Chiroptical Modulation of Gold Nanorods by Self-Assembly: End-to-End vs. Side-by-Side

Xi Mao,[a] Abrahan Martinez,[c] Samantha Williams,[b] Shenli Zou,[c,*] Jie He[a,b,*]

[a] Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, USA
[b] Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, USA
[c] Department of Chemistry, University of Central Florida, Orlando, Florida 32816, USA

Materials and instruments

1 Materials.

Hexadecyltrimethylammonium bromide (CTAB, >98%), hexadecyltrimethylammonium chloride (CTAC, >95%), sodium borohydride ($NaBH_4$, 99%), sodium oleate (NaOL, >97%), D-cysteine (D-cys, >95%), were obtained from TCI America. Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.9%), hydrochloric acid (HCl, 37 wt% in water, 12.1 M), silver nitrate ($AgNO_3$, ≥99%), L-ascorbic acid (AA, 99%), L-cysteine (L-cys, 97%), styrene (St, ≥99%), 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%) were purchased from Sigma Aldrich. Bovine serum albumin (BSA, 98%) was obtained from Equitech-bio, Inc. The ultra-pure water was produced by double distillation using a High-Q distillation system (model # 103S). Styrene was purified by passing through a basic aluminum oxide column, AIBN was recrystallized from ethanol. The reversible addition-fragmentation chain transfer polymerization (RAFT) agent 3-(benzylthiocarbonothioylthio)propanoic acid (BCTPA) was synthesized according to a previously reported method. All other chemicals were used as received without additional purification. All glassware used for synthesis of gold nanoparticles was immersed in aqua regia for 30 min, followed by washing with distilled water.

2. Methods

2.1 Synthesis of gold nanosphere (3.5 nm) seeds.

10 mL of aqueous solution containing 100 mM CTAB and 0.25 mM $HAuCl_4$ was stirred at 27 ℃ for 10 min. Then, 0.6 mL of freshly prepared 10 mM ice-cold $NaBH_4$ solution was mixed with 0.4 mL of water and injected into Au-CTAB solution under vigorous stirring. The solution color changed from yellow to brown immediately. After stirring for 3 min, the seed dispersion was kept at 27 ℃ for 3 h before use.

2.2 Synthesis of gold nanorods (AuNRs).

AuNRs with aspect ratio of 5.9 were synthesized according to following procedure.[1] Briefly, 1 L aqueous solution with 14 g CTAB and 2.468 g NaOL was stirred to dissolve at 70 ℃ for 30 min. Then the solution was cooled down to 30 ℃, followed by 24 mL of 8 mM $AgNO_3$ was added and kept undisturbed for 15 mins. 50 mL of 10 mM $HAuCl_4$ solution was injected and stirred for 1.5 h until it became colorless. Subsequently, 6 mL of HCl solution was added to adjust pH. After stirring for 15 mins, 2.5 mL of 64 mM AA solution was added into the flask under vigorous stirring. Then, 1.6 mL of 3.5 nm seeds dispersion was injected into the flask. The flask was kept undisturbed at 30 ℃ for 12 h. The final product was centrifuged at 8000 rpm for 20 min, washed by 500 mL of water and redispersed in 70 mL of water. To replace the surface ligands of long AuNRs with CTAC/NaOL, the second growth of AuNRs was carried out by using the same procedure. After that, AuNRs were concentrated by centrifugation at 8000 rpm for 20 min and redispersed in 50 mL water for further use.

2.3 Synthesis of thiol-terminated polystyrene (HS-PS) and polystyrene-*block*-poly (ethylene oxide) (PS-*b*-PEO).

HS-PS (M_n = 16.8 kDa, PDI = 1.3) and PS_{37}-*b*-PEO_{140} (M_n = 10 kDa, PDI = 1.2) were synthesized according to previous work.[2]

2.4 Preparation of dumbbell-like AuNRs.

Dumbbell-like AuNRs were obtained based on our previous work.[2] Typically, 0.5 mL of AuNRs and 1.0 mL of water were mixed in a 1.5 mL centrifuge tube and centrifuged at 7000 rpm for 20 min. Meanwhile, 2 mL of DMF solution containing PS-*b*-PEO (0.5 mg/mL) and HS-PS at different concentrations (0.25-10 μM) were prepared.

