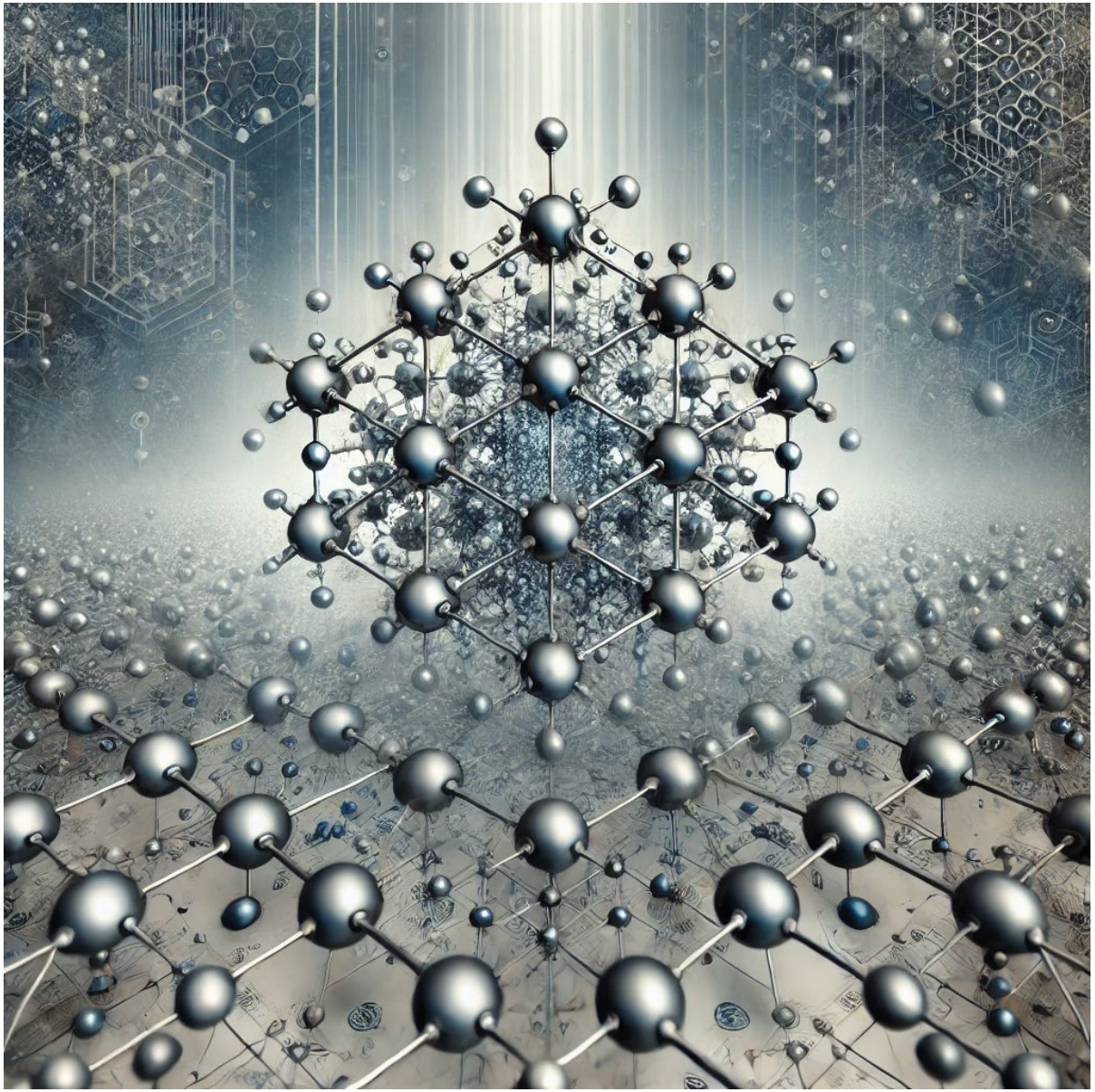
Background



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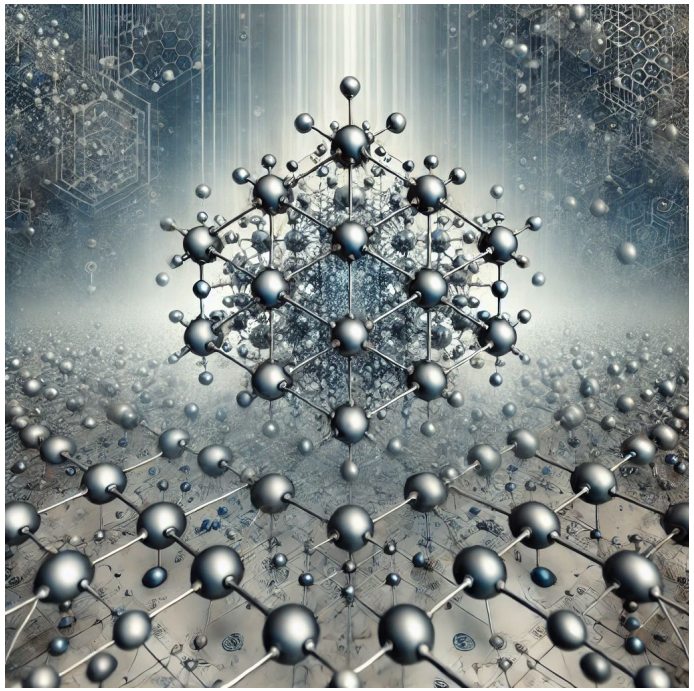

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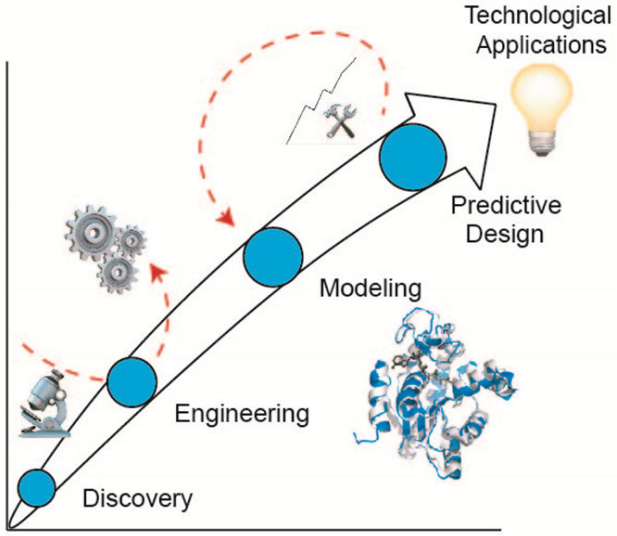

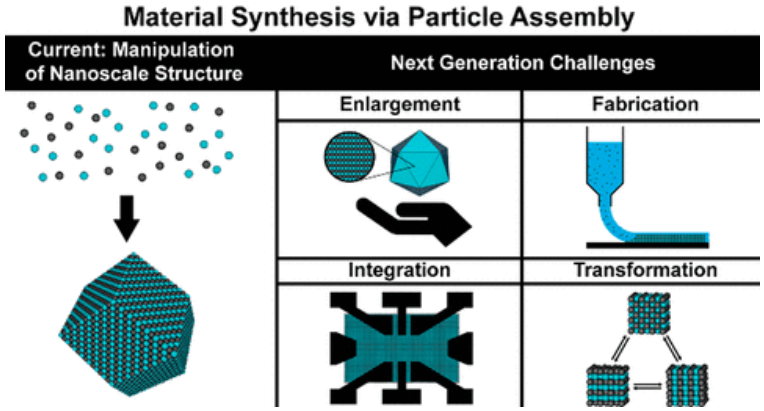

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Received 21st June 2021,
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A double helical 4H assembly pattern with secondary hierarchical complexity in an Ag_{70} nanocluster crystal†

Tao Chen,[a] Sha Yang,[b] Qinzhen Li,[a] Yongbo Song,[c] Guang Li, *[a] Jinsong Chai*[c] and Manzhou Zhu *[bc]

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Background

Supercrystal engineering of atomically precise gold nanoparticles promoted by surface dynamics

