Constructing Chiral Gold Nanorod Oligomers Using Spatially Separated Sergeants-and-Soldiers Effect

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Supporting Information

Materials

Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), silver nitrate ($AgNO_3$) were purchased from Beijing Chemical Reagent Company. Trisodium citrate was purchased from Alfa Aesar. L/D-cysteine (L/D-Cys), 4-aminophenol (4-ATP), mercaptobenzene (MB), sodium borohydride ($NaBH_4$), cetyltrimethylammonium bromide (CTAB), L-ascorbic acid (AA) were purchased from Sigma. Milli-Q Water (18 MΩ•cm) was used for the experiments. Cetylpyridinium chloride (CPC) was purchased from Ark pharm. Cetyltrimethylammonium chloride (CTAC) was purchased from TCI.

Characterizations.

CD measurements were conducted on a JASCO J-1500 CD spectrometer and the bandwidth was set at 2 nm. Zeta potentials were obtained using a zeta potential and size analyzer (Malvern, Zeta-sizer nano ZS). Extinction spectra were obtained using a Cary 60 UV-vis-NIR spectrophotometer. SEM images were taken using a Zeiss JC-Merlin SEM with a voltage of 5 kV. TEM measurement was performed on a Tecnai G2 20 S-TWIN TEM at an accelerating voltage of 200 kV. Raman spectra were obtained in solution phase using a Renishaw InVia Raman microscope with a 785 nm laser.

HRTEM images with relative strain mapping were taken using Titan G2 60-300 with image corrector (point resolution = 80 pm) operating at an accelerating voltage of 300 kV. Image analysis was done using GPA and Digital Micrograph (Gatan) software.

Spectra measurement: All extinction and CD spectra were obtained directly with solution samples in a 1 cm * 1 cm quartz cuvette.

Experimental results

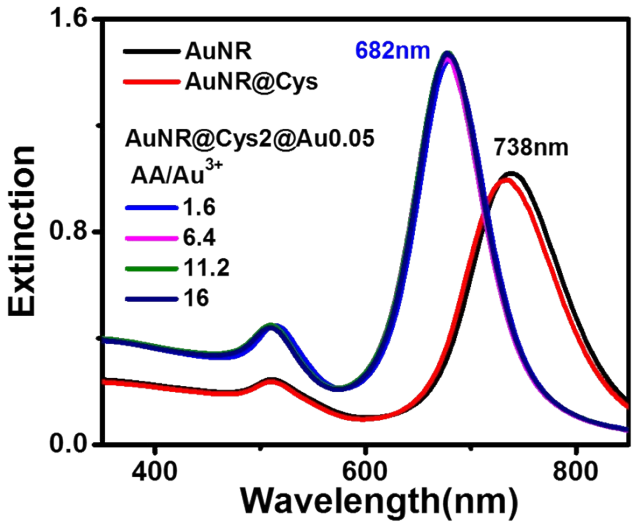

Figure S1. Effect of AA/Au^{3+} molar ratio on extinction spectra of AuNR@Cys2@Au0.05 monomers.

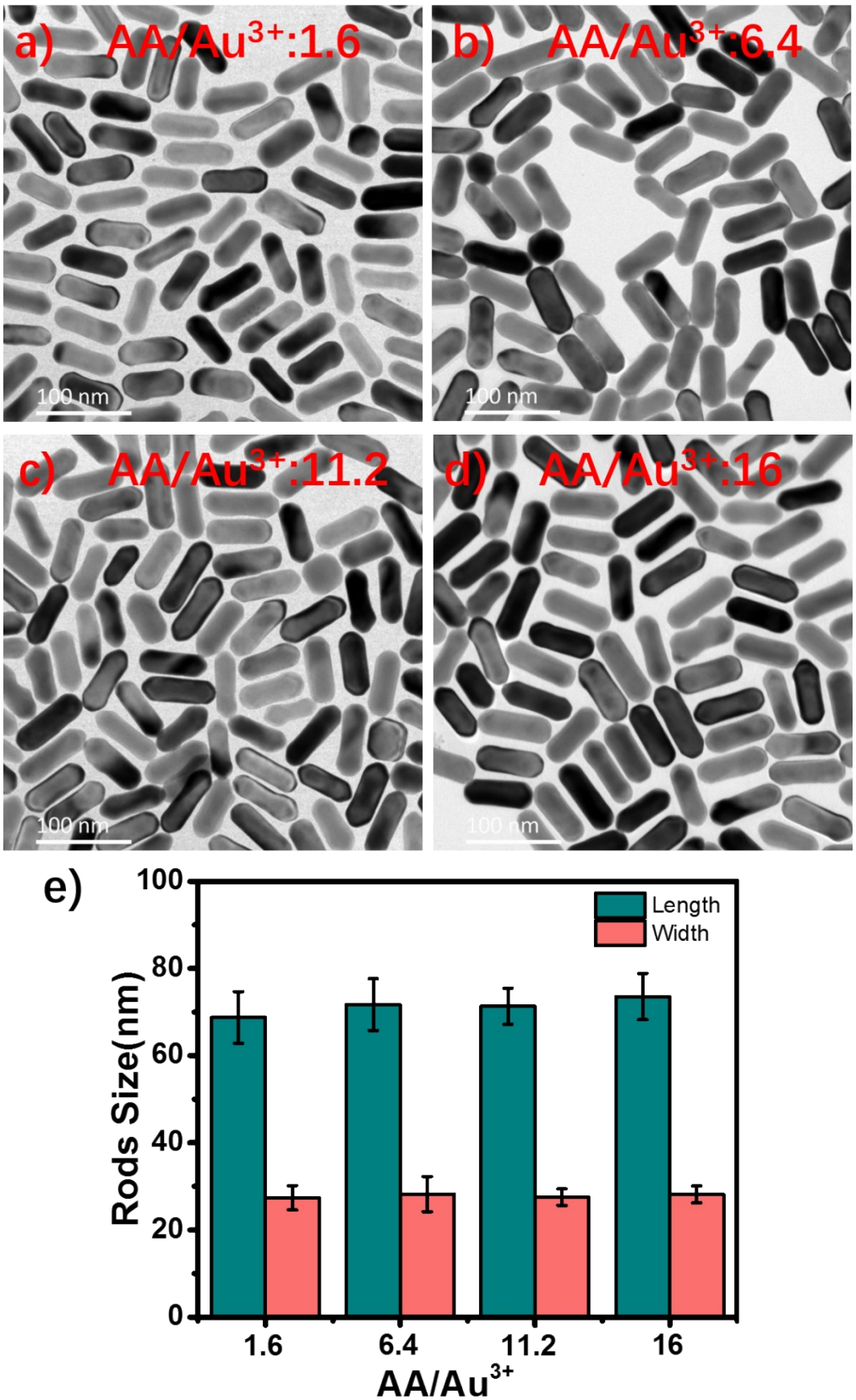

Figure S2. TEM images (a-d) of Au@Cys2@Au0.05 monomers obtained with different AA/Au^{3+} ratios. (e) rod size vs AA/Au^{3+} ratio.

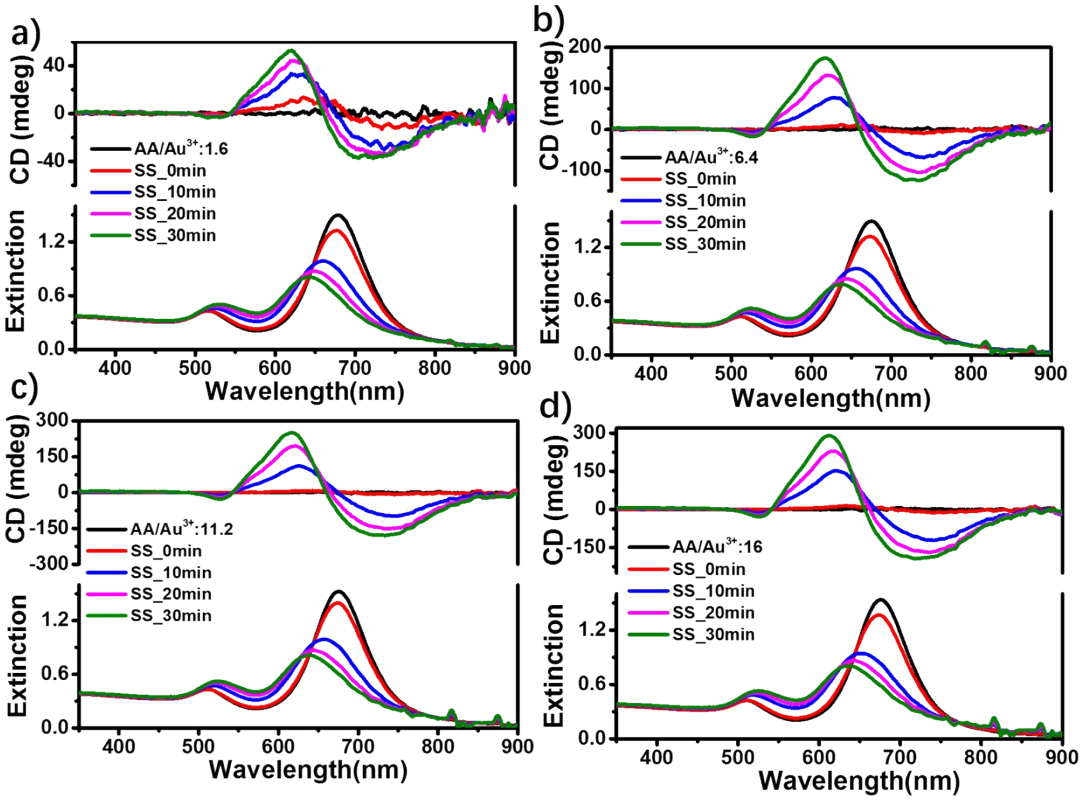

Figure S3. Changes in CD and extinction spectra of AuNR@Cys2@Au0.05 SS oligomers during 60 ℃ assembly process using monomers prepared with different AA/Au^{3+} ratios.