Then, concentrated AuNRs (10-15 μL) were obtained after removing the supernatant, and the AuNRs were added to the 2 mL polymer DMF solution under sonication. The mixture was kept for 4 h after 4 min of sonication. Then, 0.353 mL of water was added to the mixture, followed by sonication for 4 min. Subsequently, the mixture was thermally annealed at 90 °C for 30 min. AuNRs dumbbells were obtained by centrifuging the mixture in 25 mM CTAC solution (2 mL of mixture was dispersed in 10 mL CTAC solution), washing with 10 mL of water, and redispersing in 2 mL of water.

2.5 Preparation of chiral AuNRs (c-AuNRs).

The c-AuNRs were prepared as follows.[3] First, 30 μL of 10 mM $HAuCl_4$ solution were dispersed in 40 mL of 17 mM CTAB solution and stirred at 30 ℃ for 10 min, followed by 120 μL of 1 M 2-methylpyridine and 2 mL of 100 mM AA solution were injected into the mixture. Then, 100 μL of 0.1 mM cysteine solution and 1 mL of dumbbell-like AuNR seeds were added. After stirring 15 min, 30 μL of 10 mM $HAuCl_4$ solution was added. The addition of $HAuCl_4$ solution was repeated for 8 times. The diameter of c-AuNRs was tuned by adjusting the growth cycles from 4 to 12. After that, the mixture was stirred at 30 ℃ for 2 h. Then, the mixture was centrifuged at 5000 rpm for 10 min and washed by 10 mL water and redispersed in 2 mL water.

2.6 Preparation of chiral AuNR chains and disassembly.

Chiral AuNR chains were synthesized by seed-mediated growth of AuNR chains. First, achiral AuNR chains were prepared by adding 80 μL of concentrated AuNRs in 2 mL of DMF containing 0.5 mg/mL PS-*b*-PEO and 1 μM HS-PS. AuNR chains were obtained after waiting overnight and purified by centrifugation at 3000 rpm for 5 min. Then, AuNRs were redispersed in 2 mL of 17 mM CTAB solution as seeds. The chiral AuNR chains were prepared by using the same procedure of preparation of c-AuNRs. The diameter (short axis of AuNRs) of chiral chains was adjusted by growth cycles.

2.7 Side-by-side (SS) assembly of c-AuNRs.

The SS assembly of dumbbell-like c-AuNRs was carried out by mixing 100 μL of c-AuNRs with 900 μL of ethanol (EtOH). The chiral SS assemblies of dumbbell-like c-AuNRs was formed by mixing 1 mL of 1 μM BSA in 1 mM PBS butter (pH = 6.4) with 1 mL c-AuNRs in 0.3 mM CTAB solution under an ice bath.[4]

2.8 Simulations.

The discrete dipole approximation (DDA) method was used to calculate the *g*-factor of c-AuNRs, SS and EE assemblies. In the DDA method, the target can be represented with an array of polarizable cubes and the length of the cube was kept as 1 nm. Due to the weak signal (less than 10^{-4}), which poses a challenge for numerical simulations requiring at least six-digit convergence precision, we amplified the signal by over 100 times to better illustrate the trend observed in the experiment. The AuNRs with 100 nm of length and 30 nm of diameter, as well as the chiral curl has a width of approximately 3 nm and a height of 2 nm were used for the simulations.

2.9 Characterization.

The structures of chiral AuNRs and assemblies were observed by transmission electron microscopy (TEM, Tecnai 12 G2 TEM, FEI, acceleration voltage: 120 kV) and scanning electron microscope (SEM, FEI, acceleration voltage: 10 kV). The optical and chiroptical properties were performed on ultraviolet-visible (UV-vis, Cary 60, Aglient and Jasco v670, JASCO) and circular dichroism (CD, Chirascan V100, Applied Photophysics). The grafting density of polymer was measured by thermogravimetric analysis (TGA, SDT Q600, TA Instruments).