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$[Cu\{SC(O)O^{i}Pr\}]_{96}$: A Giant Self-Assembled Copper(I) Supramolecular Wheel Exhibiting Photoluminescence Tuning and Correlations with Dynamic Solvation and Solventless Synthesis

Arvind K. Gupta, Pilli V. V. N. Kishore, Jhih-Yu Cyue, Jian-Hong Liao, Welni Duminy, Werner E. van Zyl*, and C. W. Liu*

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ARTICLE | December 28, 2023

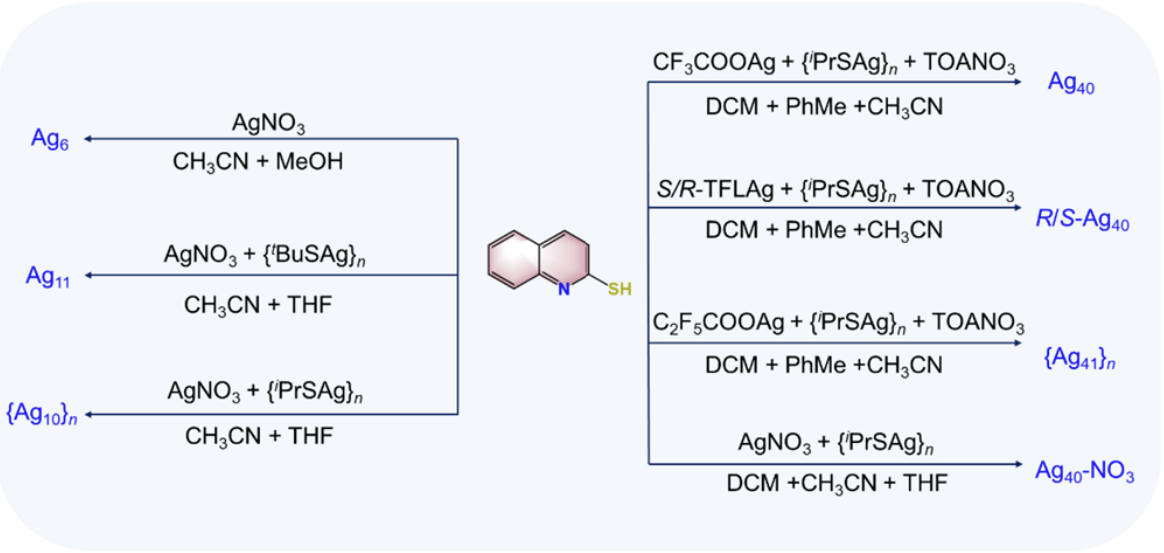
Evolution of Polynuclear Gold(I) Sulfido Complexes from Clusters and Cages to Macrocycles

Liang-Liang Yan, and Vivian Wing-Wah Yam*

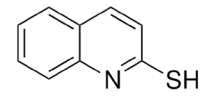
Why this paper?

- Reveals a detailed understanding of the construction of hierarchical crystalline superstructures of large-sized metal NCs from a small building block nanocluster (NC)
- The significance of metal salts, and peripheral ligands of NCs on the transformation of Ag nanowheel to complex triple and double helical superstructures and 1D chains
- Specific biomolecule recognition of Ag_{40} nanowheel through non-covalent interaction
- Role of solvent in inducing chirality in superstructures

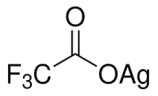
Results & discussion



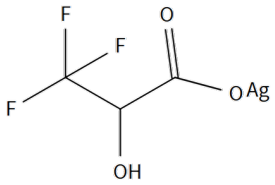
Supplementary Figure 3. Synthetic routes of Ag_6, Ag_{11}, $\{Ag_{10}\}_n$, Ag_{40}, *R*-Ag_{40}, *S*-Ag_{40}, $\{Ag_{41}\}_n$ and Ag_{40}-NO_3 protected by QL-2-SH ligand.



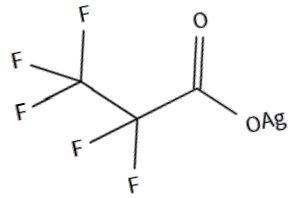
Quinoline-2-thiol [QL-2-SH]



