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Research Article

Spontaneous Resolution of Chiral Multi-Thiolate-Protected Ag_{30} Nanoclusters

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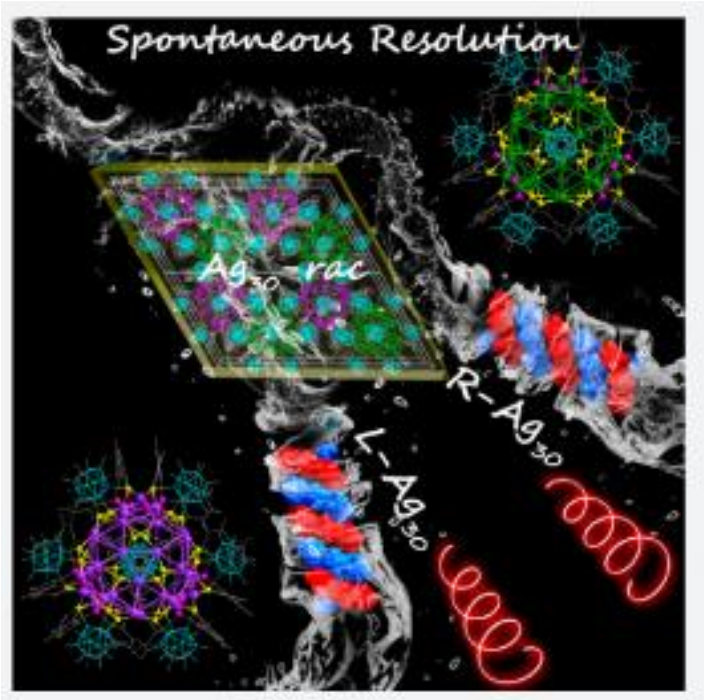
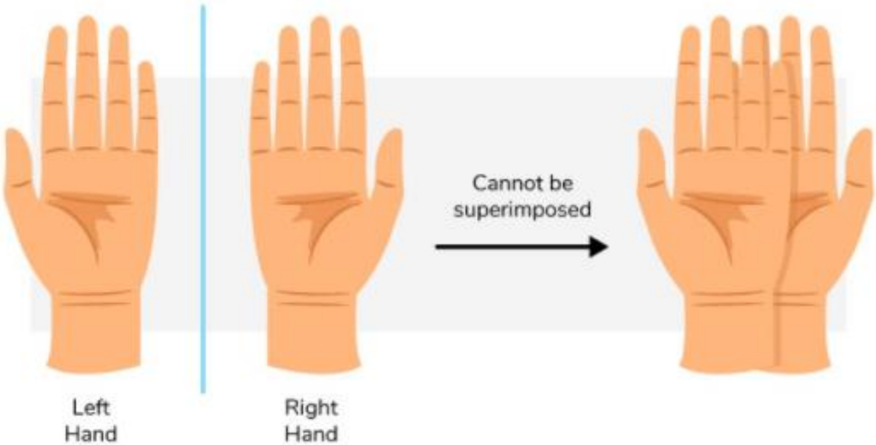