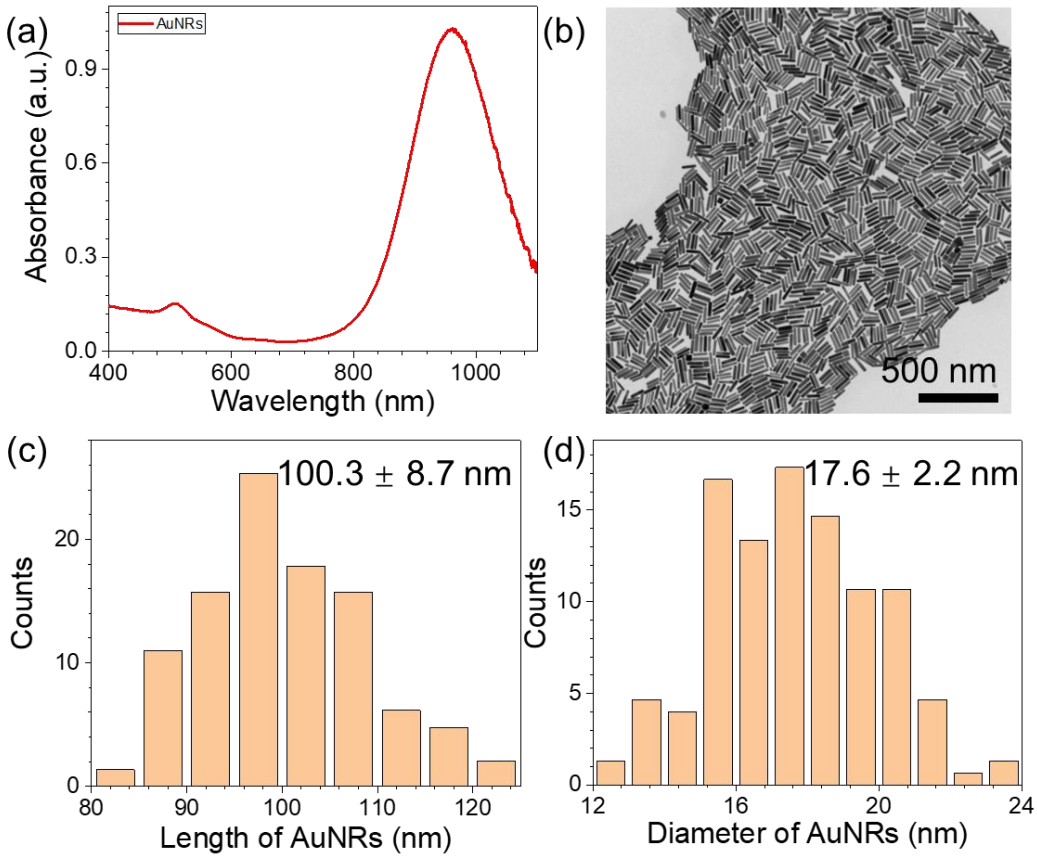


Figure S1. Characterization of CTAC stabilized AuNRs: (a) UV-vis spectrum, (b) TEM image, (c, d) statistic column chart of length and diameter of AuNRs, respectively.