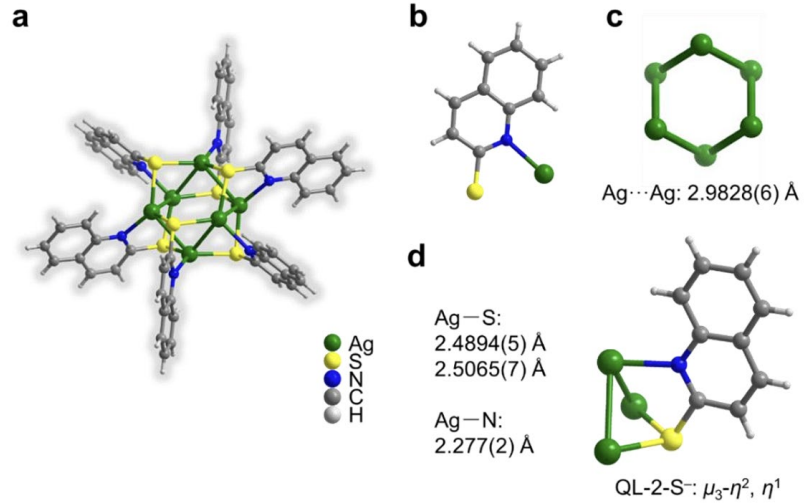
Silver trifluoro acetate



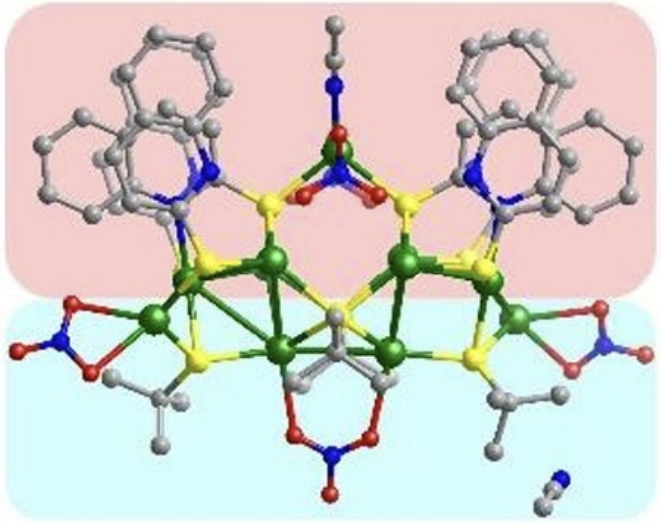
S/R- silver trifluorolactate



C_2F_5COOAg

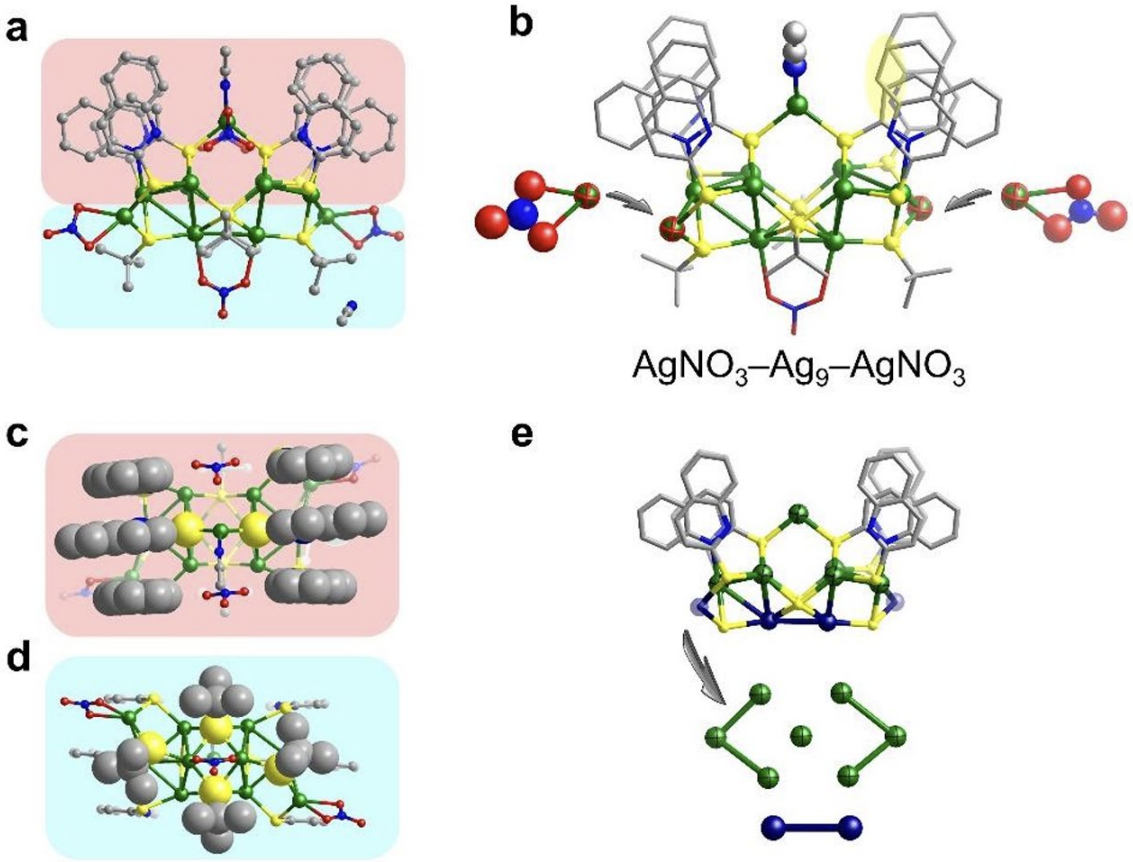


S4. structure analysis for $Ag_6(QL\text{-}2\text{-}S)_6$ (Ag_6) based on SCXRD.



S5. Crystal structure of Ag_{11}

Results & discussion



S5. Crystal structure of Ag_{11}. (a) The total structure of Ag_{11}, $Ag_{11}(QL\text{-}2\text{-}S)_2(HQL\text{-}2\text{-}S)_4(tBuS)_4(NO_3)_5(CH_3CN)\cdot CH_3CN$, where their thiol ligands with different steric hindrance exhibit a 'Janus' distribution mode. (b) Two $AgNO_3$ as capping agents located on both sides of the Ag_9 building block in Ag_{11}. (c) Six quinoline-2-thiol ligands including 2 QL-2-S– and 4 HQL-2-S, distributed on the same side of Ag_{11}. (d) Four ^{t}BuS– ligands distributed on the same side of Ag_{11}. (e) Ag_2 (dark blue) and Ag_7

Results & discussion

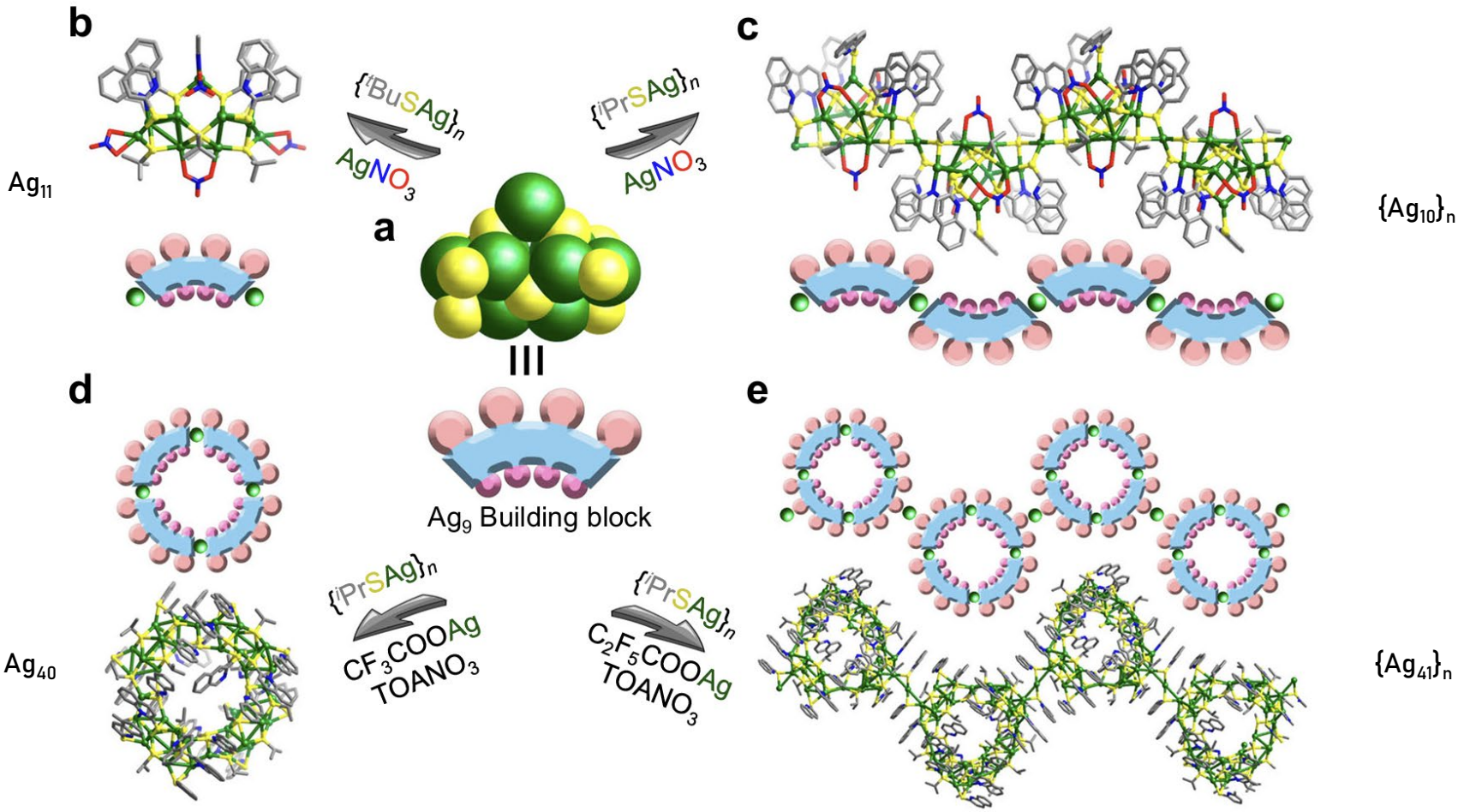
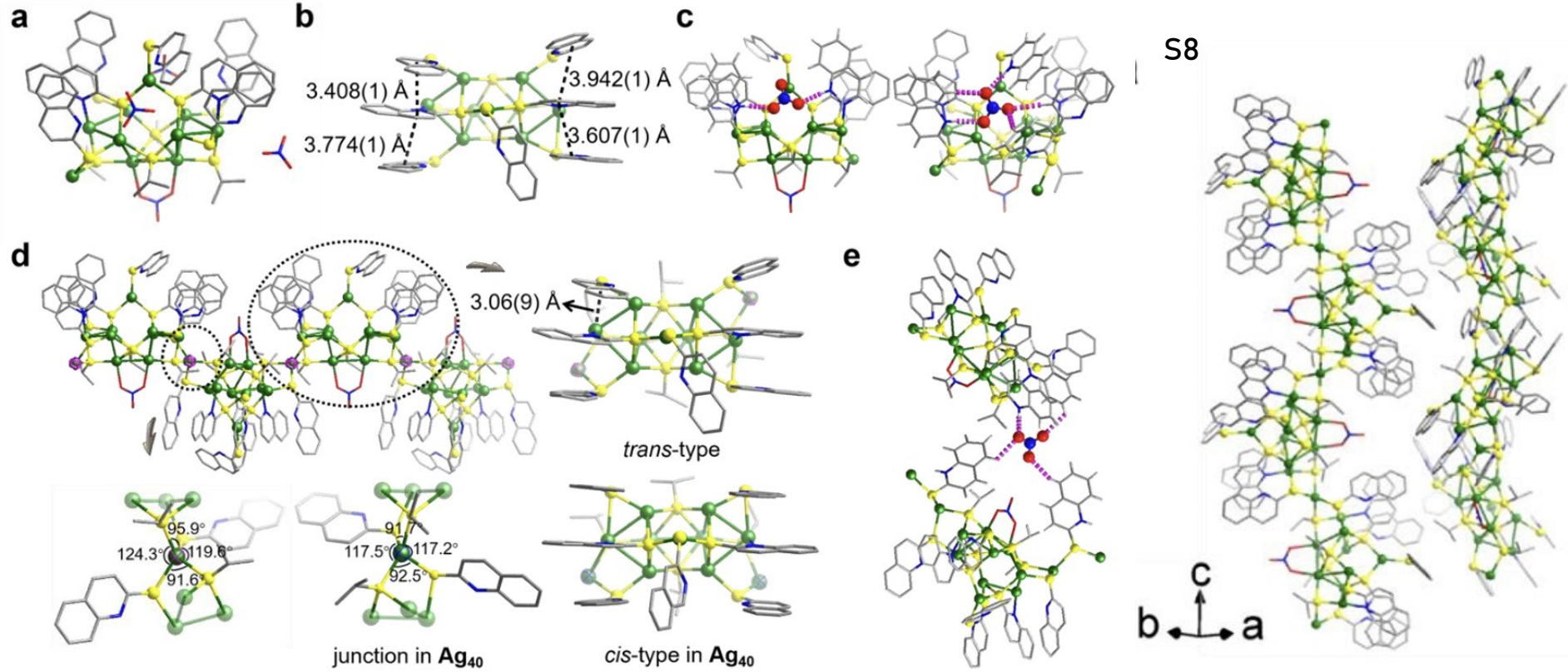