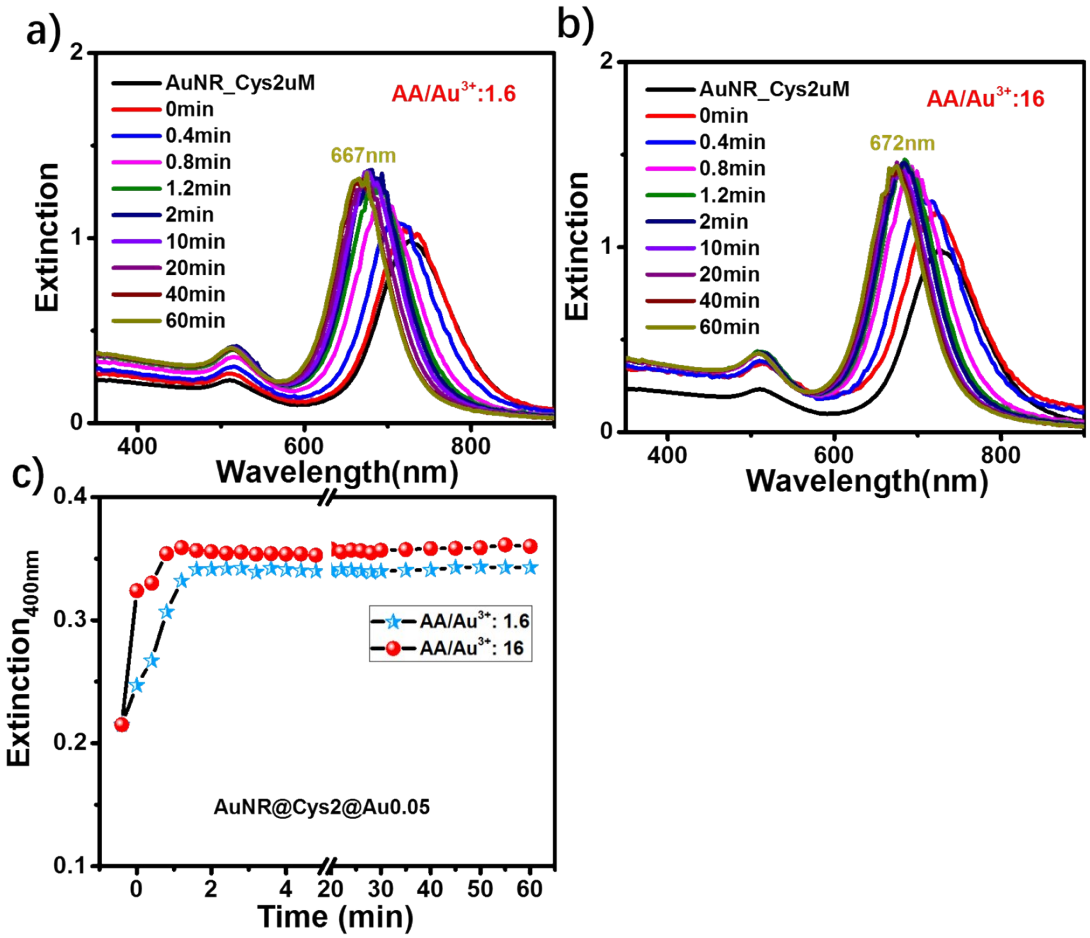

Figure S4. The evolutions (a, b) of extinction spectra of Au@Cys2@Au0.05 monomers during the overgrowth with AA/Au^{3+} ratios of 1.6 and 16, respectively. (c) Extinction value at 400 nm vs Au shell growth time.

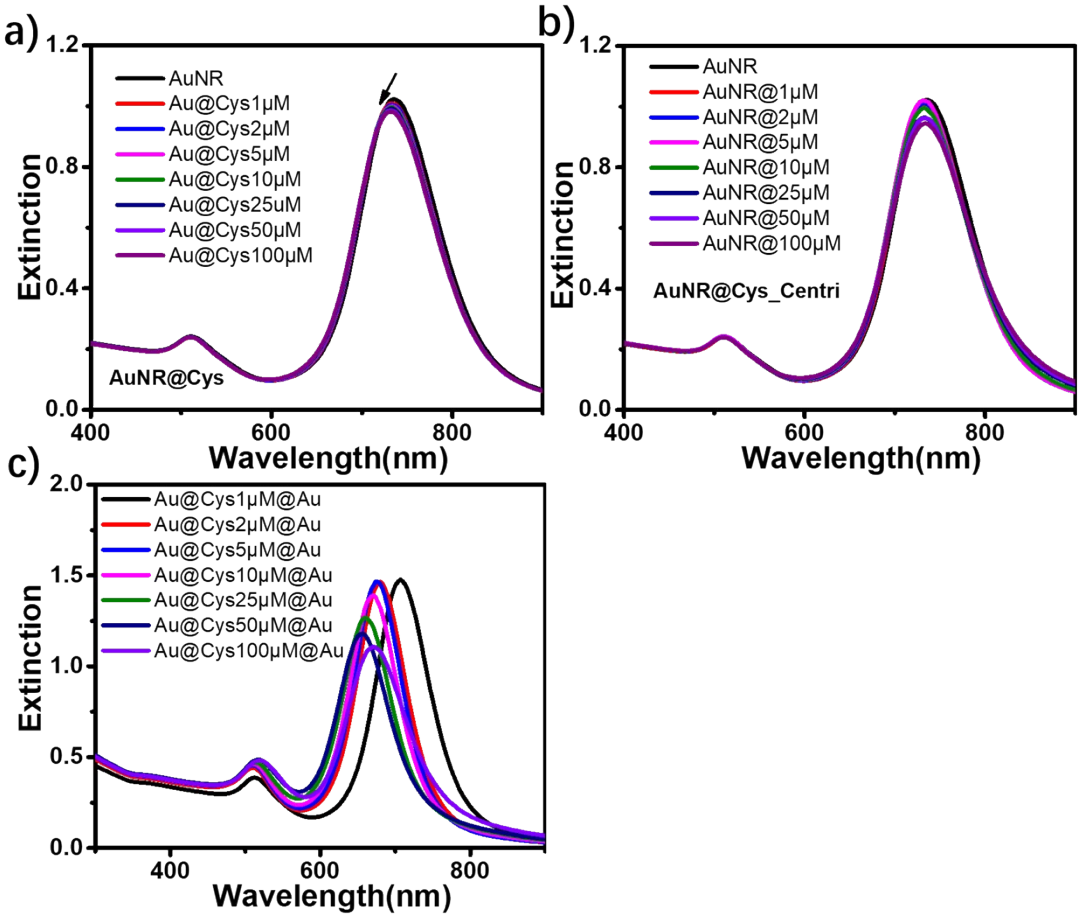

Figure S5. Extinction spectra of AuNRs incubated with different concentrations of cysteine before (a) and after (b) centrifugation and those of AuNR@CysX@Au0.05 after Au overgrowth (c).

Increasing Cys incubation concentration from 1 μM to 100 μM, the longitudinal SPR band showed a slight blue-shift and intensity damping, indicating that more Cys molecules adsorbed on the Au core surface (Fig.S5a). After centrifugation, AuNR@Cys monomers with [Cys]≥10 μM exhibited a slight aggregation, as witnessed by a long wavelength tailing and LSPR intensity decreasing (Fig.S5b). After Au shell overgrowth, the effect of Cys concentration was more obvious. The longitudinal SPR band showed a blue-shift trend with decreased intensity upon increasing Cys incubation concentration (Fig.S5c).

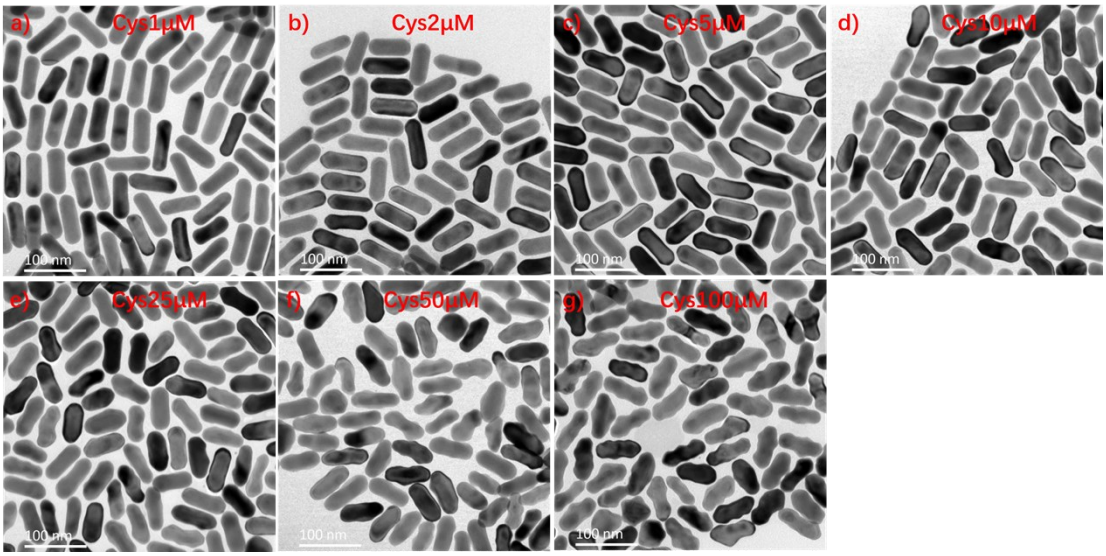

Figure S6. TEM images of AuNR@Cys**X**@Au0.05 monomers.