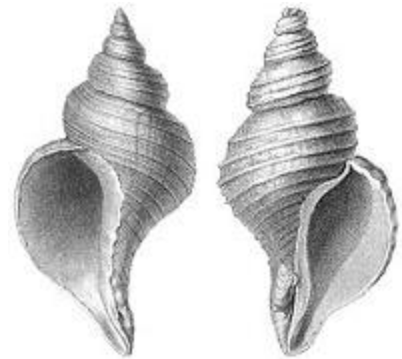
Arijit Jana

27.02.2021

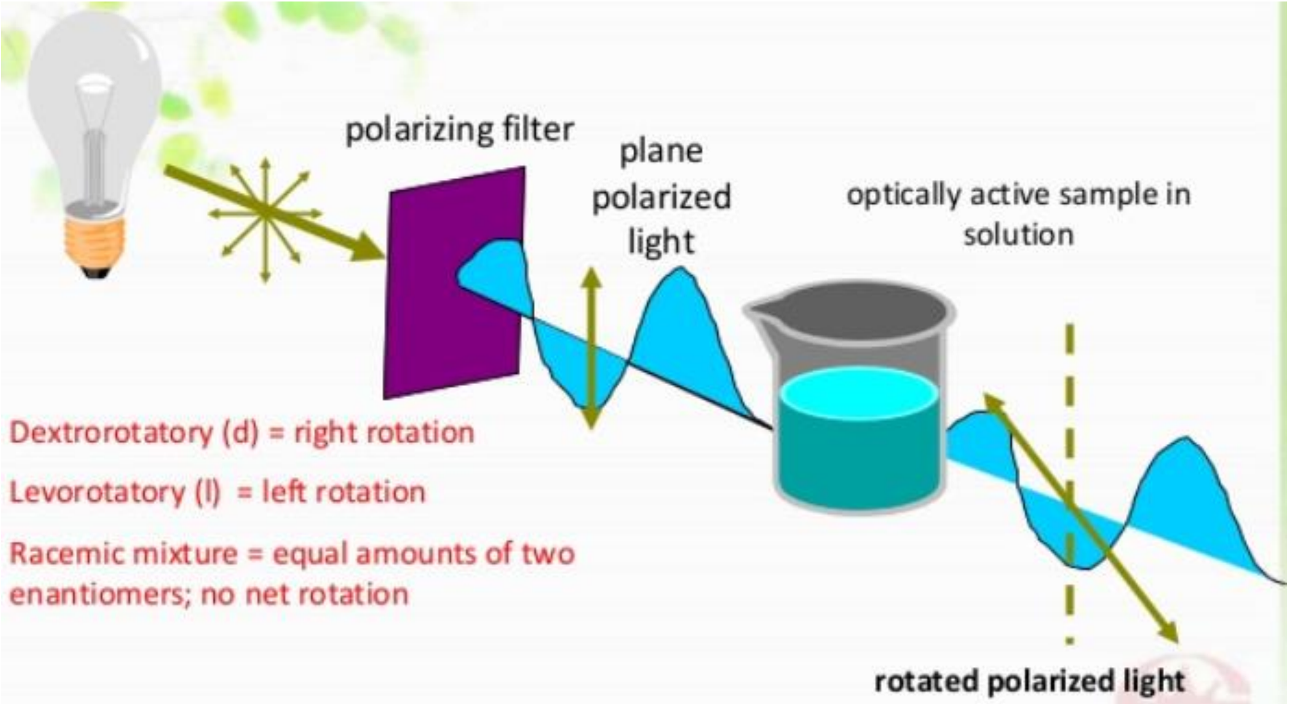
Chirality

An object that cannot be superimposed on its mirror image is called chiral

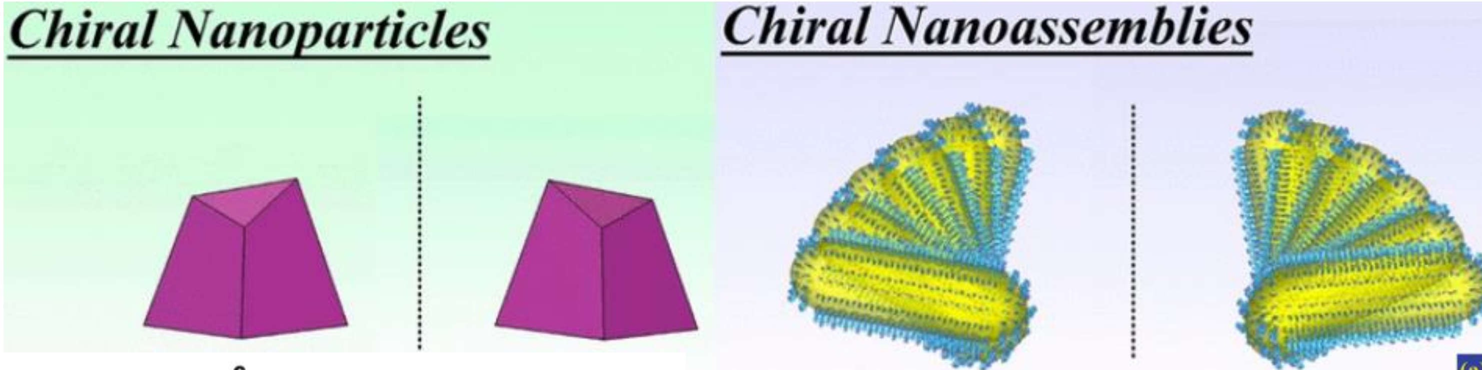


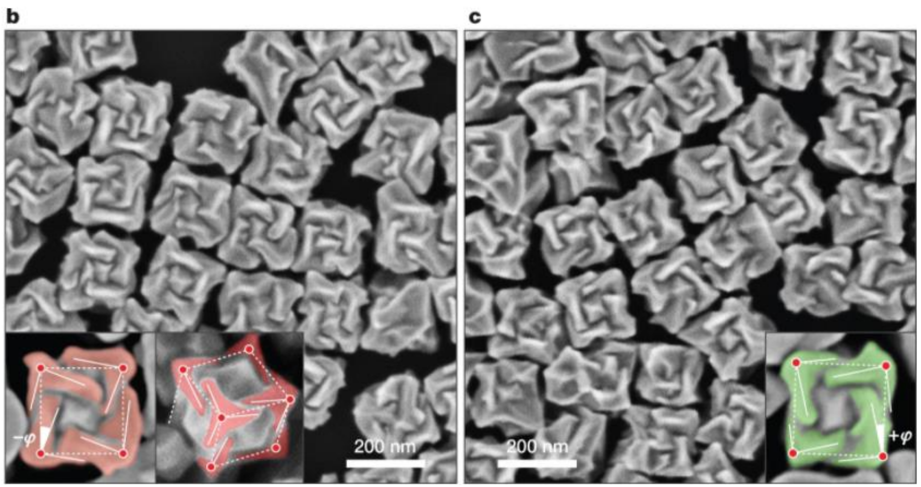


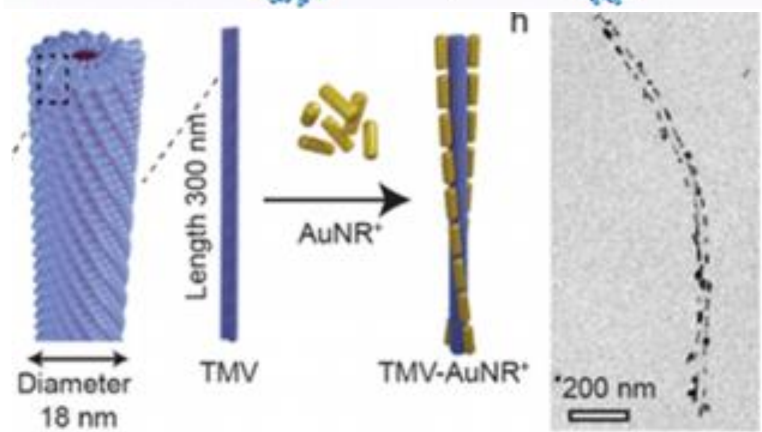
Interaction with plane polarized light :

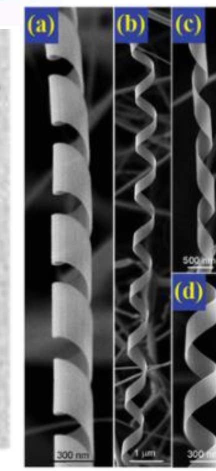


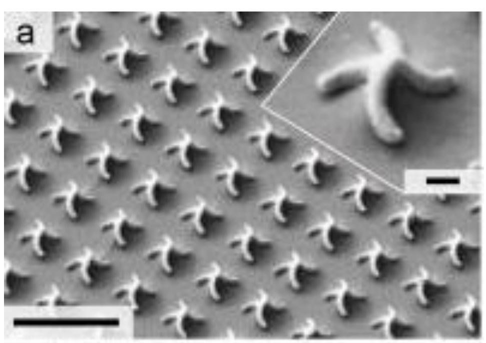
Chirality at nanoscale…………..

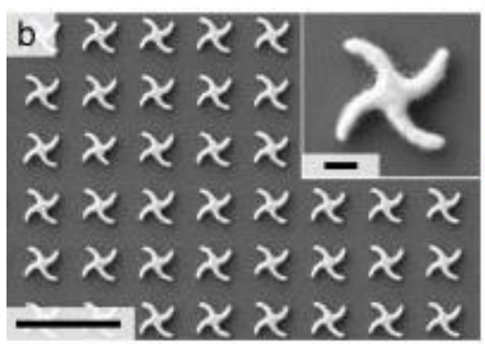


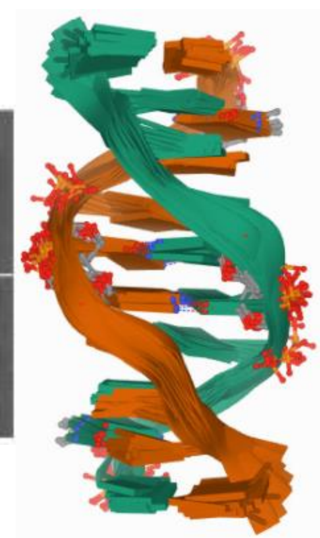


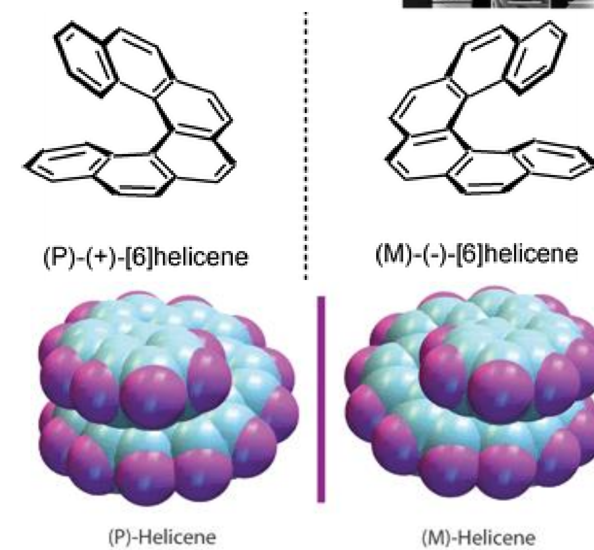












Introduction to the paper:

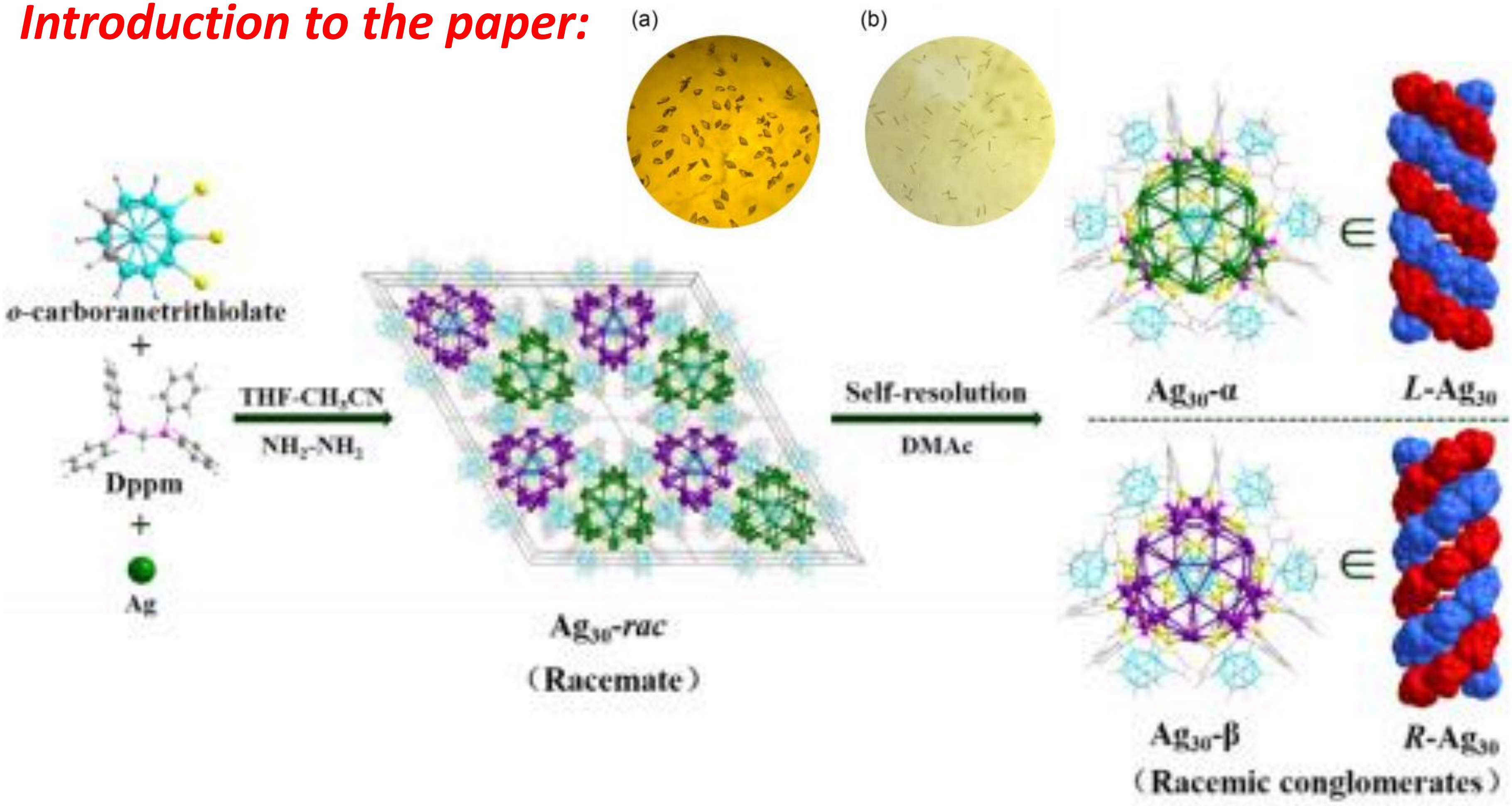
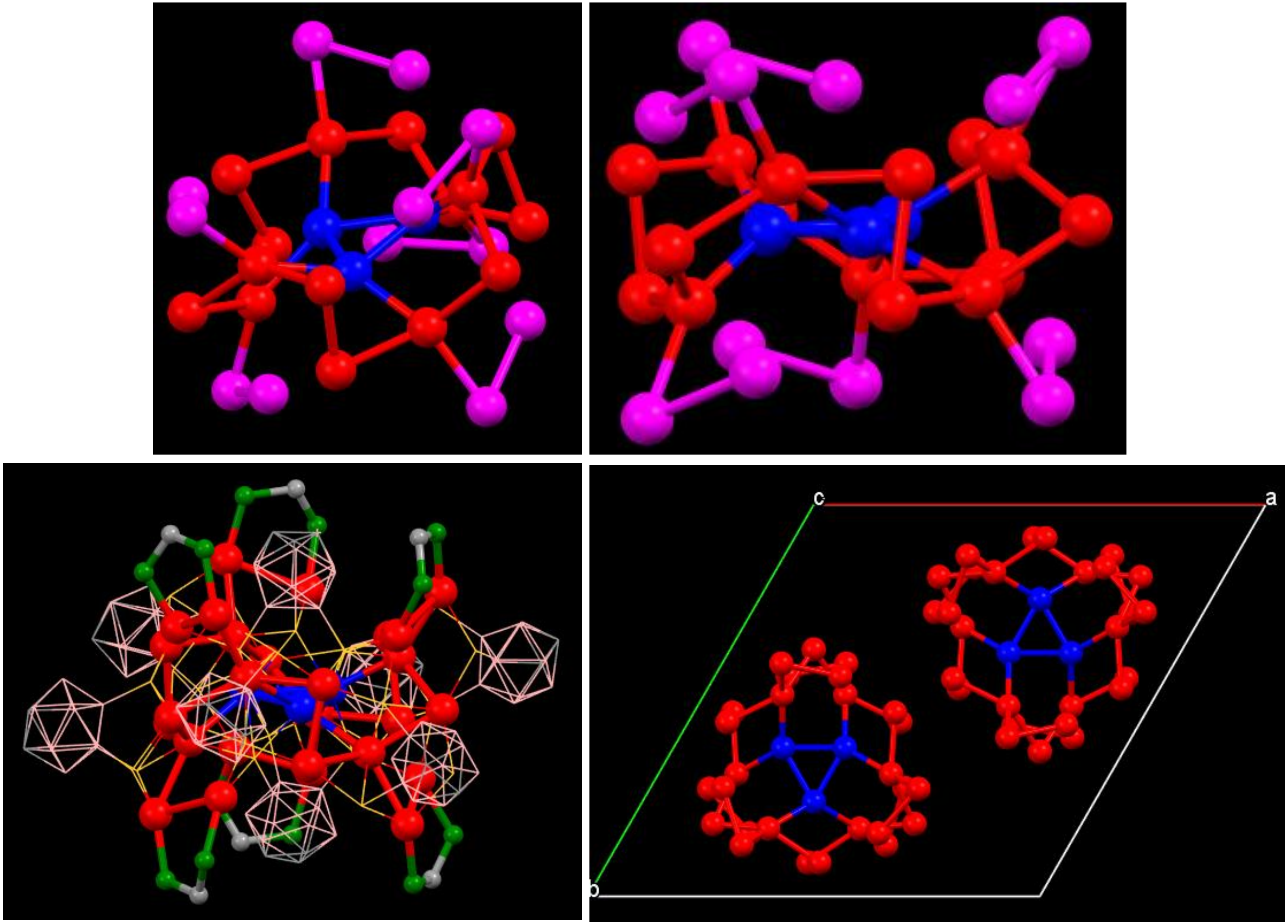


Figure 1. Schematic illustration of the synthesis and self-resolution of the racemic **Ag_{30}**-*rac*. Color labels: green, blue, red, and violet, Ag; yellow, S; pink, P; gray, C; cyan, B; light gray, H.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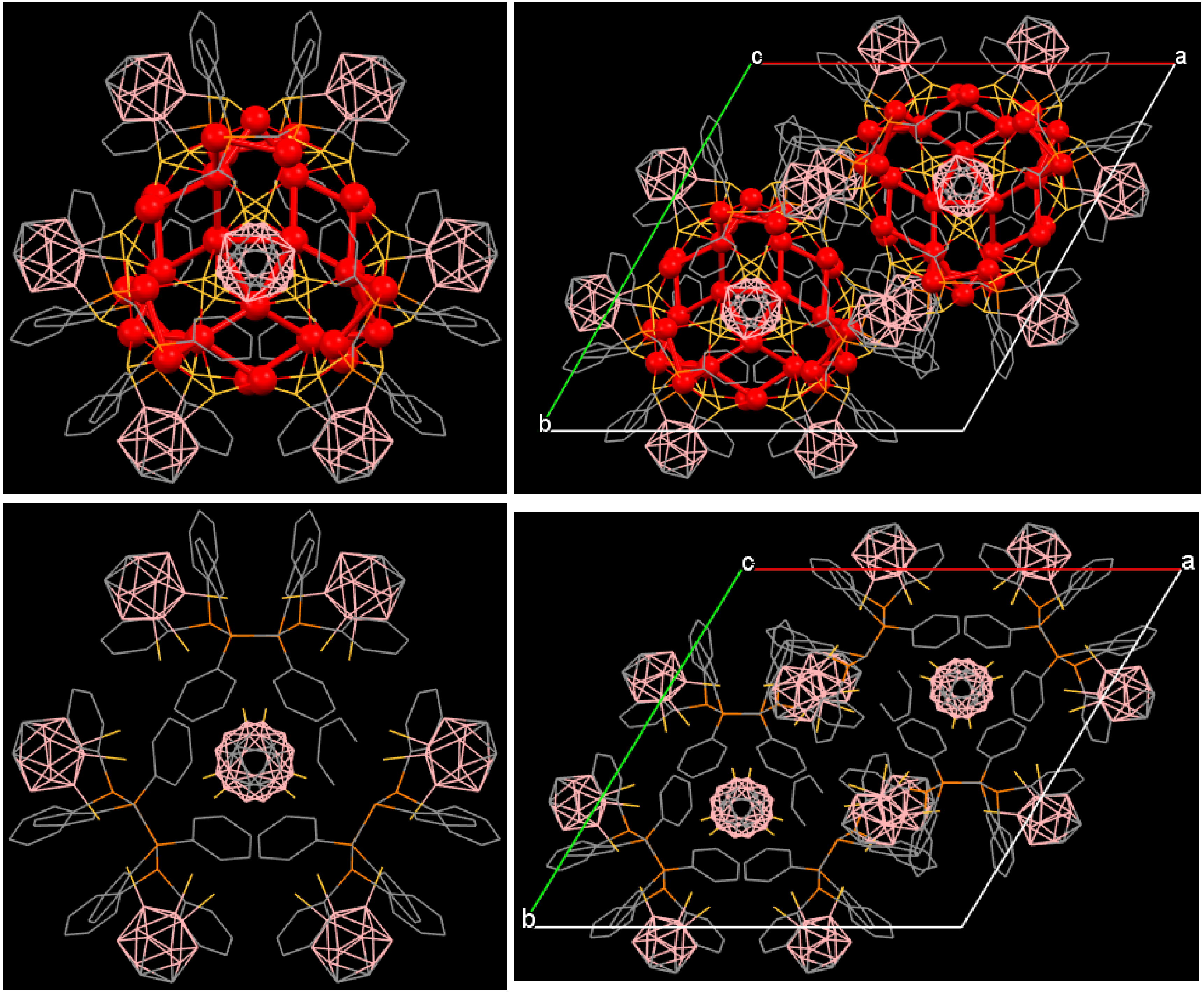
c
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c
a
b