Fig. 1 Hierarchical assembly based on Ag_9PBBs. a Ag_9 building block, protected by two types of thiol ligands. b Monomer Ag_{11}, blocked by two $AgNO_3$ molecules at both ends, inhibited further aggregation. c One-dimensional aggregate $\{Ag_{10}\}_n$, where Ag_9 PBBs are connected by Ag+ ions to form an infinite structure. d Tetramer Ag_{40} nanowheel, in which four PBBs are gathered together through the silver nodes to form a discrete structure. e One-dimensional aggregate $\{Ag_{41}\}_n$, in which Ag_{40} nanowheels are connected by additional Ag atoms to form an infinite structure.

Results & discussion



S7. Crystal structure of $\{Ag_{10}\}_n$. (a) Asymmetric unit, $\{Ag_{10}(QL\text{-}2\text{-}S)_2(HQL\text{-}2\text{-}S)_5(iPrS)_4(NO_3)_4\}_n$. (b) Intramolecular face-to-face π···π stacking interactions. (c) NO_3^- anions confined in local cavity between the HQL-2-S ligands via electrostatic interaction, N(sp2)–H···O, C(sp2)–H···O interactions and weak coordination. (d) The differences between the junctions, Ag_9 building block and connection types in $\{Ag_{10}\}_n$ and Ag_{40}. S8. Packing structures of $\{Ag_{10}\}_n$ in single crystals.

Results & discussion

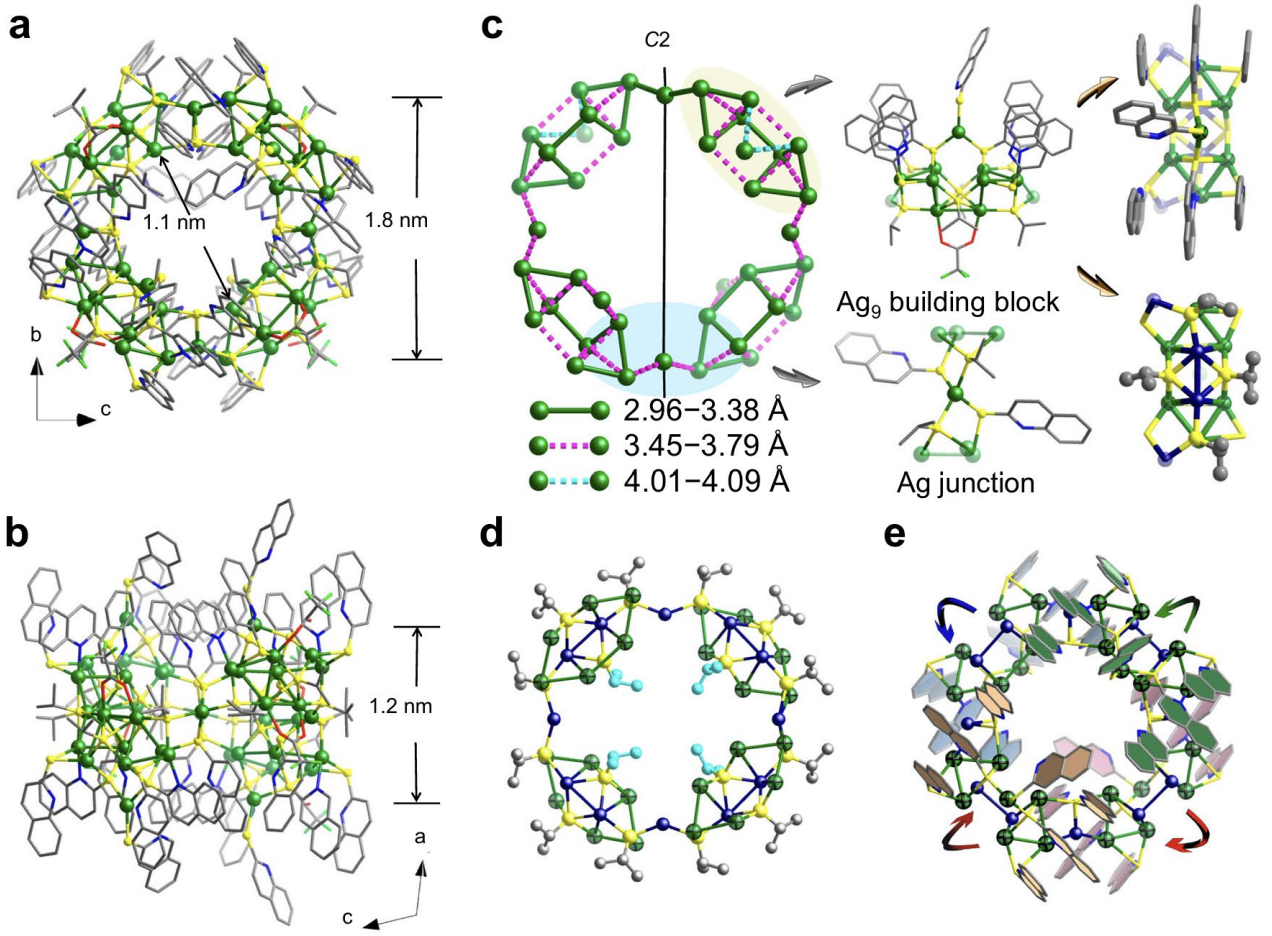
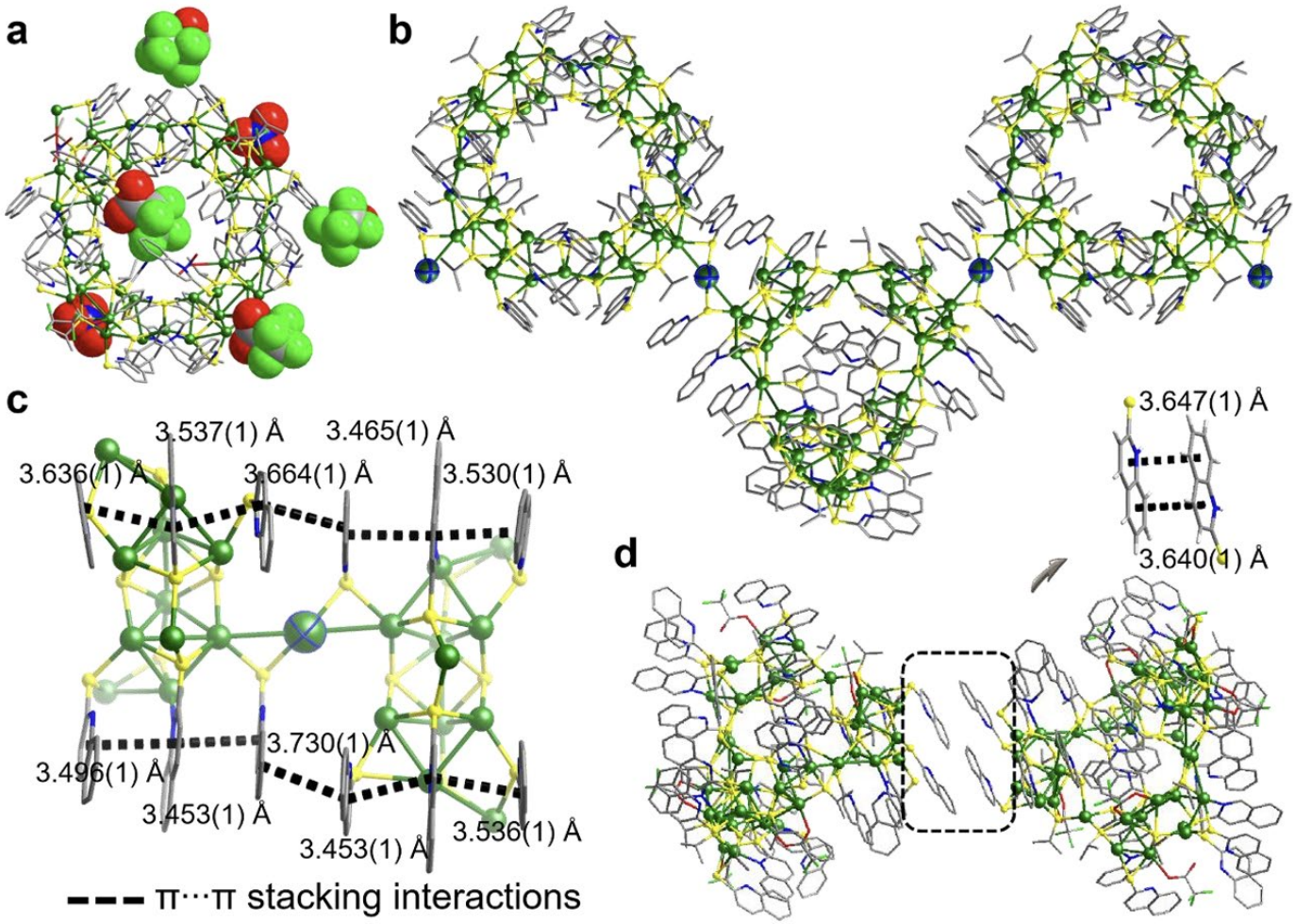