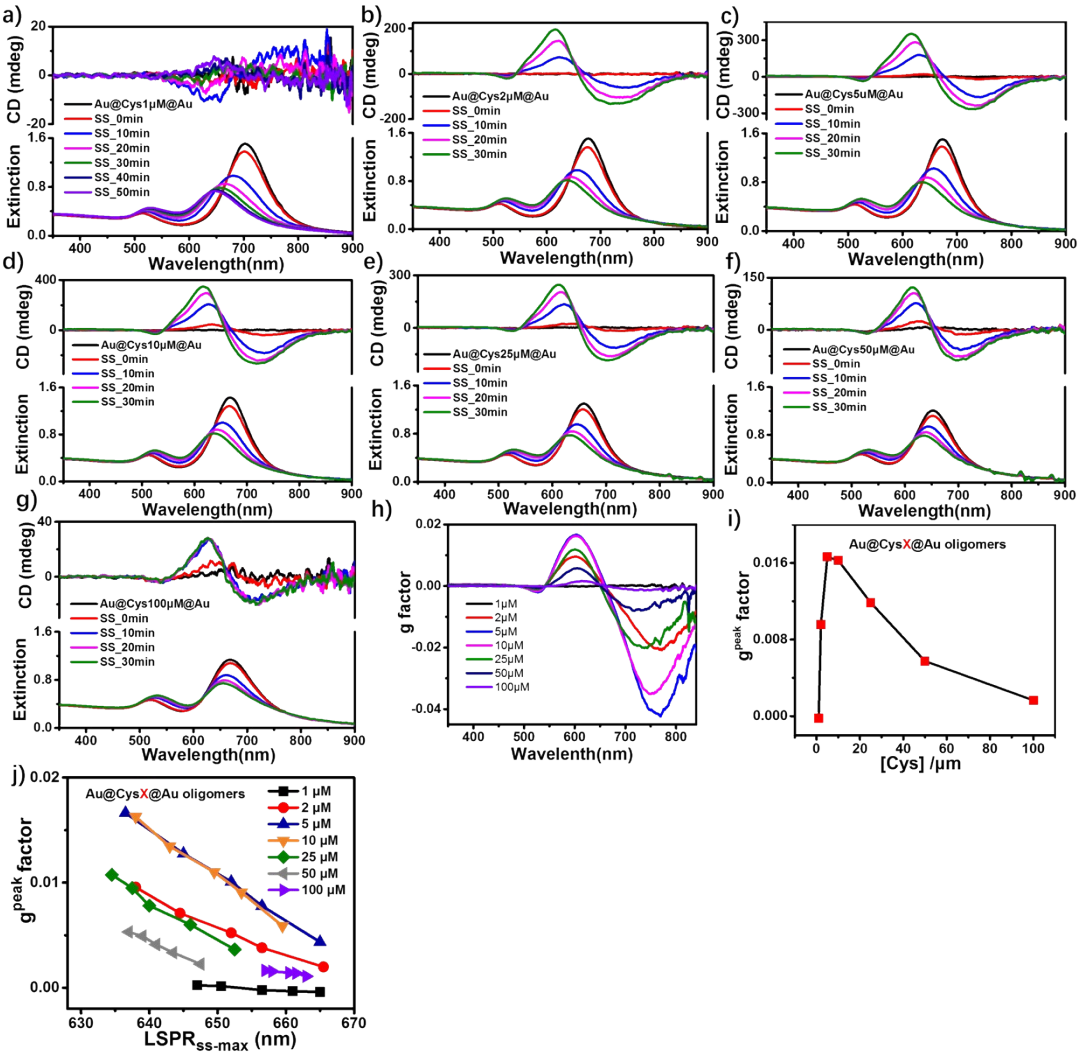

Figure S7. Effect of Cys incubation concentration on the PCD responses of AuNR@CysX@Au0.05 oligomers. (a-g) Evolution of CD and extinction spectra of Au@CysX@Au0.05 oligomers during

SS assembly processes at 60℃. (h) g factor spectra. (i) The g^{peak} value after 30 min assembly vs Cys concentration. (j) Relationship between g^{peak} value and $LSPR_{SS\text{-}max}$.

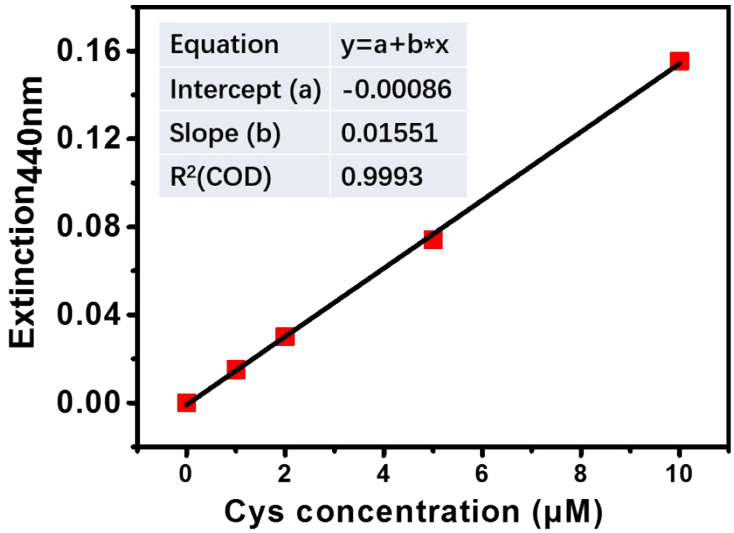

Figure S8. Standard curve for determining Cys adsorption amount.

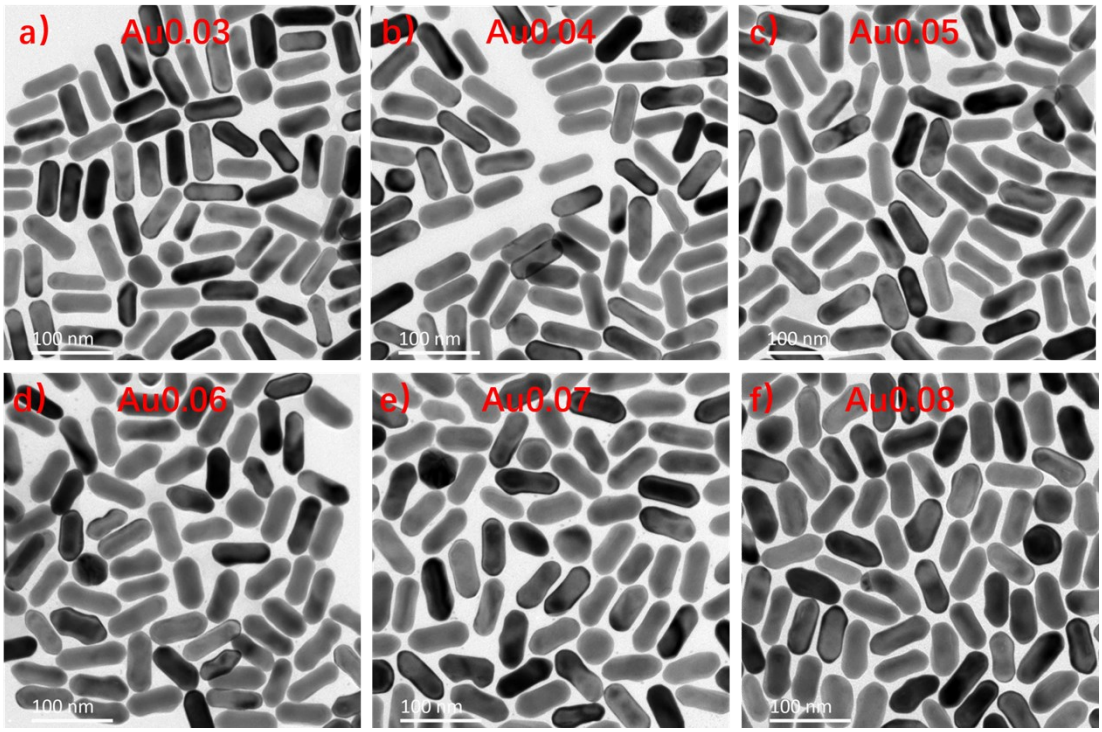

Figure S9. TEM images of AuNR@Cys5@AuY monomers.

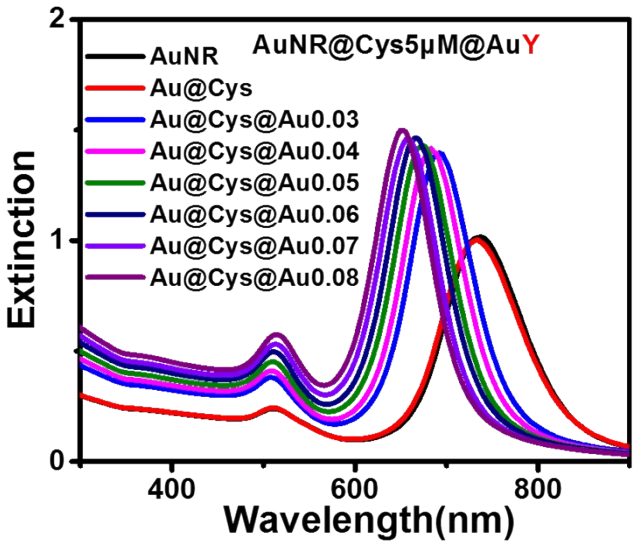

Figure S10. Extinction spectra of Au@Cys5@AuY monomers with different shell thicknesses by changing $HAuCl_4$ concentration from 0.03 mM to 0.08 mM.

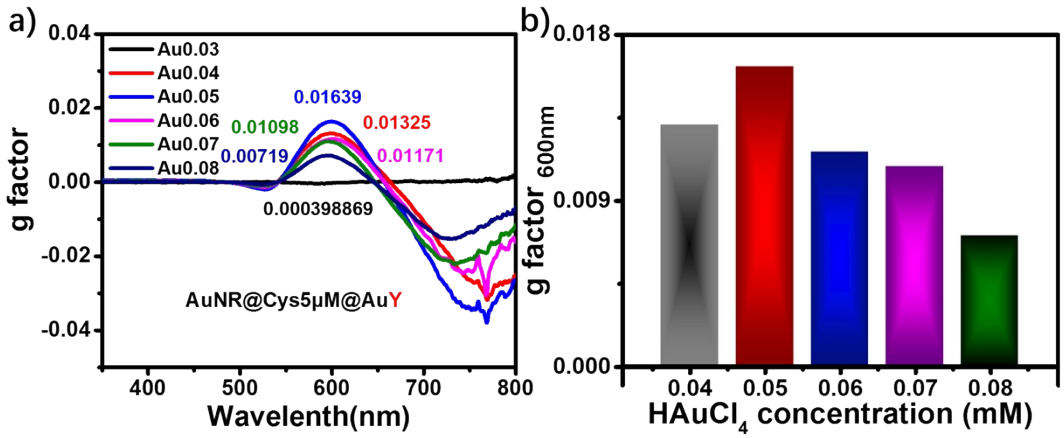

Figure S11. Effect of Au shell thickness on the PCD responses of AuNR@Cys5@AuY (Y= 0.03-0.08 mM) oligomers. (a) g factor spectra and (b) g factor value at 600 nm vs $HAuCl_4$ concentration after assembled at 60℃ for 30 min.