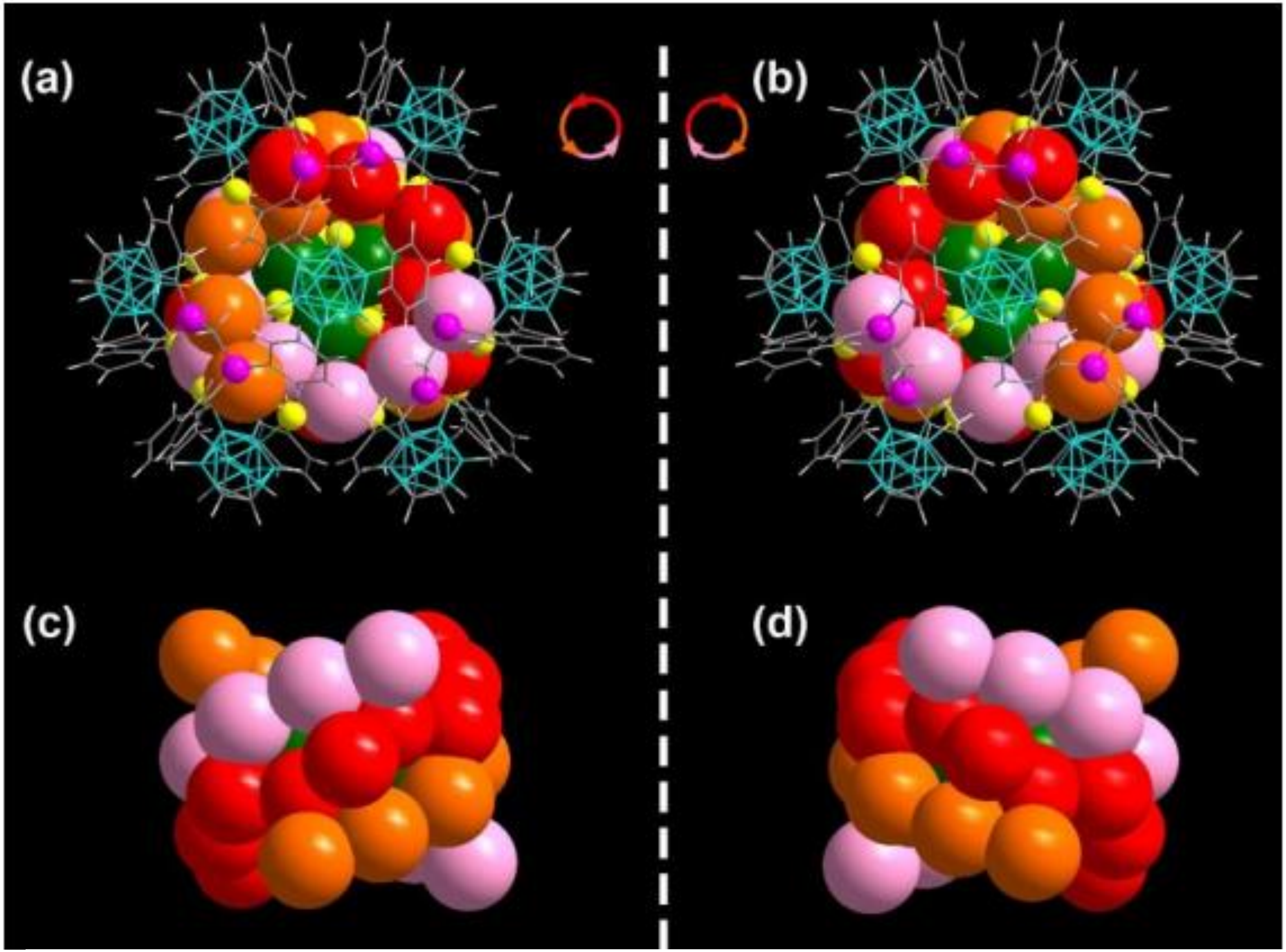


Figure S9. (a) (b) Overall structure of the enantiomers in **Ag_{30}-*rac*** viewed from the top. (c) (d) Arrangements of Ag atoms viewed from the side. Color labels: green, red, orange and light pink, Ag; yellow, S; pink, P; gray, C; cyan, B; white, H.