Fig. 2 Crystal structures of Ag_{40}. a,b View of nanowheel Ag_{40} in the a-axis (a) and b-axis (b) directions. c Metal skeleton with a C_2 symmetry of Ag_{40}, constructed by four $[Ag_9(QL\text{-}2\text{-}S)_2(HQL\text{-}2\ S)_5(^iPrS)_4(CF_3COO)]^{2+}$ PBBs (Ag_9, pale yellow shadow) and four $[Ag(^iPrS)_2(HQL\text{-}2\ S)_2]^-$ junctions (pale blue shadow). d Distribution of small sterically hindered $^iPrS-$ ligands on the metal skeleton of Ag_{40}, highlighting the four $^iPrS-$ ligands inside the nanowheel (blue) and a ring composed of 12 metal atoms in almost the same plane (dark blue). e Distribution of quinoline-2-thiol ligands with larger steric hindrance on the metal skeleton of Ag_{40}, highlighting the ligands on different PBBs in different colors. .

Results & discussion



S9. Crystal structure of $\{Ag_{41}\}_n$. (a) Asymmetric unit of $\{Ag_{41}\}_n$. (b) One-dimensional aggregate $\{Ag_{41}\}_n$, in which Ag_{40} nanowheels are connected by additional Ag atoms (front ellipses style with blue inner lines) to form an infinite structure. (c) Intrachain face-to-face π···π stacking interactions. (d) Intermolecular face-to-face π···π stacking interactions of Ag_{40}.

Results & discussion

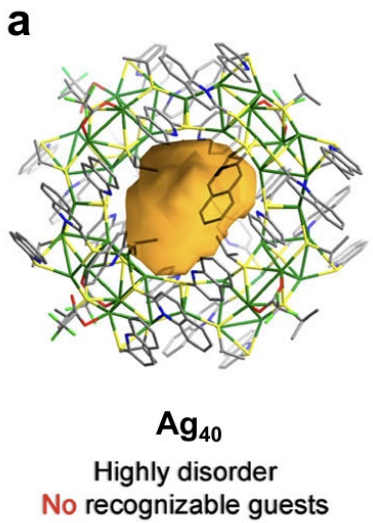
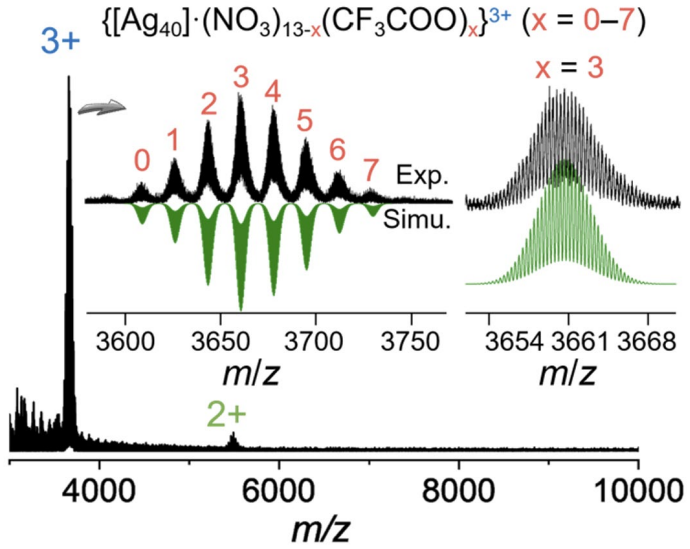
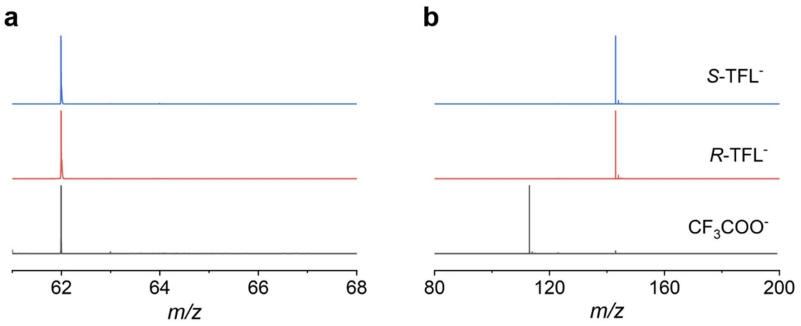


Fig. 3 a Ag_{40} with an internal nanospace.



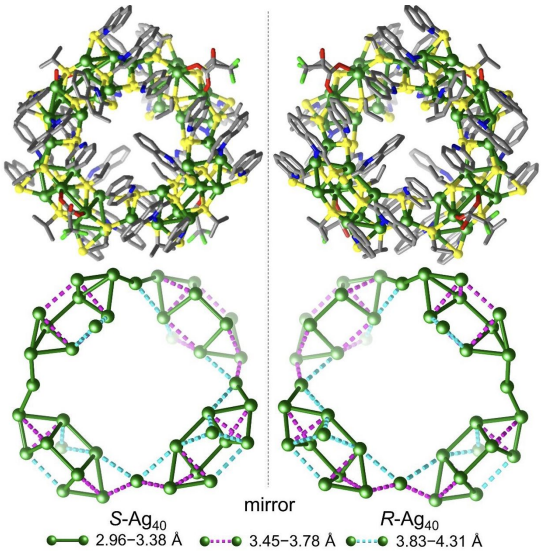
S23. ESI-MS of Ag_{40} dissolved in DCM collected in positive mode.