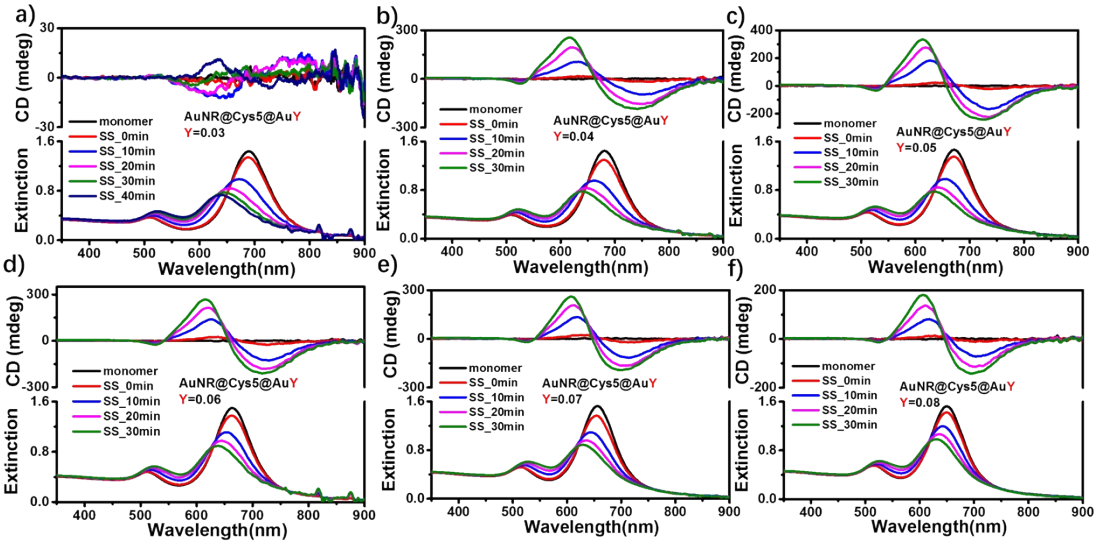

Figure S12. Evolutions of CD and extinction spectra of Au@Cys5@AuY (Y = 0.03 to 0.08 mM) oligomers during 60℃ assembly process.

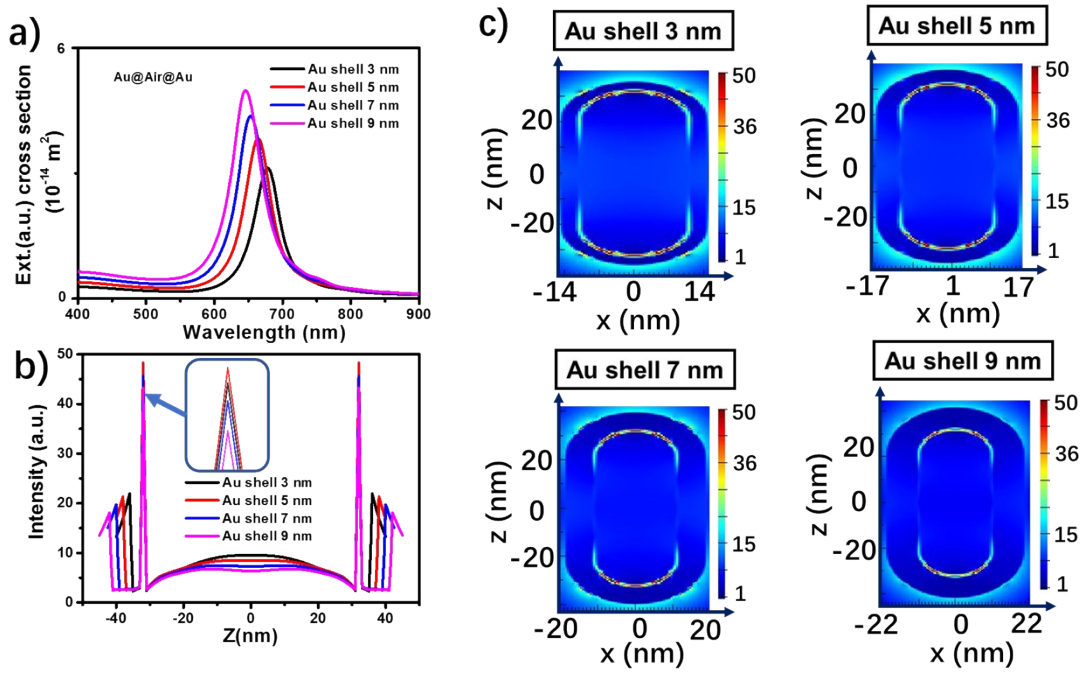

Figure S13. FDTD simulation of AuNR @1 nm air-gap @Au nanostructures with varying shell thickness. (a) Extinction spectra, (b) local electromagnetic field distribution along z axis, and (c) local electromagnetic field at the LSPR maximum.

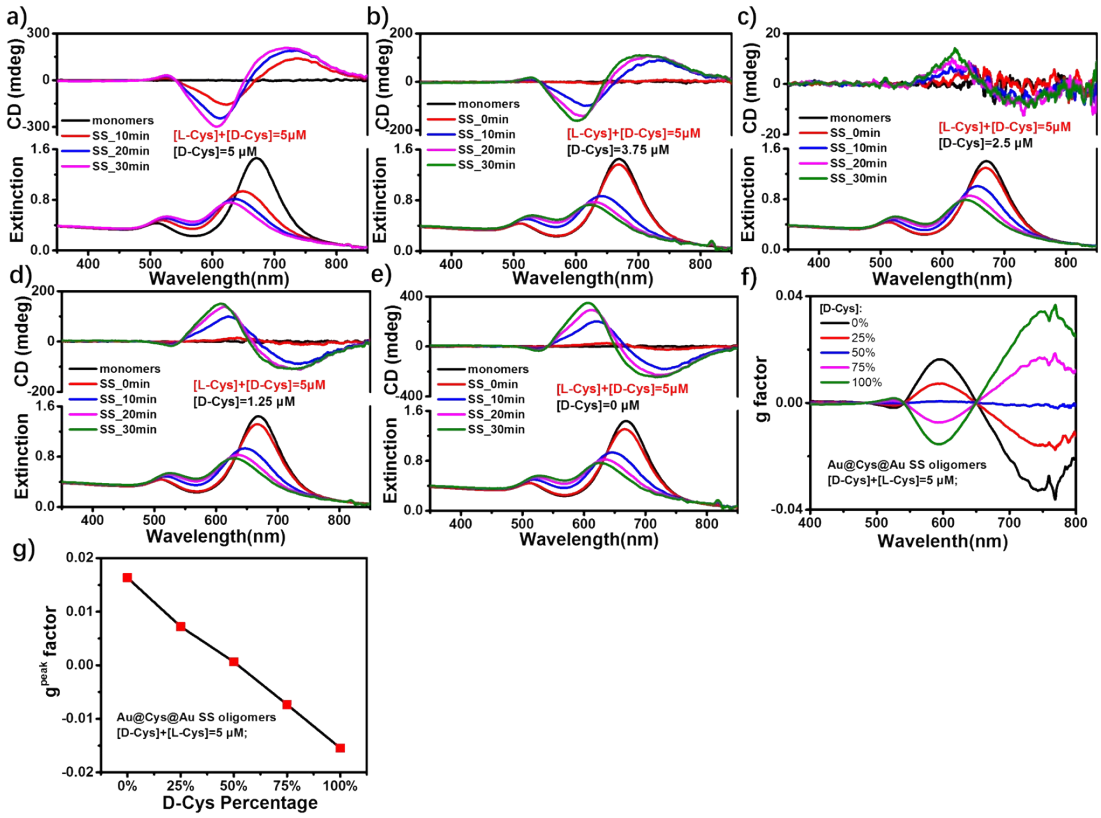

Figure S14. (a-e) Evolutions of CD and extinction spectra of AuNR@Cys5@Au0.05 oligomers during 60℃ assembly process with L- and D-Cys molar ratio of 1, 0.75, 0.5, 0.25 and 0. (f) g factor spectra at different ee values and (g) g^{peak} at 600 nm vs ee. [L-Cys]+[D-Cys] = 5 μM.

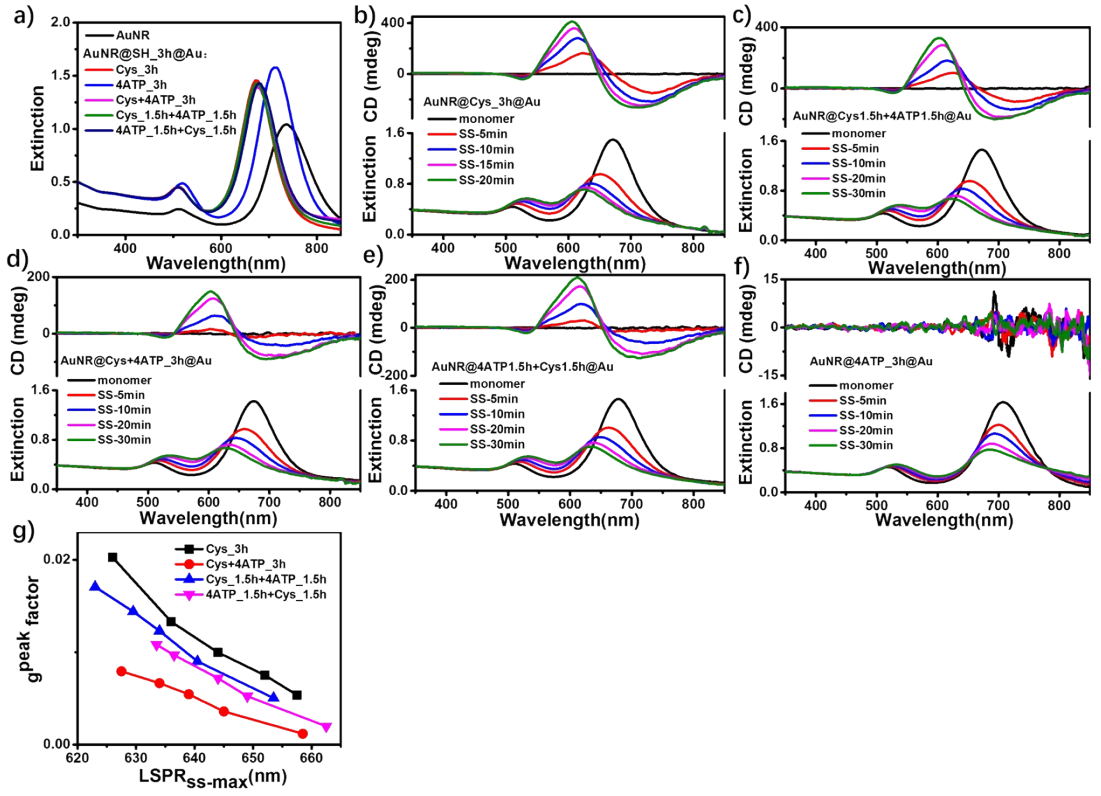

Figure S15. (a) Extinction spectra of AuNR@RSH@Au0.05 monomers obtained under different thiol (4-ATP and/or Cys) incubation conditions. (b-f) Evolutions of CD and extinction spectra of AuNR@RSH@Au0.05 oligomers during 60℃ assembly process. (g) g^{peak} value vs $LPSR_{SS\text{-}max}$. [Cys] = 2 μM, [4-ATP] = 2 μM.