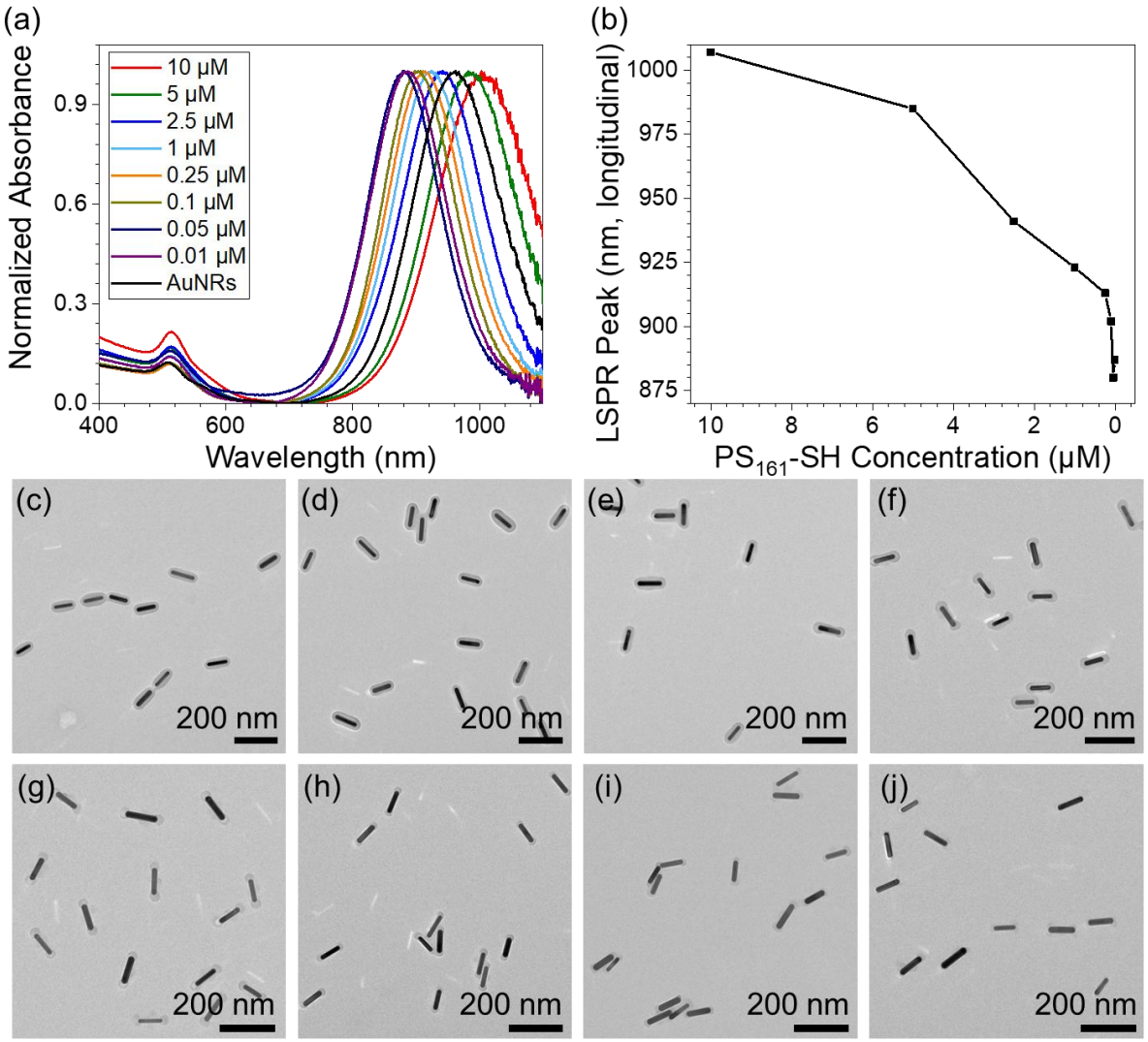


Figure S2. UV-vis spectra (a), longitudinal LSPR peak (b) and TEM images (c-j) of Au@PS prepared at different PS_{161}-SH concentrations ($C_{PS161\text{-}SH}$): (c) 10 μM, (d) 5 μM, (e) 2.5 μM, (f) 1 μM, (g) 0.25 μM, (h) 0.1 μM, (i) 0.05 μM, (j) 0.01 μM.