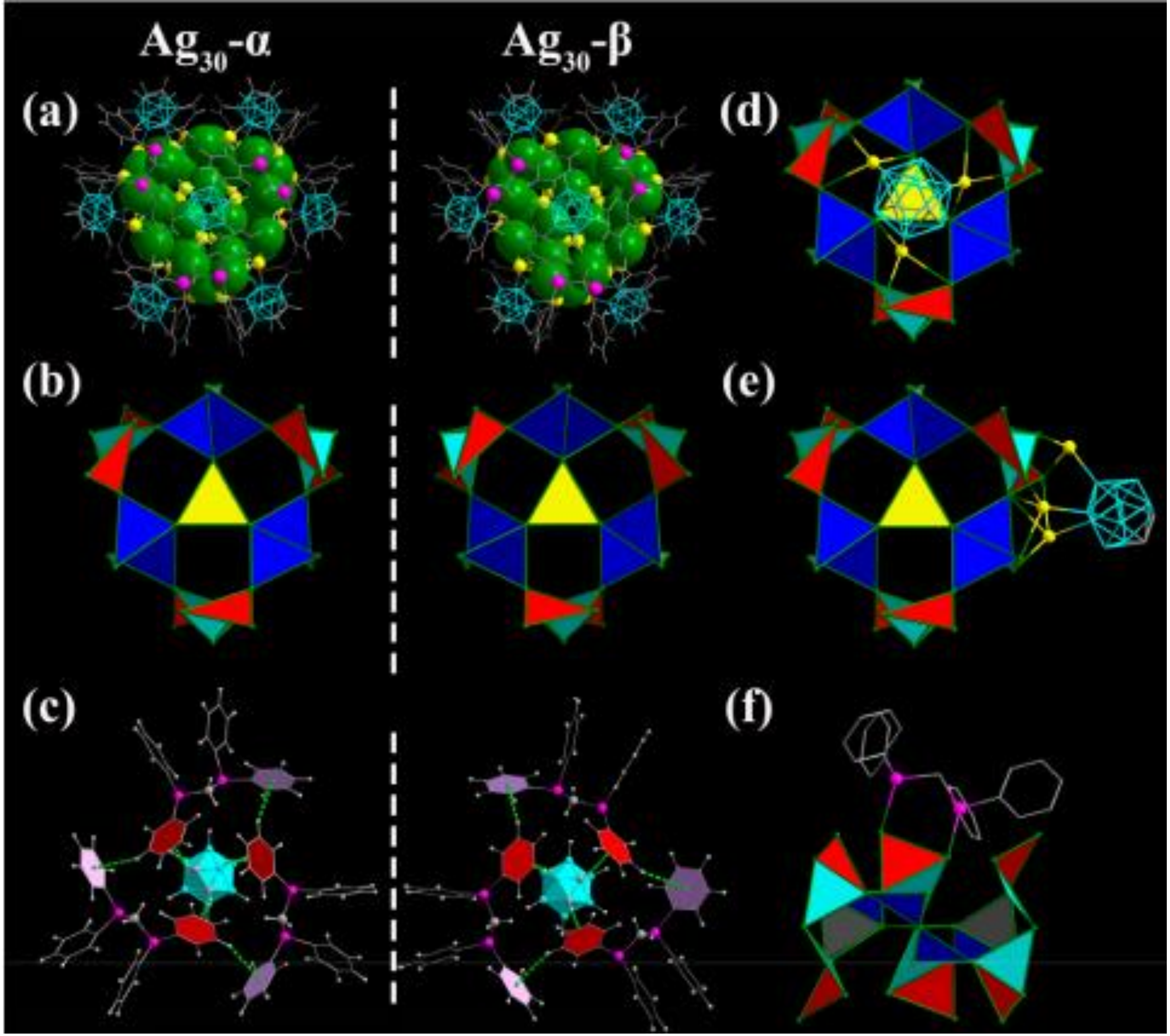


Figure 2. Atomic structure of the cluster in Ag30-rac. (a) Overall structure of the enantiomers. (b) Chiral triangle-based metal architectures in the enantiomers. (c) Illustration of the intracluster noncovalent interactions in the enantiomers. (d−f) Binding modes of carboranetrithiolate and phosphine in Ag30-α.

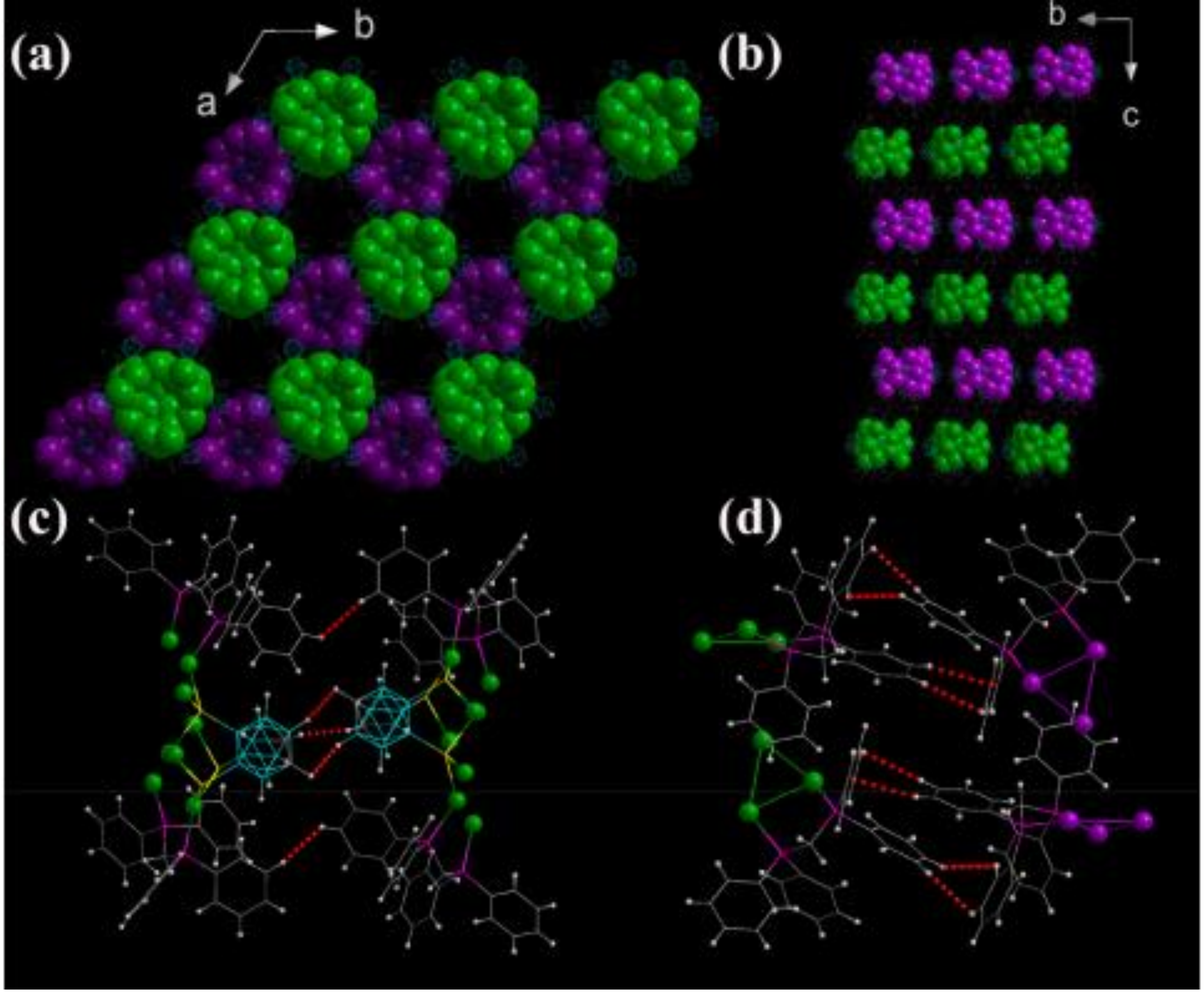


Figure 3. Packing of enantiomers in the lattice of Ag30-rac. (a, b) Packing structures viewed along the c and a axis. (c) Intercluster weak interactions in the same layer. (d) Intercluster weak interactions between neighboring layers. Color labels: green and violet, Ag; yellow, S; pink, P; gray, C; cyan, B; white, H. Red dashed lines indicate the week interaction.