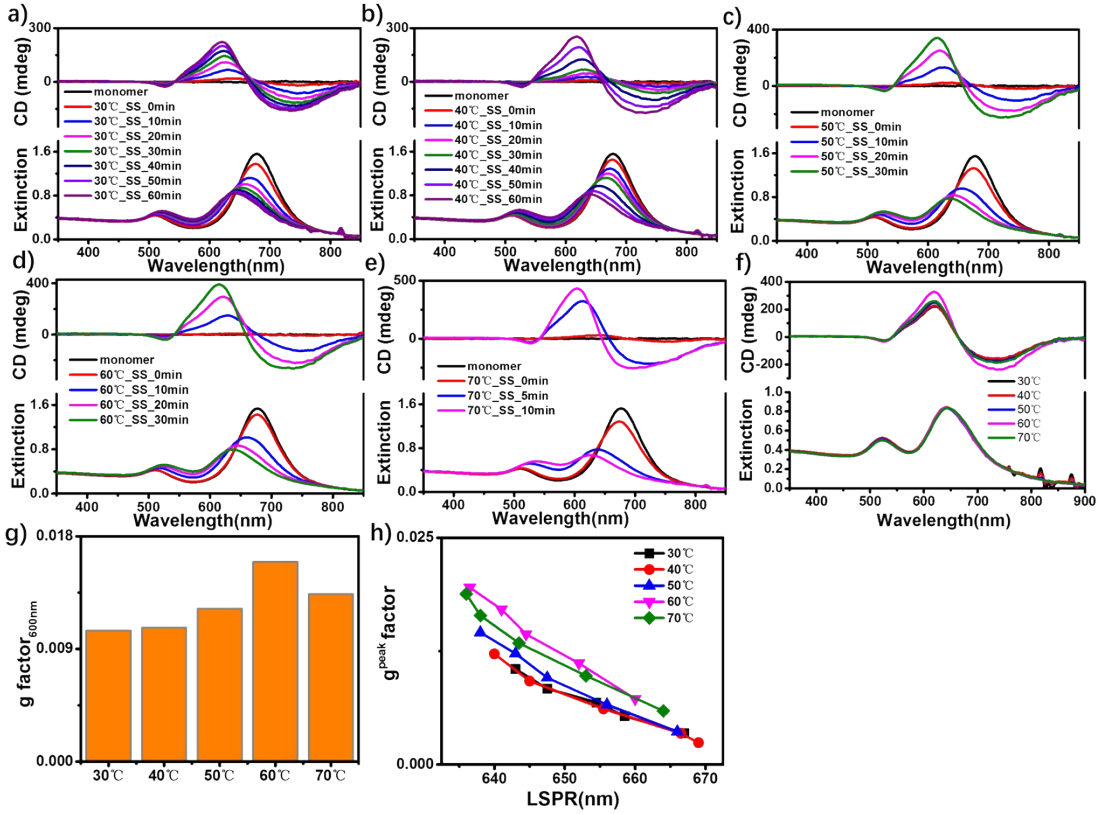

Figure S16. (a-e) Evolutions of CD and extinction spectra of Au@Cys5@Au0.05 oligomers during assembly process at different assembly temperatures from 30℃ to 70℃. (f) The g^{peak} value vs $LSPR_{SS\text{-}max}$ at different assembly temperatures. (g) The g factor value at 600 nm vs assembly temperature at similar assembly degrees. (h) g^{peak} value vs $LPSR_{SS\text{-}max}$ at different assembly temperature. [CTAB] = 2 mM.

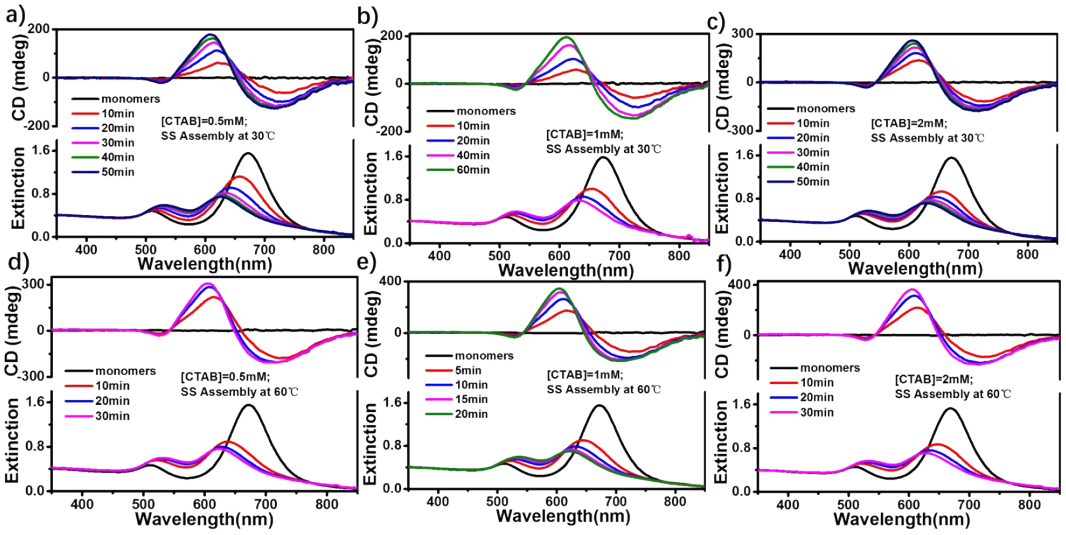

Figure S17. Evolutions of CD and extinction spectra of Au@Cys5@Au0.05 oligomers during SS assembly processes at 30 and 60℃, respectively, at different CTAB concentrations.

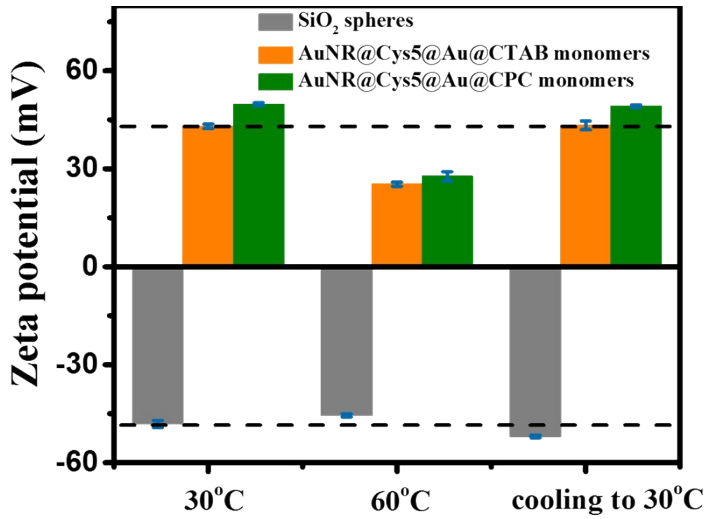

Figure S18. Effect of measurement temperature on Zeta potential of AuNR@Cys5@Au0.05 monomers (0.1 nM) coated with CTAB- and CPC-bilayer, respectively.

Compared with the control of negatively charged SiO_2 spheres, raising measuring temperature from 30°C to 60°C greatly reduced the zeta potential of AuNR@Cys5@Au0.05 monomers coated with CTAB- or CPC-bilayer. When cooling back to 30°C, the zeta potential recovered. This result indicates that enhanced Brownian motion at high temperature damages the packing order of CTAB- and CPC-bilayer on rod surface.

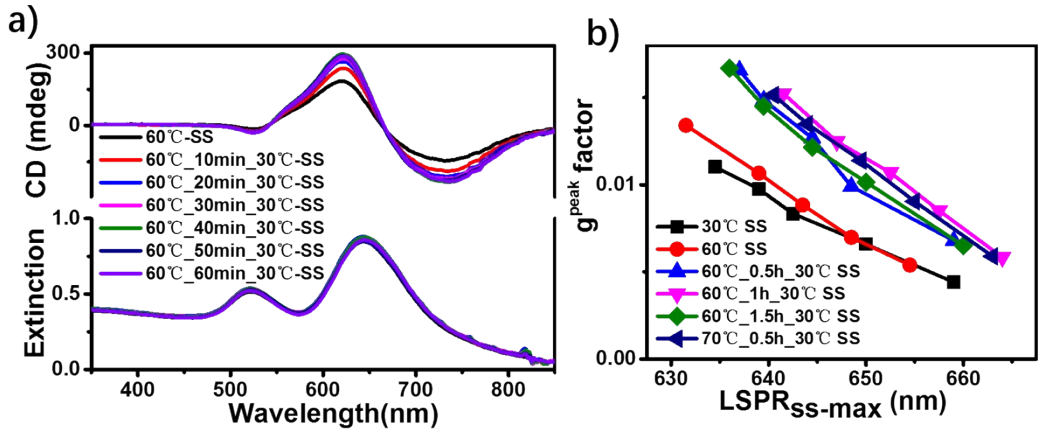

Figure S19. (a) CD and extinction spectra of AuNR@Cys5@Au0.05 oligomers and (b) g^{peak} value vs $LSPR_{SS\text{-}max}$ under different pretreatment conditions.