	$\{[Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{13-x}(CF_3COO)_x]\}^{3+}$ (x = 0–7)
0	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{13}\}^{3+}$
1	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{12}(CF_3COO)_1\}^{3+}$
2	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{11}(CF_3COO)_2\}^{3+}$
3	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{10}(CF_3COO)_3\}^{3+}$
4	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{9}(CF_3COO)_4\}^{3+}$
5	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{8}(CF_3COO)_5\}^{3+}$
6	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{7}(CF_3COO)_6\}^{3+}$
7	$\{Ag_{40}(QL\text{-}2\text{-}S)_8(HQL\text{-}2\text{-}S)_{20}(^{i}PrS)_{16}(NO_3)_{6}(CF_3COO)_7\}^{3+}$

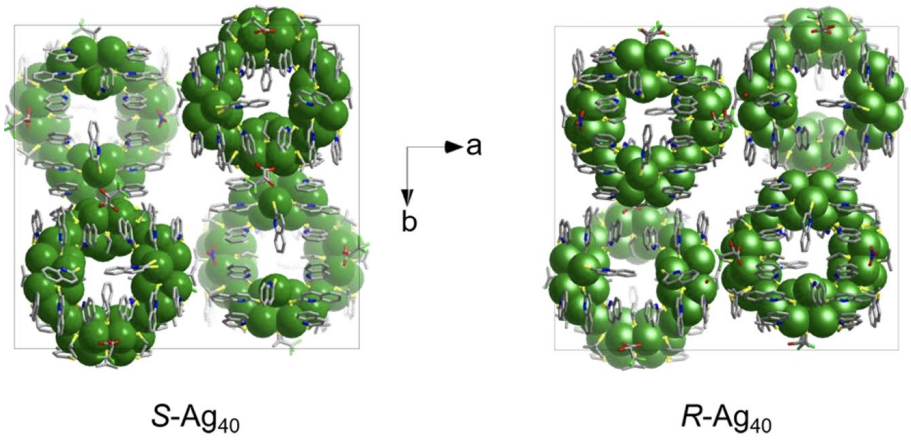


S23. Mass spectrum of Ag_{40} and S-/R-Ag_{40} in negative-ion mode, confirming the presence of NO^{3-} (a), CF_3COO^- and S-/R-TFL– (b)

Results & discussion



S19. Ball-and-stick representation of the enantiomers and their metal skeletons of S-Ag_{40} and R-Ag_{40}.



S20. Unit cells of S-Ag_{40} (a) and R-Ag_{40} (b), in which exist four chiral nanowheel molecules.

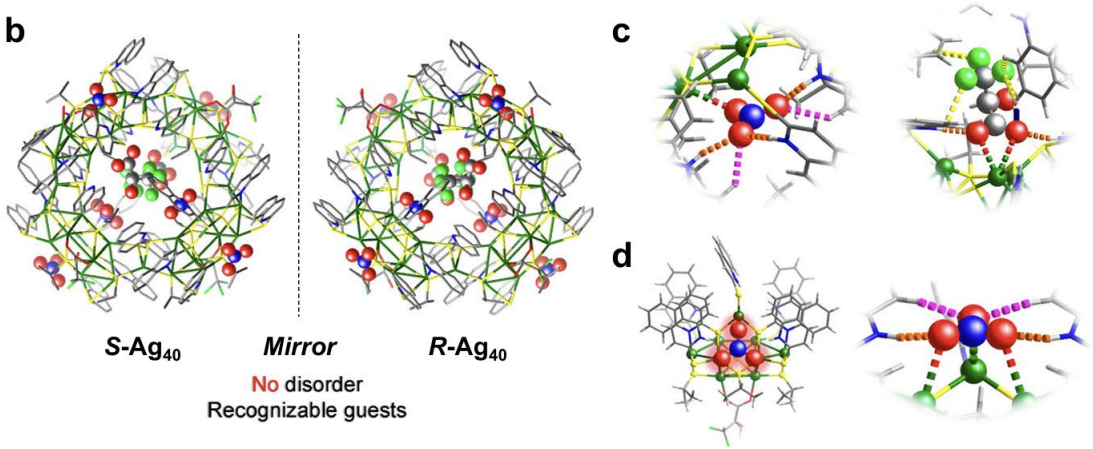


Fig. 3 b *S*-Ag_{40} and *R*-Ag_{40} nanowheels with C_1 symmetry, *S*-Ag_{40} and *R*-Ag_{40} display the chiral structure and the non-coordinated guest anions (NO_3^- and *S-/R*-TFL^-) in the internal nanospace. c, d Non-coordinated guest anions confined in the internal or outer nanospace via hydrogen bonding and weak coordination.

Results & discussion

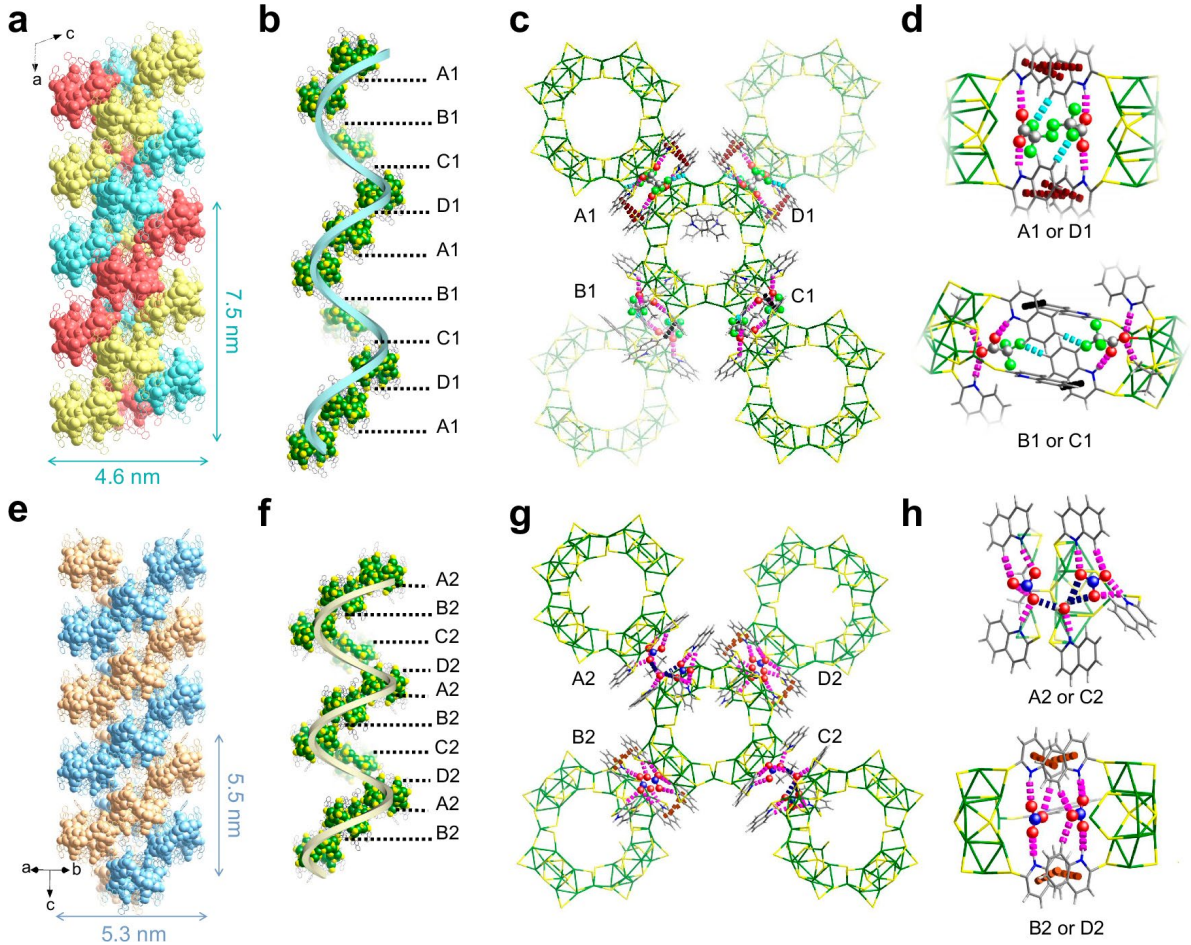
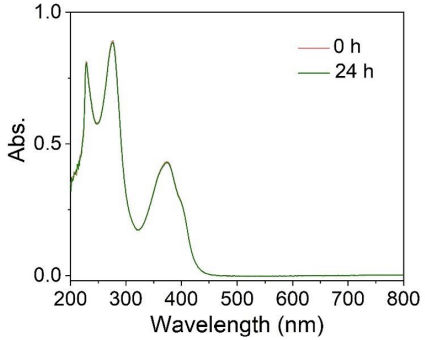
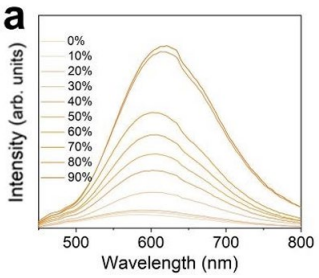