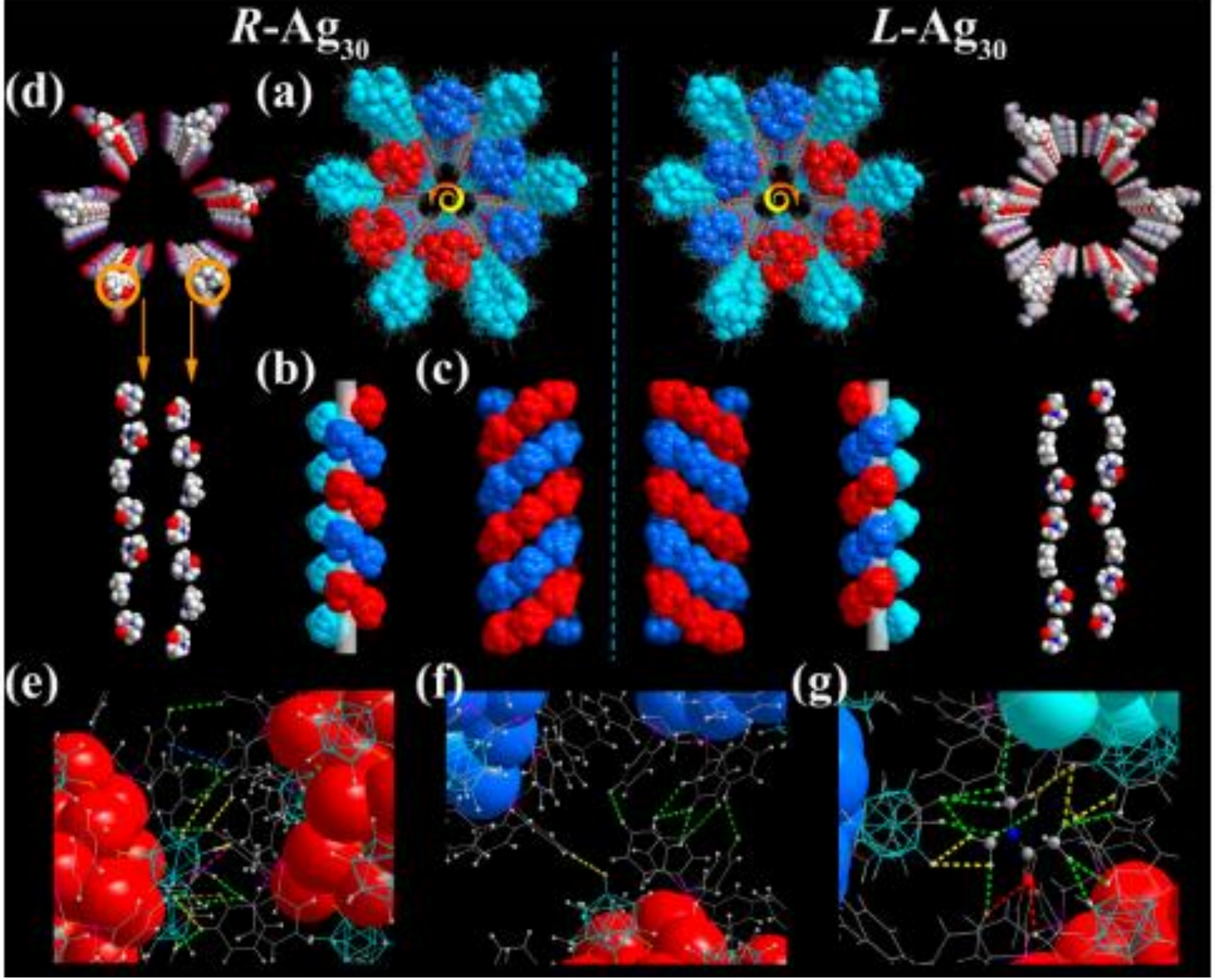


Figure 4. Packing mode analysis of the R-Ag30 and L-Ag30. (a) Perspective diagram of the superstructure viewed along the c axis. (b) Smaller helix surrounding the helical tubes. (c) Helical tubes built with double helical arranged nanoclusters. (d) Helically organized DMAc molecules in the crystal lattice. (e−g) Weak interactions among the nanoclusters and DMAc molecules. Color labels of the dashed lines: green, H(C)···H(C); yellow, H(B)···H(C); purple, B− H···π; blue, π···π; red, C−H···O.

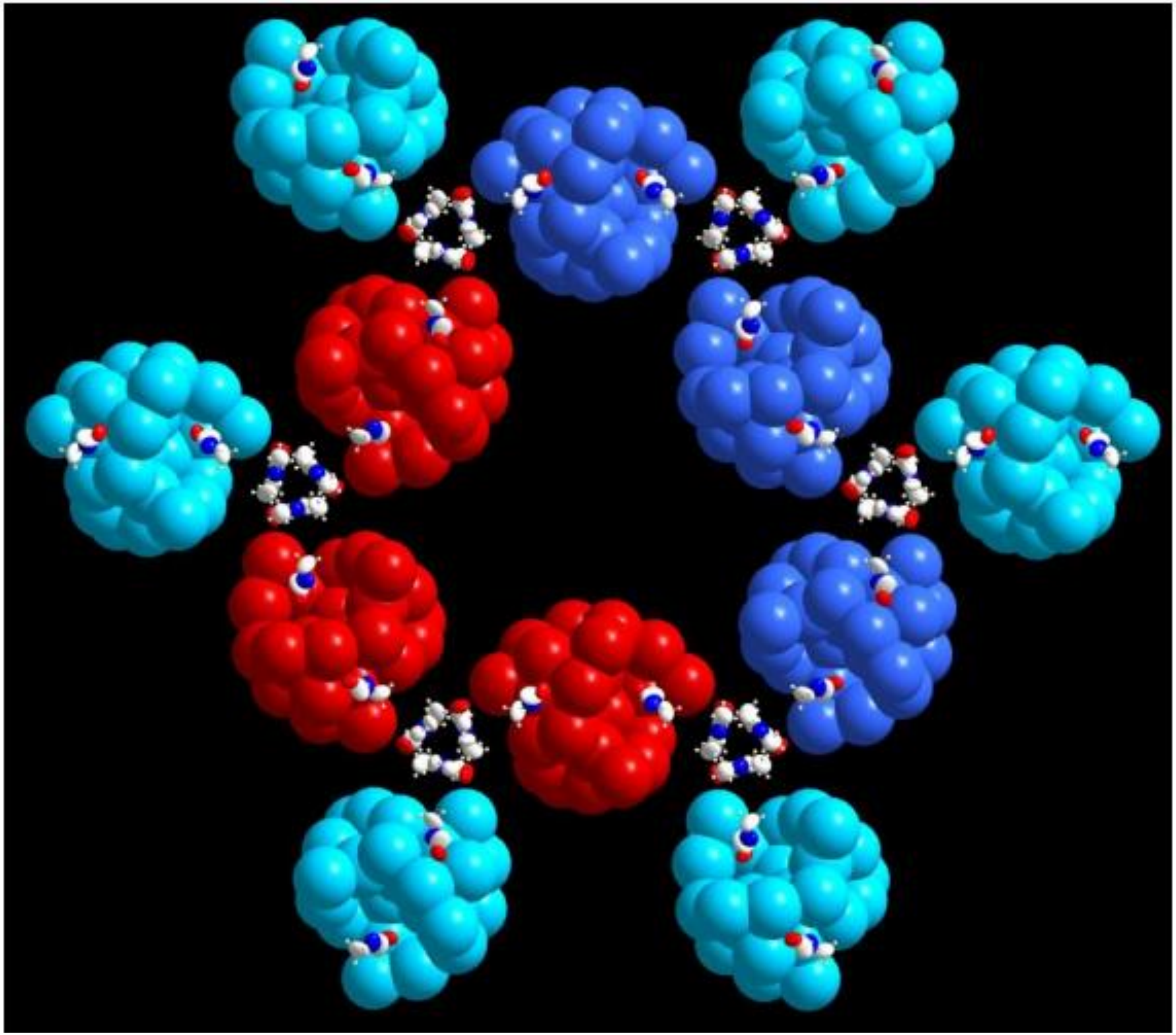


Figure S11. The arrangement of DMAc molecules in the lattice. Color labels: cyan, blue, and deep red, Ag; blue, N; red, O; white, H.