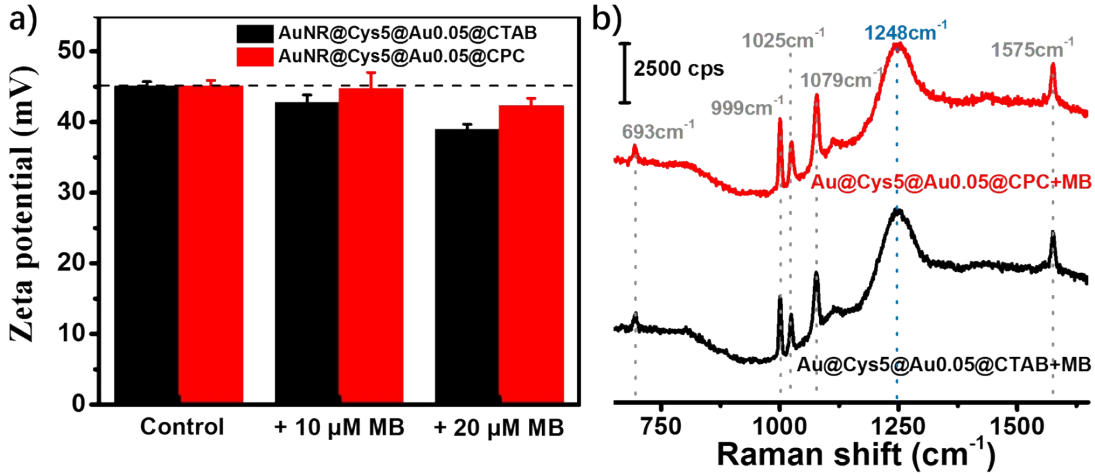

Figure S20. MB addition in AuNR@Cys5@Au0.05 monomers (0.1 nM) reducing Zeta potential of nanorods (a) and appearance of MB SERS signals (b) due to the adsorption of MB on rod surface. [CTAB] = 2 mM; [CPC] = 2 mM.

SERS bands at 693, 999, 1025, 1079, and 1575 cm^{-1} come from adsorbed MB molecules.

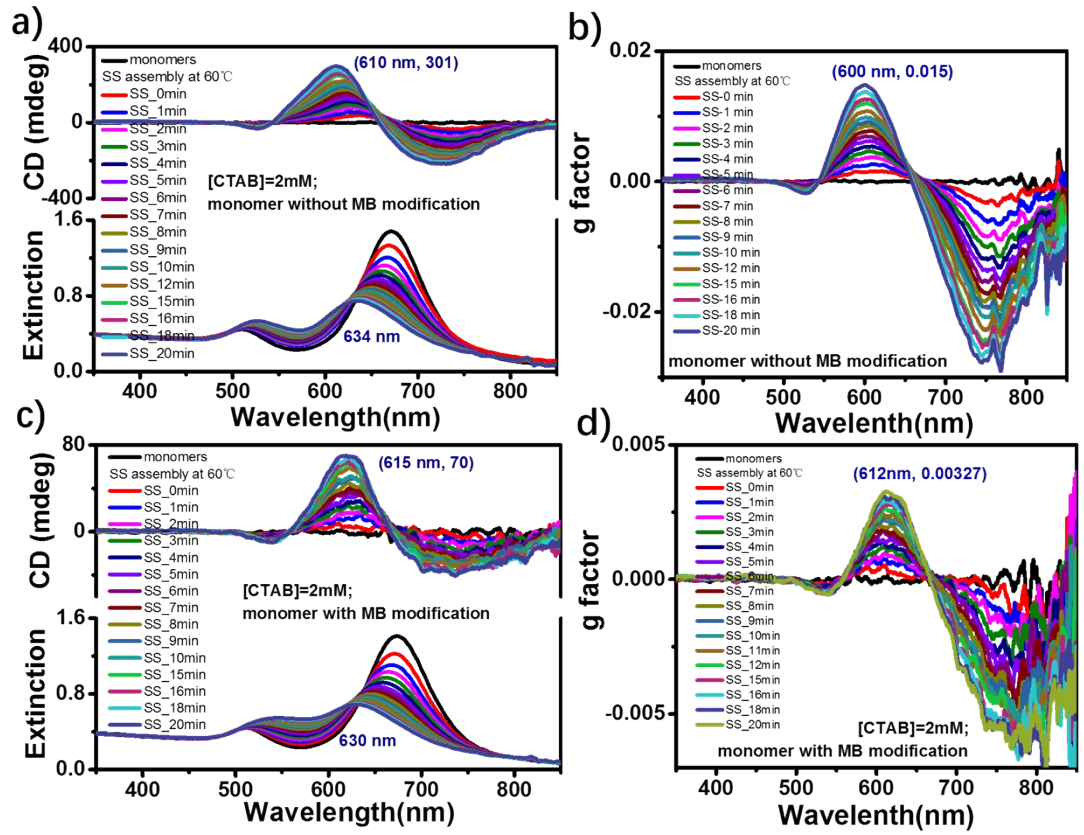

Figure S21. Evolutions of CD, extinction, g factor spectra of oligomers assembled at 60℃ using AuNR@Cys5@Au0.05 monomers with (a and b) and without MB modification (c and d). MB modification was done by incubating 20 μM MB with 0.1 nM AuNR@Cys5@Au0.05 monomers at 30° C for 30 min.

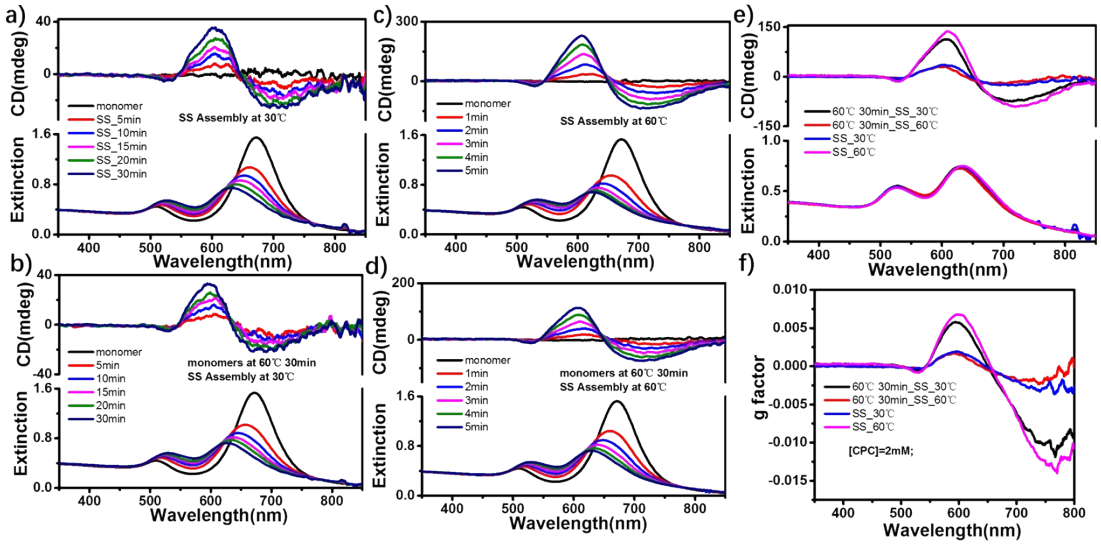

Figure S22. CPC as achiral surface ligands. (a-d) Evolutions of CD and extinction spectra of Au@Cys5@Au0.05 oligomers under different assembly and monomer pre-treatment conditions. e) CD and extinction spectra and (f) g factor spectra at similar assembly degrees.

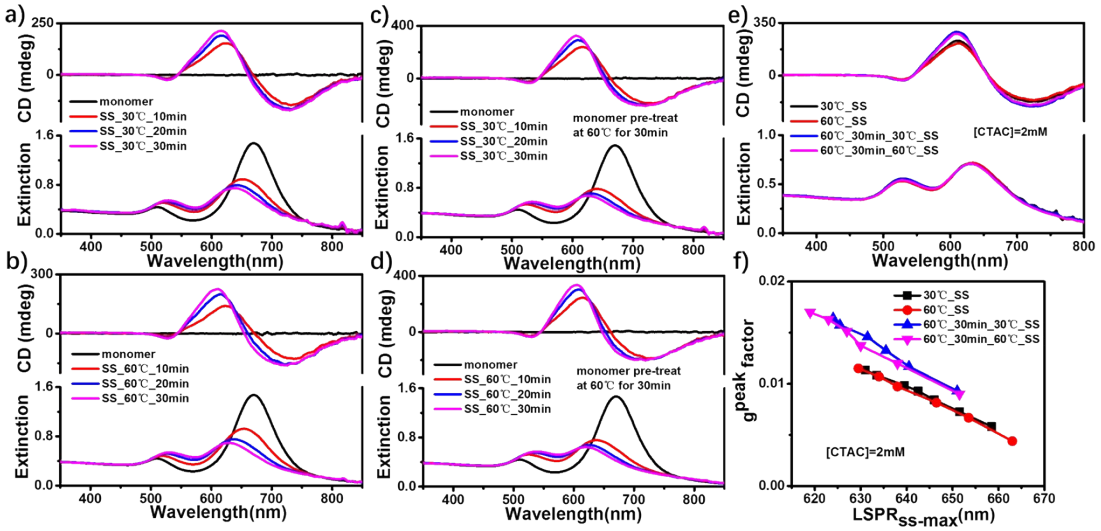

Figure S23. CTAC as achiral surface ligands. (a-d) Evolutions of CD and extinction spectra of Au@Cys5@Au0.05 oligomers under different assembly and monomer pre-treatment conditions. (e) CD and extinction spectra at a similar assembly degree. (f) The g^{peak} value vs $LSPR_{SS\text{-}max}$.