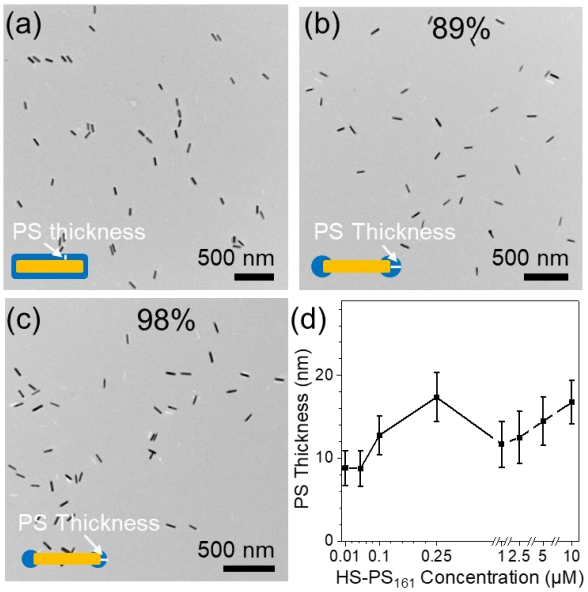
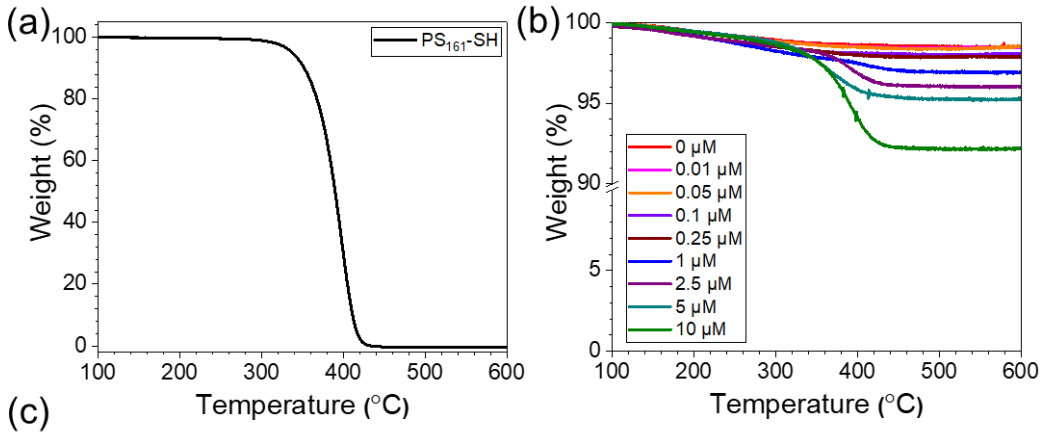


Figure S3. TEM images of AuNRs@PS at different $C_{PS161\text{-}SH}$: (a) 10 μM, (b) 0.25 μM, (c) 0.1 μM. (d) Plot of PS thickness and PS_{161}-SH concentration.



(c)

PS_{161}-SH concentration	Weight loss (%)	Overall σ (chains/nm²)	σ (tip)
0 μM	1.52		
0.01 μM	1.54	0.045	0.303
0.05 μM	1.48	0.043	0.290
0.1 μM	1.95	0.058	0.385
0.25 μM	2.15	0.063	0.424
1 μM	3.11	0.093	0.620
2.5 μM	4.00	0.120	
5 μM	4.79	0.145	
10 μM	7.82	0.245	

Figure S4. TGA curves of PS_{161}-SH (a) and Au@PS prepared at different $C_{PS161\text{-}SH}$ (b). (c) Table summary of grafting densities (σ) of Au@PS prepared at different $C_{PS161\text{-}SH}$.

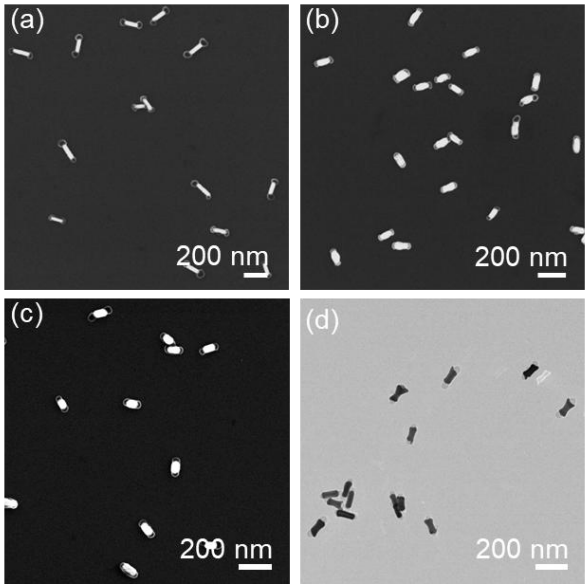


Figure S5. SEM images of dumbbell-like AuNRs (a) and L-AuNRs (b) and D-AuNRs (c). (d) TEM image of AuNRs/WO-cys.

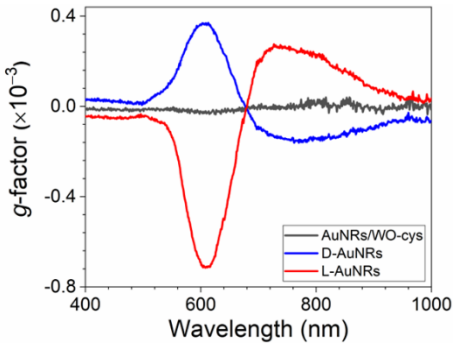


Figure S6. *g*-factor spectra of L-/D-AuNRs and AuNRs/WO-cys.