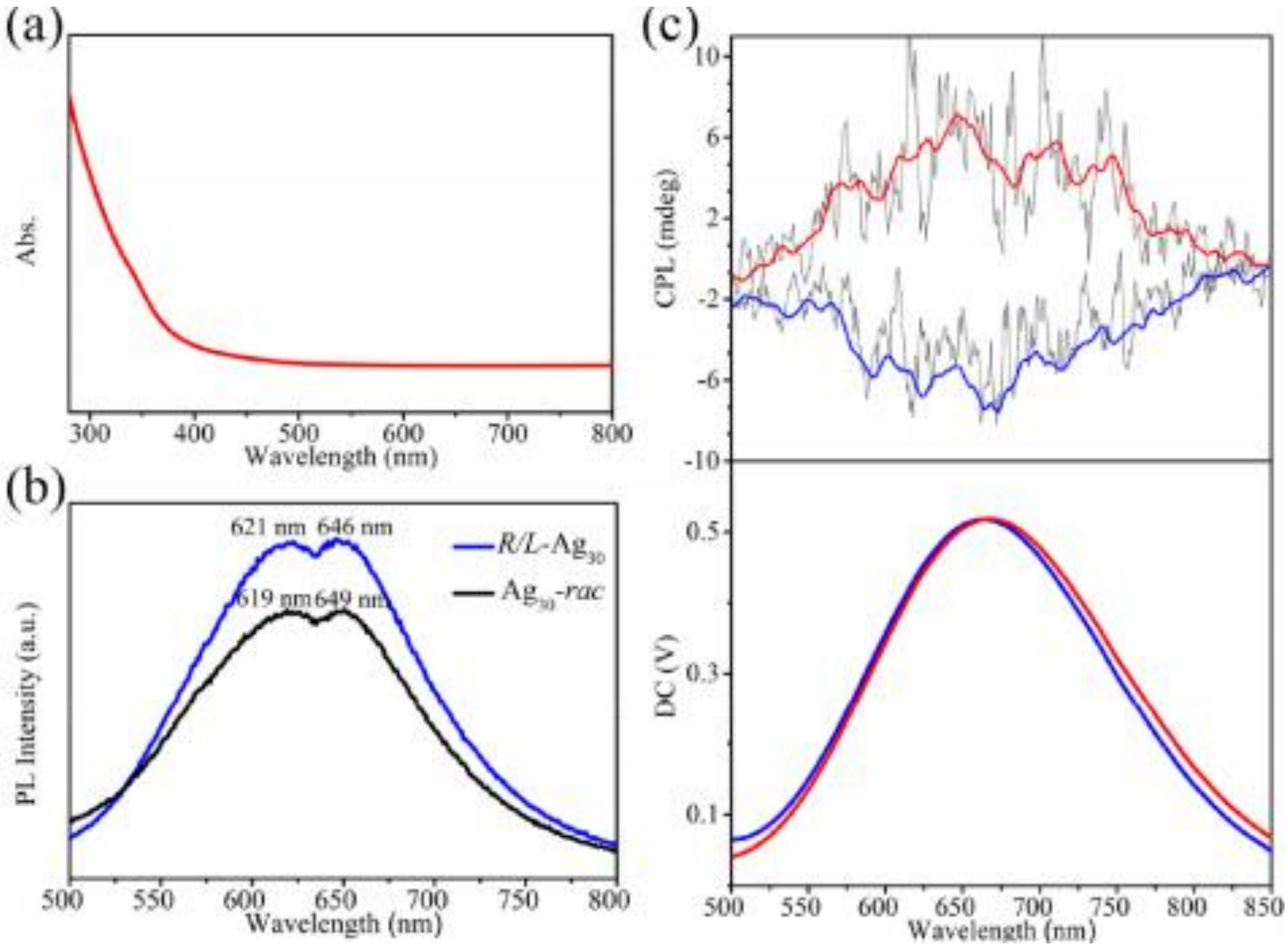
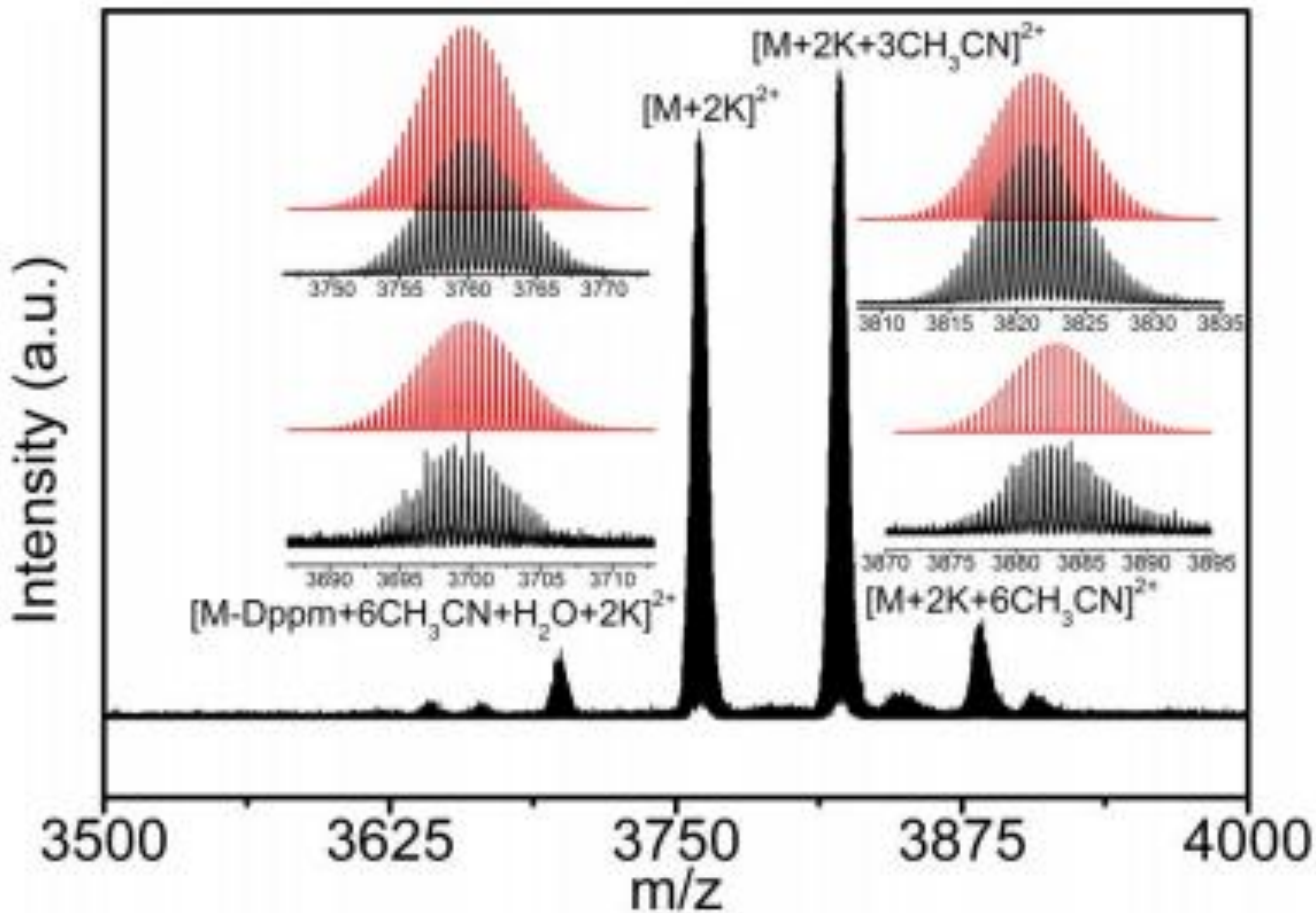


Figure 5. Photophysical properties. (a) UV−vis absorption spectrum of Ag30-rac in DMAc. (b) Solid-state emission spectra of Ag30-rac and the racemic conglomerates R/L-Ag30. (c) CPL spectra of R-Ag30 and L-Ag30 excited at 367 nm.

Conclusion…….

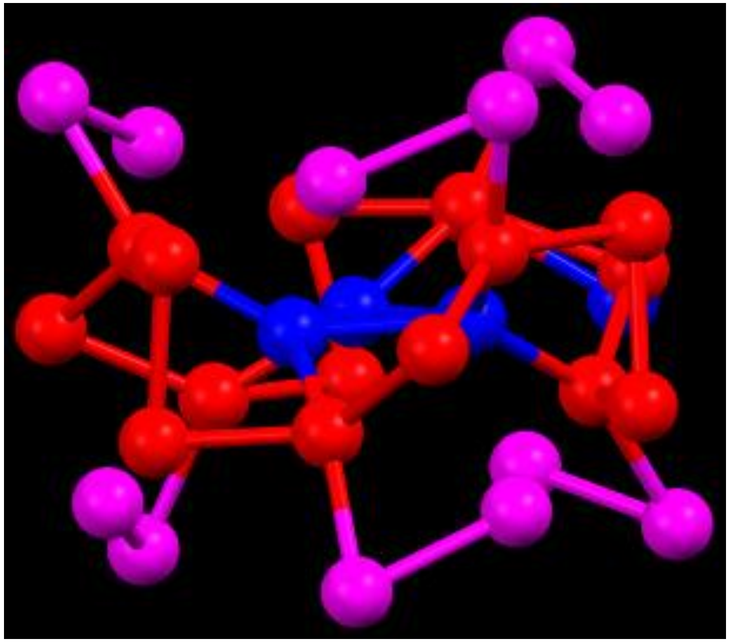
- The synthesis of racemic Ag_{30}-rac nanoclusters by a facile one-pot method with carboranetrithiolate and phosphine as coprotective ligands utilizing hydrazine as the reducing agent.
- Crystal structure analysis revealed that the chirality of the nanocluster arises from the spiral arrangement of the ligands directed by unusual B−H···π and C−H···π bonding interactions among the carborane cages and the benzene rings.
- The racemate underwent a spontaneous self-resolution upon recrystallization in DMAc and formed a mechanic mixture of racemic conglomerates.
- The Ag_{30} nanoclusters display red luminescence in both solid and solution states, and the mirror-image CPL Spectra.