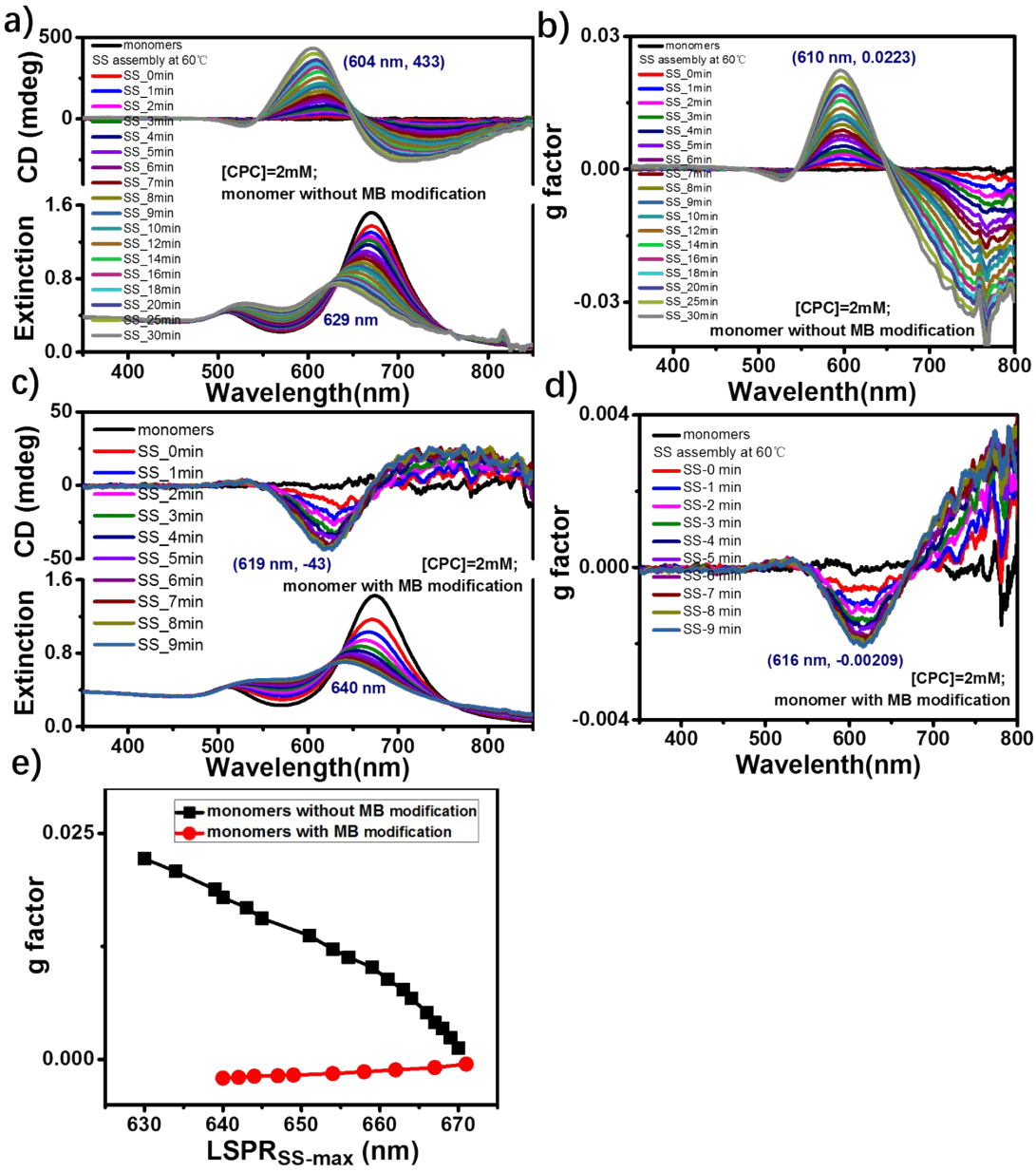

Figure S24. (a-d) Evolutions of CD, extinction and g factor spectra of CPC-coated AuNR@Cys5@Au0.05 SS oligomers during 60℃ assembly processes with and without monomers pre-incubation with 20 μM MB at 30° C for 30 min. (e) g^{peak} vs $LSPR_{SS\text{-}max}$. [CPC] = 2 mM.

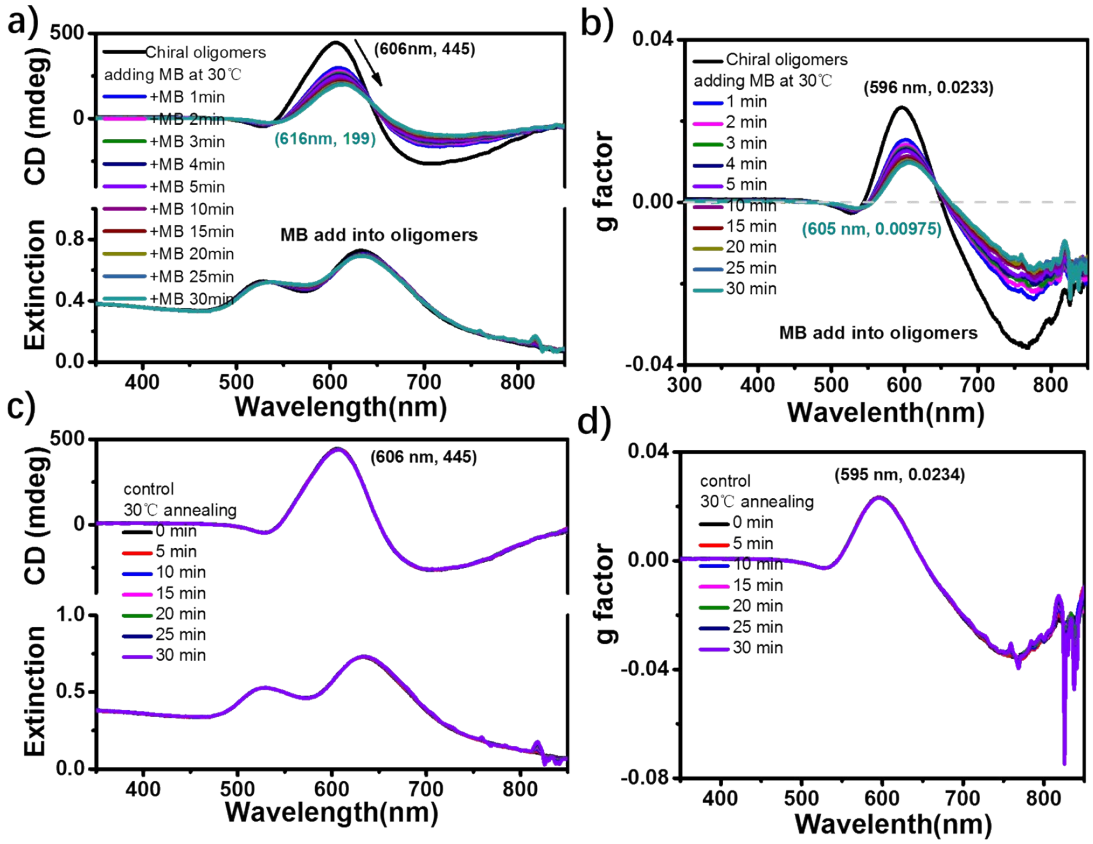

Figure S25. (a-d) Evolutions of CD, extinction and g factor spectra of CPC-coated AuNR@Cys5@Au0.05 chiral oligomers during 30°C annealing with and without adding 20 μM MB. [CPC] = 2 mM.

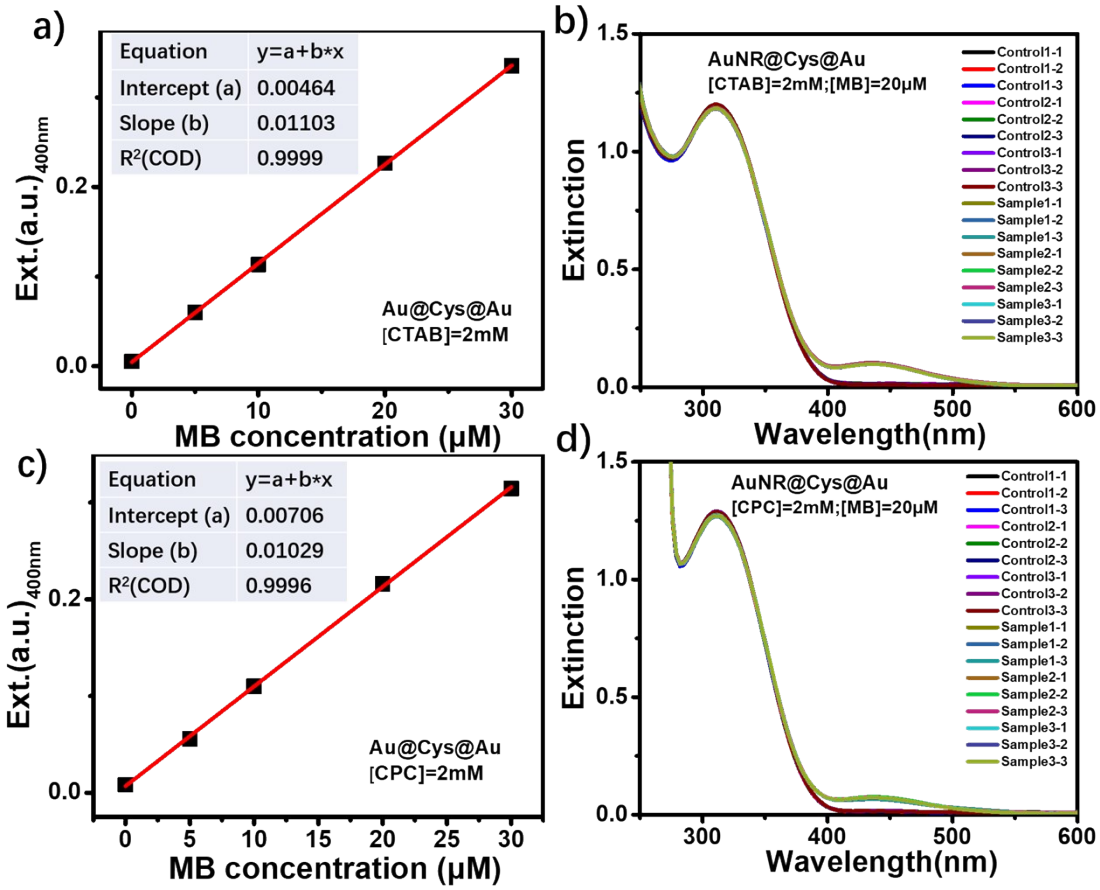

Figure S26. Standard curves (a and c) for determining MB adsorption amount and the extinction spectra of supernatants of CTAB- (b) or CPC-coated (d) AuNR@Cys5@Au0.05 monomers after MB adsorption. ([CTAB] or [CPC]= 2 mM, [MB]= 20 μM).

The measured MB adsorption amount of CTAB-coated and CPC-coated monomer was 10.2 μM and 13.8 μM, respectively.