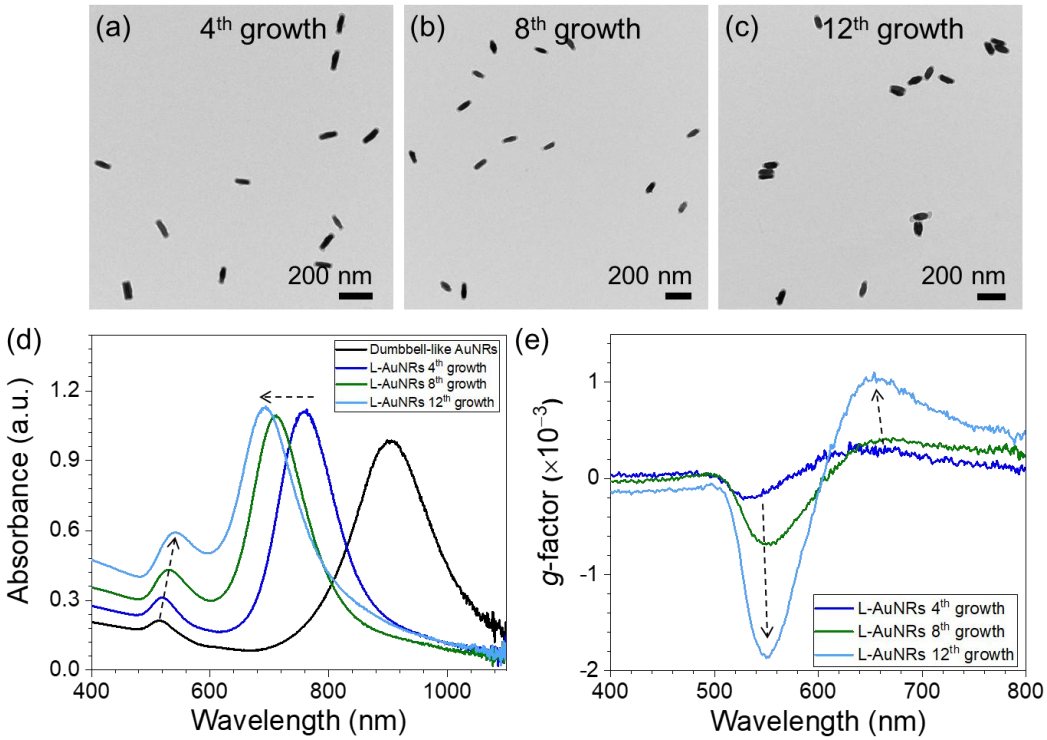


Figure S7. TEM images (a-c), and UV-vis (d), CD spectra (e) of L-AuNRs with different growth cycles.

Table S1. Summary of diameter and *g*-factor for L-/D-AuNRs and L-/D-Chains.

		Growth cycle	**Diameter (nm)**	***g*-factor at TSPR[a]**	***g*-factor at LSPR[b]**
Batch 1	L-AuNRs	8^{th}	38.6 ± 6.7	-7.1×10^{-4}	1.5×10^{-4}
	D-AuNRs	8^{th}	40.9 ± 6.2	3.7×10^{-4}	-2.6×10^{-4}
Batch 2	L-AuNRs	4^{th}	34.3 ± 3.9	-2.1×10^{-4}	3.1×10^{-4}
	L-AuNRs	8^{th}	42.3 ± 5.4	-6.9×10^{-4}	3.7×10^{-4}
	L-AuNRs	12^{th}	48.3 ± 6.9	-1.9×10^{-3}	1.0×10^{-3}
	L-Chains	4^{th}	27.7 ± 3.5	-5.7×10^{-4}	/
	L-Chains	8^{th}	34.8 ± 8.8	-2.5×10^{-3}	/
	L-Chains	12^{th}	38.7 ± 8.7	-3.3×10^{-3}	/
	D-Chains	4^{th}	26.7 ± 3.3	3.7×10^{-4}	/
	D-Chains	8^{th}	32.5 ± 5.8	1.6×10^{-3}	/
	D-Chains	12^{th}	40.0 ± 7.3	2.6×10^{-3}	/

[a] TSPR refers to transverse localized surface plasmon resonance; [b] LSPR means longitudinal localized surface plasmon resonance.