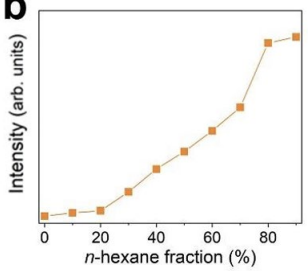
Fig. 4 a Self-assembly of Ag_{40} NCs into a triple-helical structure. b Helical linear chain of the triple-helical superstructure oriented and connected by two different surface motif pairs of Ag_{40} (A1/D1 and B1/C1). c Four types of motif matching between the neighboring nanowheels in the Ag_{40} supercrystal. d Intermolecular interactions of the two different surface motif pairs of Ag_{40}, e Self-assembly of S-Ag_{40} NCs into a double-helical structure. f Helical linear chain of the double-helical superstructure is orientally connected by two different surface motif pairs of S-Ag_{40} (A2/C2 and B2/D2). g Four types of motif matching between neighboring nanowheels in the S-Ag_{40} supercrystal. h Intermolecular interactions of two different surface motif pairs of S-Ag_{40}

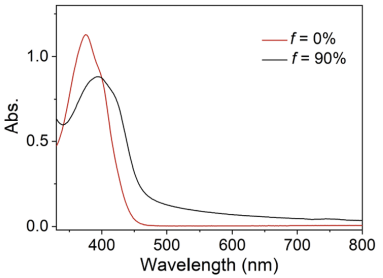
Results & discussion

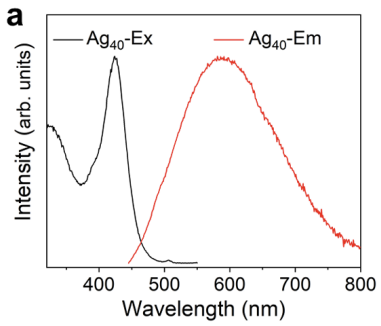
Aggregation-induced emission enhancement (AIEE) behavior