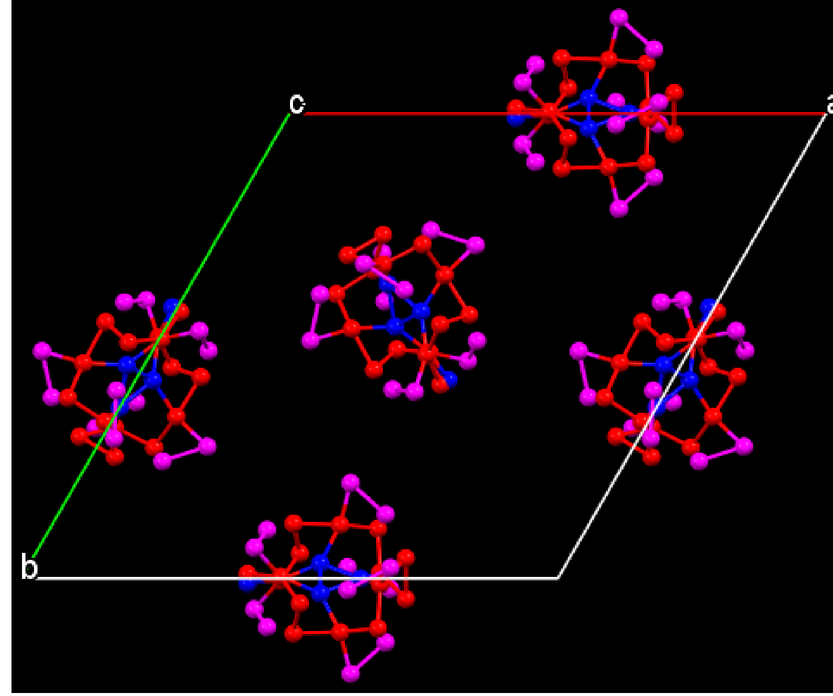
Thank you



[M+2K+3CH3CN]2+
[M+2K]2+
[M-Dppm+6CH3CN+H2O+2K]2+
[M+2K+6CH3CN]2+
3750 3755 3760 3765 3770
3810 3815 3820 3825 3830 3835
3690 3695 3700 3705 3710
3870 3875 3880 3885 3890 3895
Intensity (a.u.)
3500 3625 3750 3875 4000
m/z

Identification code	Ag_{30}-*rac*	*R*-Ag_{30}	*L*-Ag_{30}
CCDC number	2010140	2010153	2010157
Empirical formula	$C_{166}H_{204}Ag_{30}B_{80}P_{12}S_{24}$	$C_{182}H_{240}Ag_{30}B_{80}N_4O_4P_{12}S_{24}$	$C_{182}H_{240}Ag_{30}B_{80}N_4O_4P_{12}S_{2}$
Formula weight	7441.11	7789.75	7789.75
Temperature/K	200.00(10)	100.00(2)	100.00(10)
Crystal system	trigonal	trigonal	trigonal
Space group	*P*-31*c*	$P3_221$	$P3_121$
a/Å	22.084(2)	34.9242(3)	34.8668(13)
b/Å	22.084(2)	34.9242(3)	34.8668(13)
c/Å	35.768(1)	24.1417(2)	24.0968(6)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
Volume/Å^3	15107(2)	25500(5)	25370(2)
Z	2	3	3
ρ_{calc}g/cm^3	1.636	1.522	1.530
μ/mm^{-1}	17.61	15.689	15.77
F(000)	7148	11298	11298
Crystal size/mm^3	0.15 × 0.17 × 0.2	0.12 × 0.08 × 0.06	0.15 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.62 to 124.994	4.684 to 129.996	5.854 to 130.996
Index ranges	-25 ≤ h ≤ 24, -25 ≤ k ≤ 21, -34 ≤ l ≤ 41	-22 ≤ h ≤ 41, -40 ≤ k ≤ 20, -26 ≤ l ≤ 28	-28 ≤ h ≤ 39, -41 ≤ k ≤ 41, -14 ≤ l ≤ 28
Reflections collected	44730	81938	81583
Independent reflections	8046 [R_{int} = 0.1607,	28183 [R_{int} = 0.0432,	28374 [R_{int} = 0.1020,

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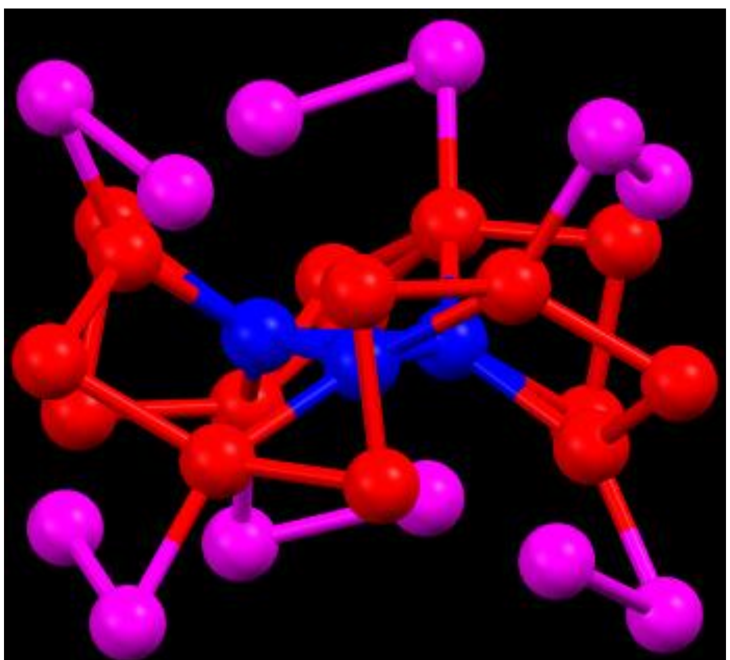

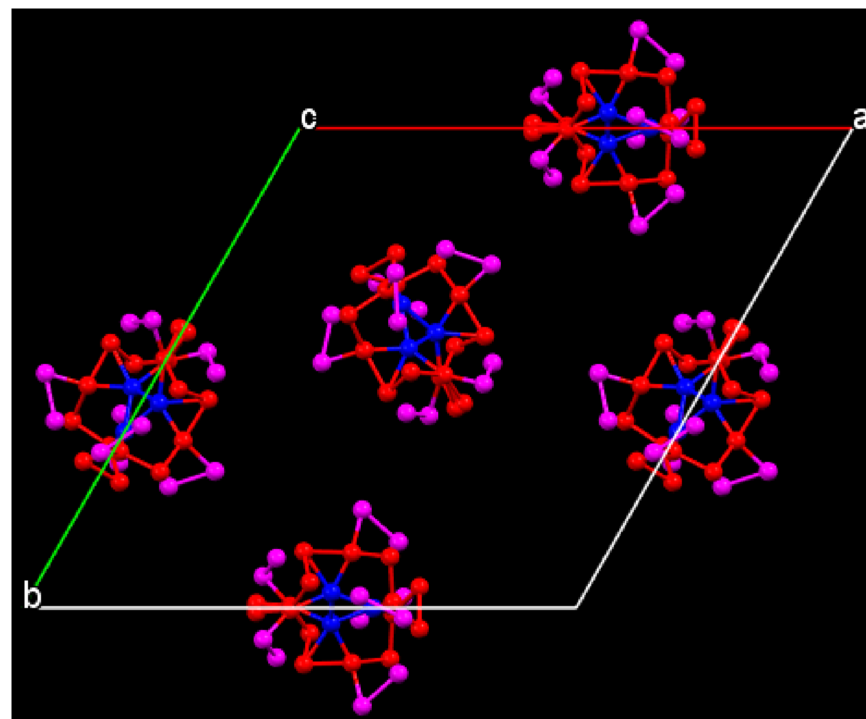
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