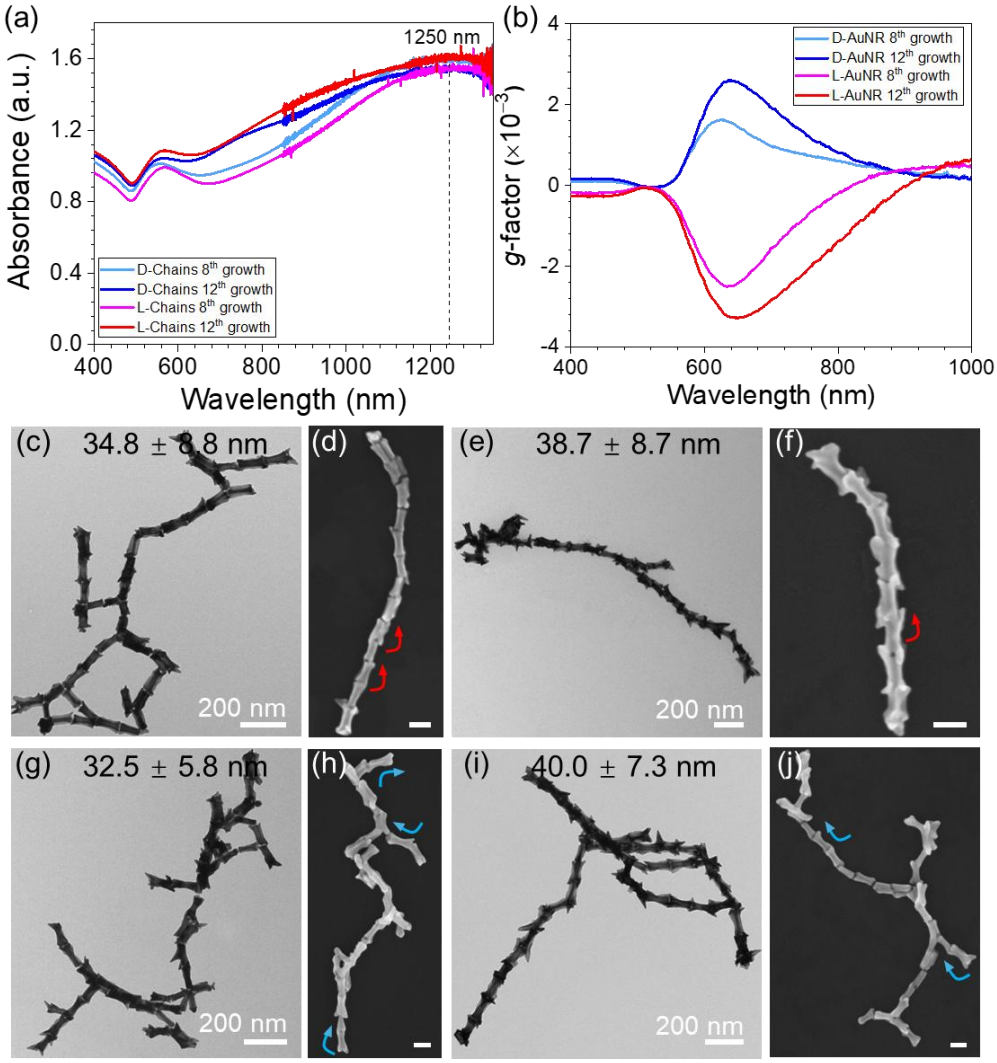


Figure S8. UV-vis (a), CD spectra (b) TEM and SEM images of L-/D-Chains with different growth cycles: (c, d) L-Chains with 8 times growth; (e, f) L-Chains with 12 times growth; (g, h) D-Chains with 8 times growth; (i, j) D-Chains with 12 times growth. The scale bars in (d, f, h, j) are 100 nm.