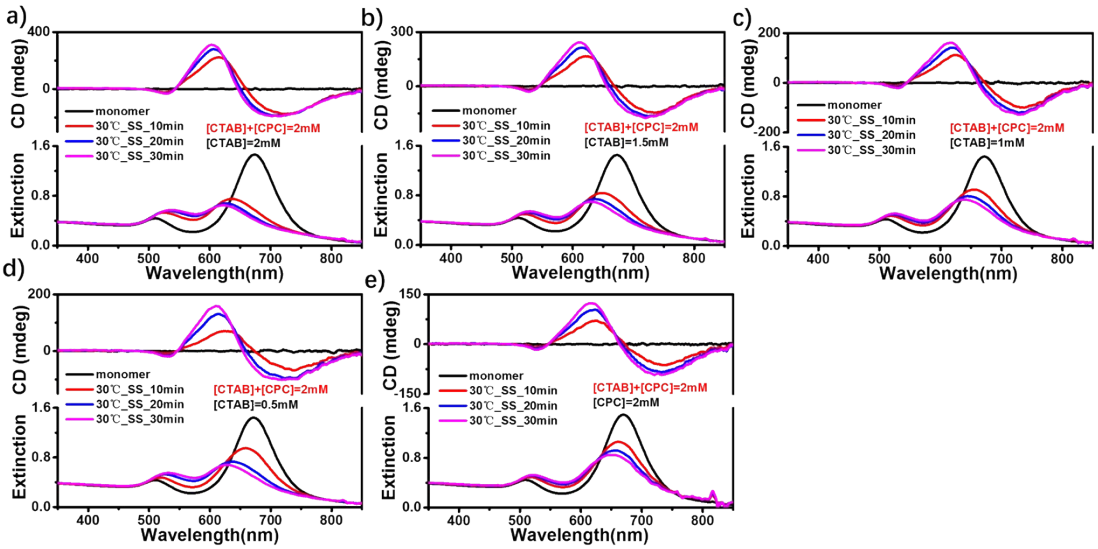

Figure S27. (a-e) Evolutions of CD and extinction spectra of AuNR@Cys5@Au0.05 oligomers

using the mixture of CTAB and CPC as surface layer during 30℃ assembly processes. [CPC] + [CTAB] = 2 mM

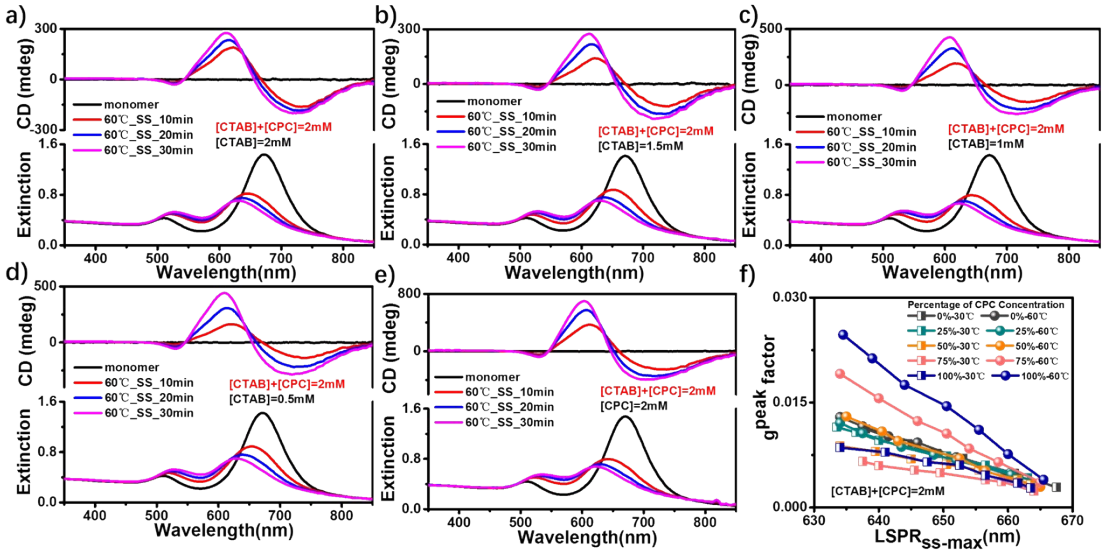

Figure S28. (a-e) Evolutions of CD and extinction spectra of AuNR@Cys5@Au0.05 oligomers using the mixture of CTAB and CPC as surface layer during 60℃ assembly processes. [CPC] + [CTAB] = 2 mM. (f) The g^{peak} value vs $LSPR_{SS\text{-}max}$ at assembly temperature of 30℃ and 60℃, respectively.

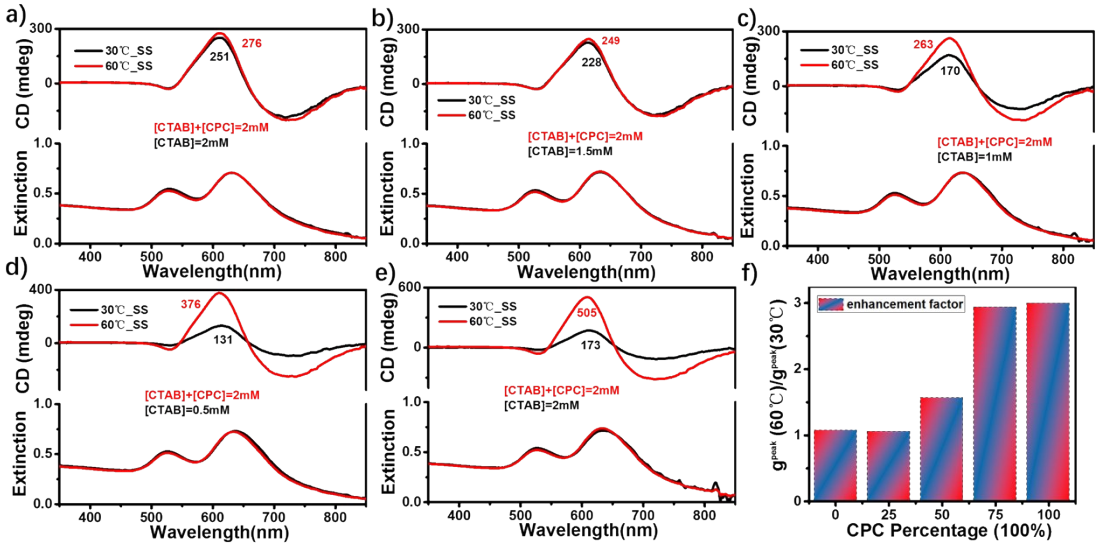

Figure S29. (a-e) CD and extinction spectra of AuNR@Cys5@Au0.05 oligomers using the mixture of CTAB and CPC as surface layer at similar assembly degrees. (f) g^{peak} (60°C)/ g^{peak} (30°C) vs CPC percentage.

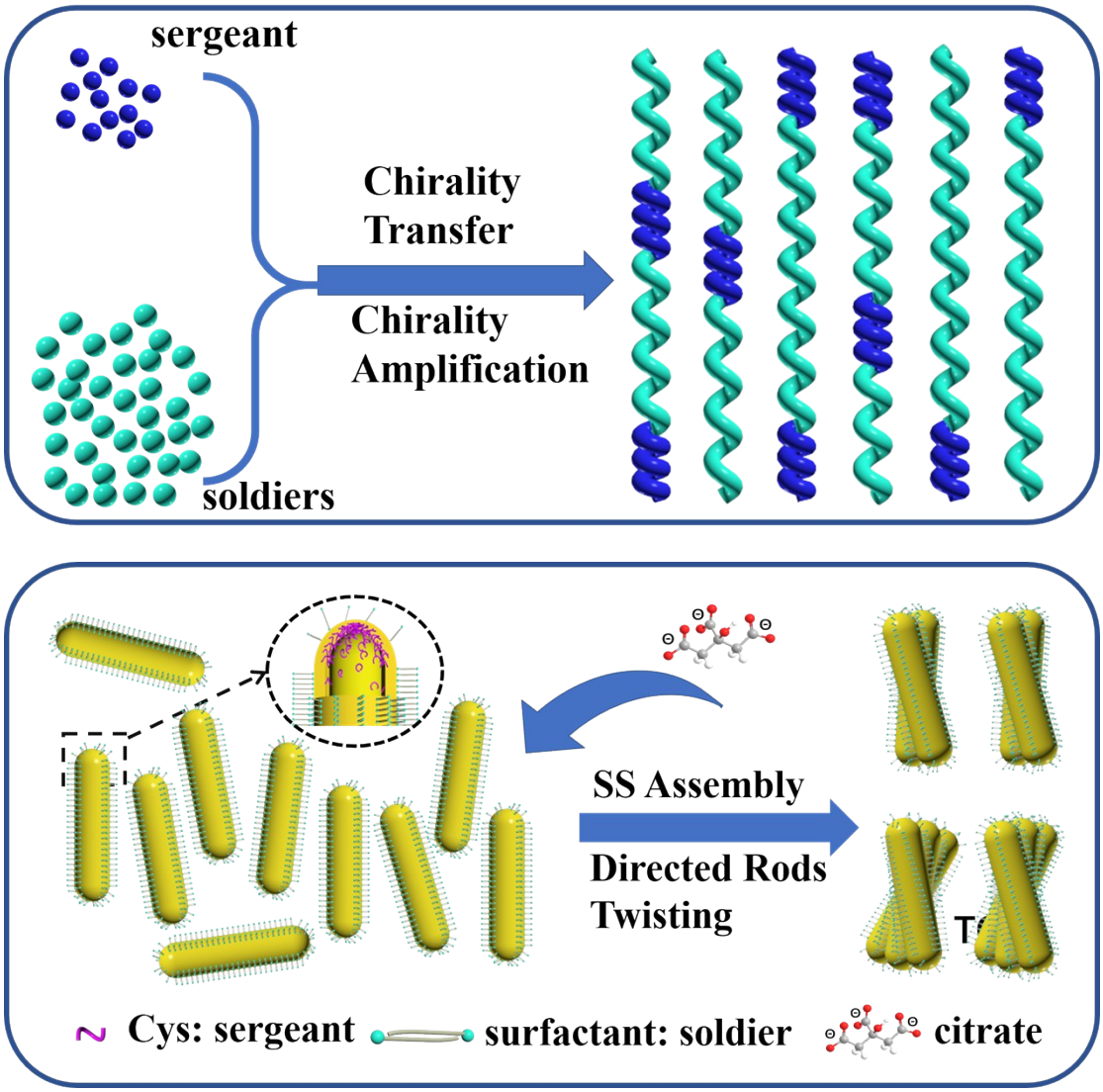

Figure S30. Schematic drawing of the S&S effect in supramolecular assemblies (upper panel) and in plasmonic assemblies (lower panel), respectively.