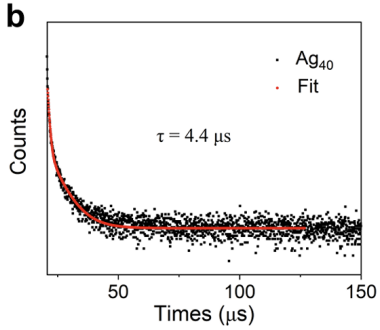


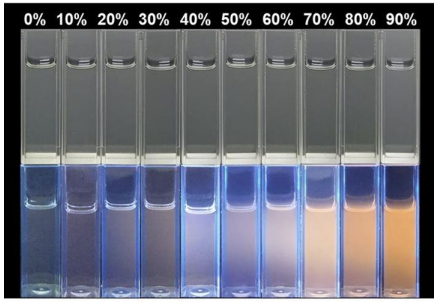


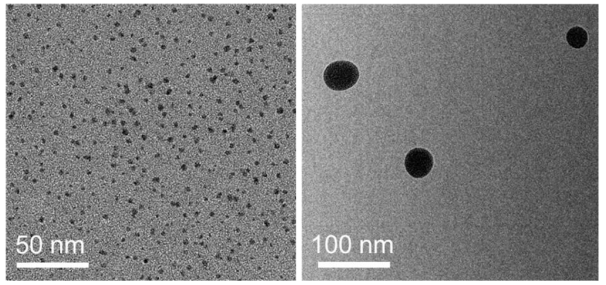


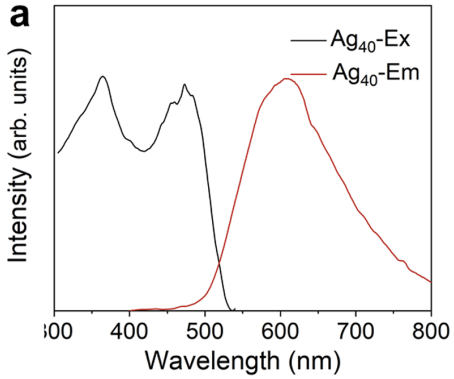


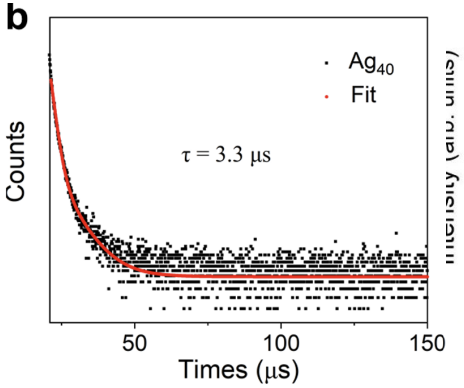


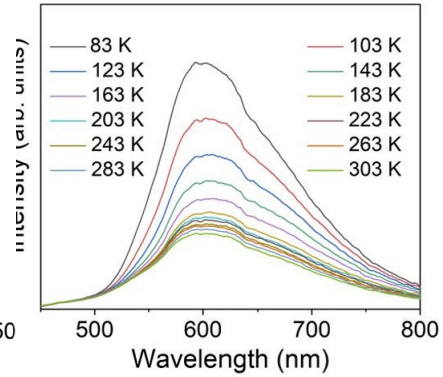


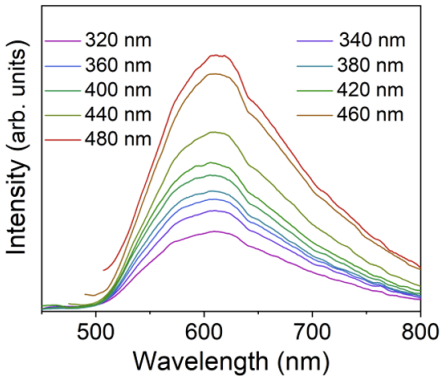












Results & discussion

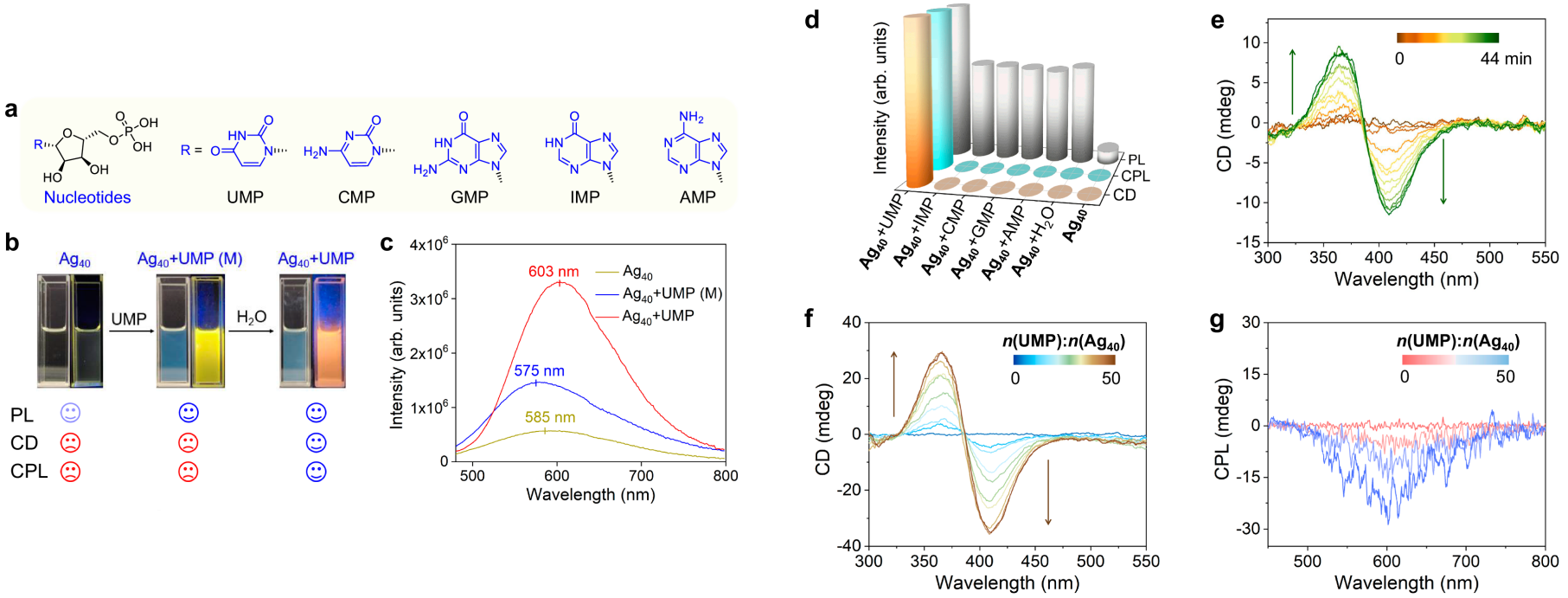


Fig. 5 a Molecular structure of various nucleotides. b CD and CPL activities triggered by the co-assembly process of Ag_{40} in DCM with UMP (dissolved in DMSO) and H_2O c Emission spectra of different stages (initial, Ag_{40}; intermediate, Ag_{40} + UMP (M); final, Ag_{40} + UMP + H_2O, abbreviated as Ag_{40} + UMP) in the recognition (λ_{ex} = 430 nm). d Column chart of the emission intensity of the PL, CD, and CPL spectra for Ag_{40}, Ag_{40} + H_2O, and the co-assemblies with nucleotides. e Time-dependent CD spectra of the co-assemblies formed by Ag_{40} (1×10^{-5} mol L^{-1}) in 3 mL of DCM with 20 µL of UMP (3×10^{-2} mol L^{-1}) in DMSO and 20 µL of H_2O. Interval: 4 min. f CD spectra of the co-assemblies formed by Ag_{40} (1×10^{-5} mol L^{-1}) in 3 mL of DCM with 0–50 µL of UMP (3×10^{-2} mol L^{-1}) in DMSO and 20 µL of H_2O. Interval: 5 µL. g CPL spectra of the co-assemblies formed by Ag_{40} (1×10^{-5} mol L^{-1}) in 3 mL of DCM with 0–50 µL of UMP (3×10^{-2} mol L^{-1}) in DMSO and 20 µL of H_2O. Interval: 5 µL.

Results & discussion

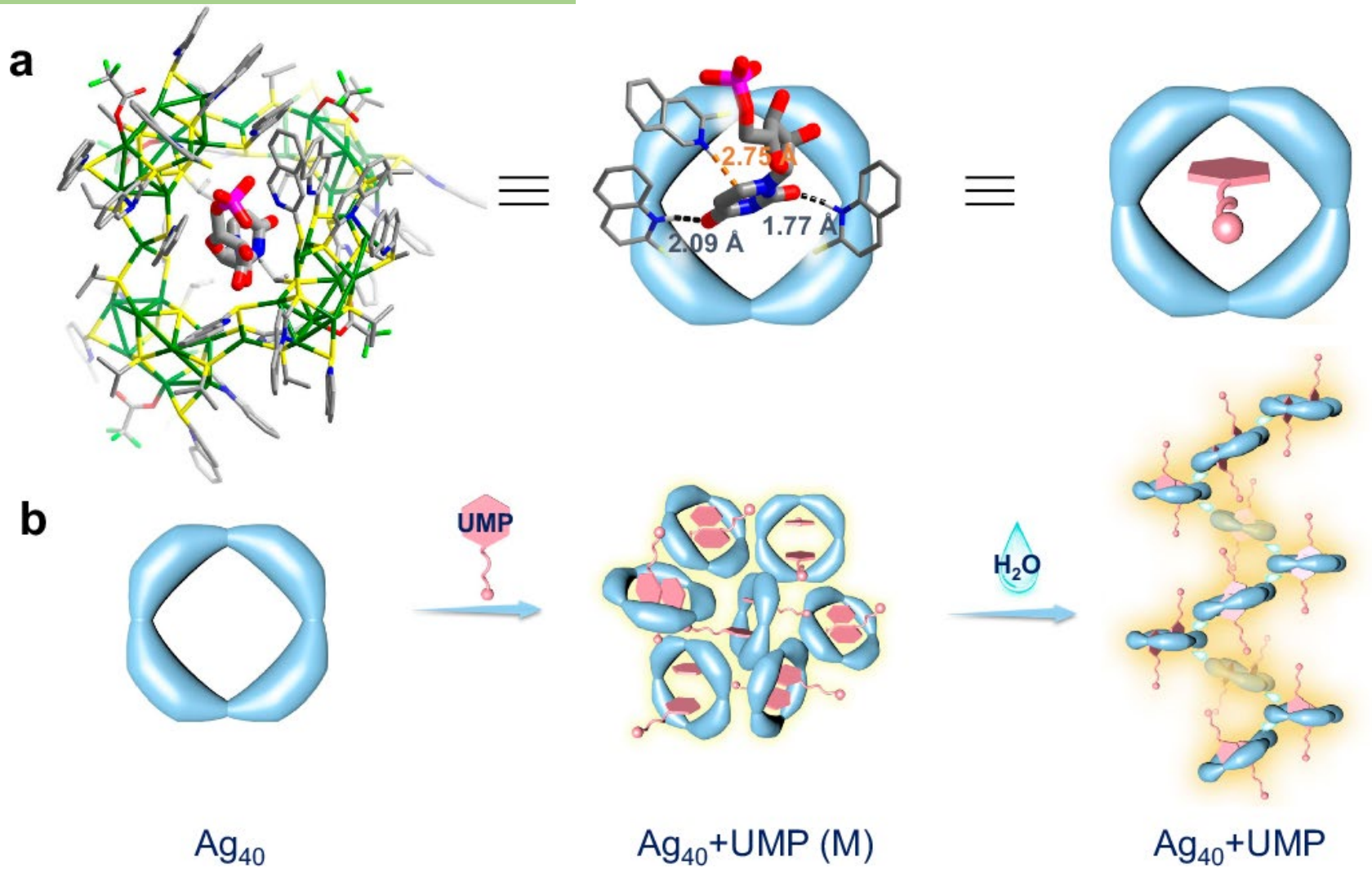


Fig. 6 a DFT (PBE0/def2-SVP)-calculated structure of the Ag_{40} and UMP co-assembly, dotted lines indicate non-covalent interactions, including N-H···O (black line) and N-H···π (orange line). Color codes: Ag green, S yellow, C gray, N blue, F cyan, O red, H white. b Scheme showing the chiral co-assembly process of Ag_{40} and UMP mediated by H_2O.

Conclusion

- It developed a series of molecules from small NCs like Ag_6, Ag_{11} to one-dimensional $\{Ag_{10}\}_n$ chain, tetrameric Ag_{40} nanowheel, S/R- chiral Ag_{40} nanowheel, ID chain of {Ag41}n based on primary building blocks Ag_9
- Formation of triple and double-helical assembly of Ag_{40} nanowheel by regulating the surface anions of the NCs
- It shows how subtle changes in solvent, and surface anions can regulate the formation of complex hierarchical structure
- Specific co-assembly formation of Ag_{40} nanowheel with UMP nucleotide and induction of chirality into the co-assembly mediated by water