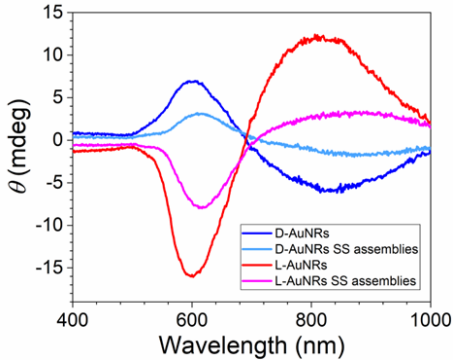


Figure S9. CD spectra of L-/D-AuNRs and their SS assemblies.

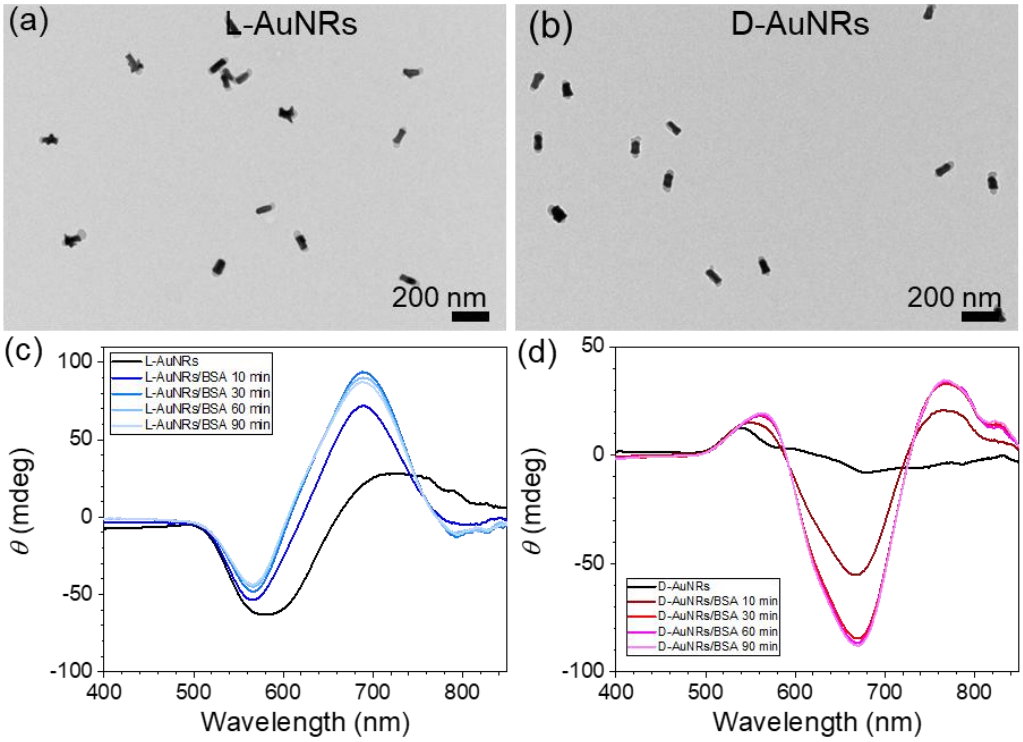


Figure S10. (a, b) TEM images of L-/D-AuNRs with diameter of 44.4 ± 7.2 nm and 39.2 ± 5.6 nm, respectively. (c, d) CD spectra of BSA induced SS assembly of L-AuNRs (c) and D-AuNRs (d).

REFERENCES

1. X. Ye, C. Zheng, J. Chen, Y. Gao and C. B. Murray, *Nano Lett.*, 2013, **13**, 765-771.
2. H. Duan, Z. Jia, M. Liaqat, M. D. Mellor, H. Tan, M.-P. Nieh, Y. Lin, S. Link, C. F. Landes and J. He, *ACS Nano*, 2023, **17**, 12788-12797.
3. N.-N. Zhang, M. Mychinko, S.-Y. Gao, L. Yu, Z.-L. Shen, L. Wang, F. Peng, Z. Wei, Z. Wang, W. Zhang, S. Zhu, Y. Yang, T. Sun, L. M. Liz-Marzán, S. Bals and K. Liu, *Nano Lett.*, 2024, **24**, 13027-13036.
4. J. Zhou, Y. Gao, D. Zhang, K. Ren, M. Dai, H. Wang and L. Qi, *Nat. Commun.*, 2025, **16**, 6897.