Supporting Information

Plasmonic Polymers with Strong Chiroptical Response for Sensing Molecular Chirality

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1. Synthesis of gold nanorods (GNRs)

GNRs were synthesized by a seed-mediated method[1]. Firstly, CTAB-capped gold seeds were synthesized by chemical reduction of $HAuCl_4$ with $NaBH_4$: 7.5 mL of CTAB (0.1 M) aqueous solution was mixed with 100 μL of $HAuCl_4$ (24 mM) and diluted with water to 9.4 mL. Then, 0.6 mL of ice-cold $NaBH_4$ (0.01 M) was added with magnetic stirring. After 3 min, the stirring was stopped and the seed solution was kept undisturbed at 30 ℃ prior to any further experimentation. The seeds can be used within 2-5 hr after preparation. After that, the growth solution of the GNRs was prepared, which consisted of CTAB (0.1 M, 100 mL), $HAuCl_4$ (25.5 mM, 1.96 mL), $AgNO_3$ (0.01 M, 0.45 mL), H_2SO_4 (0.1 M, 2 mL), and AA (0.1 M, 0.8 mL). Then 240 μL of seed solution was added to the growth solution to initiate the growth of the GNRs. After 12 h, GNRs were obtained. The GNRs were purified by centrifugation (12000 rpm for 10 min). The precipitates were collected and redispersed in deionized water. The GNRs were purified again by centrifugation (9000 rpm for 5 min) to remove the superfluous CTAB. The precipitates were collected and redispersed in deionized water. The final concentration of GNRs was ~0.9 nM. For preparaing zigzag and collinear chains of GNRs, Zeta potential of the GNR monomers in the range of 45 -57mV was regulated by adding different concentrations of CTAB.

All chemicals: sodium borohydride ($NaBH_4$), hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), cetyltrimethylammonisum bromide (CTAB), silver nitrate ($AgNO_3$) L-ascorbic acid (AA), were purchased from Sigmal and used as received. Pure Milli-Q grade water was used in all sample preparations.

2．Linear assembly of GNRs: preparation, electron microscopic chracterization, and statistical analyses of bond angles

As-prepared GNR/CTAB (~0.9 nM) colloidal solution was mixed with L-Cys, D-Cys, or D,L-Cys solution (27×10^{-6} M) under a volume ratio of 2:1 before subjected to extinction and CD measurements. Dynamic extinction and CD spectra were used to monitor the linear assembly process of GNRs. At a specific assembly time, the assembled products were capsulated by negatively charged poly (styrene sulfonic acid) sodium salt (PSS, MW 70000, 2g/L, 6×10^{-3} M NaCl), so as to stabilize the assembled cluster structures. Then the as-prepared clusters preserved by PSS encapsulation were separated by natural sedimentation method, and redispersed in DI water. Silicon substrates (with positive charges at the surfaces) were immersed in the sample solutions for 0.5-1 hr. The adsorbed samples on silicon substrates were dried for SEM structural characterization. In addition, after the excess solutions on the substrates were removed by filter paper, the adsorbed samples at a wet condition were subjected to ESEM anayses. For TEM microstructural characterization, 6μL PSS-capsulated clusters were dropped onto a copper surface, then the samples were dried before test.
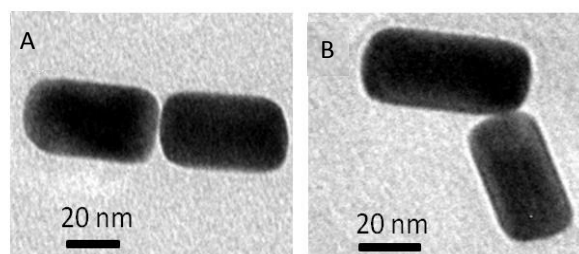

Figure S1. Typical TEM images of L-Cys mediated GNR dimers acquired at early assembly stage: (A) collinear case with the average nanogap of 0.9 ± 0.6 nm; (B) zigzag case with the average nanogap of 0.8 ± 0.6 nm.
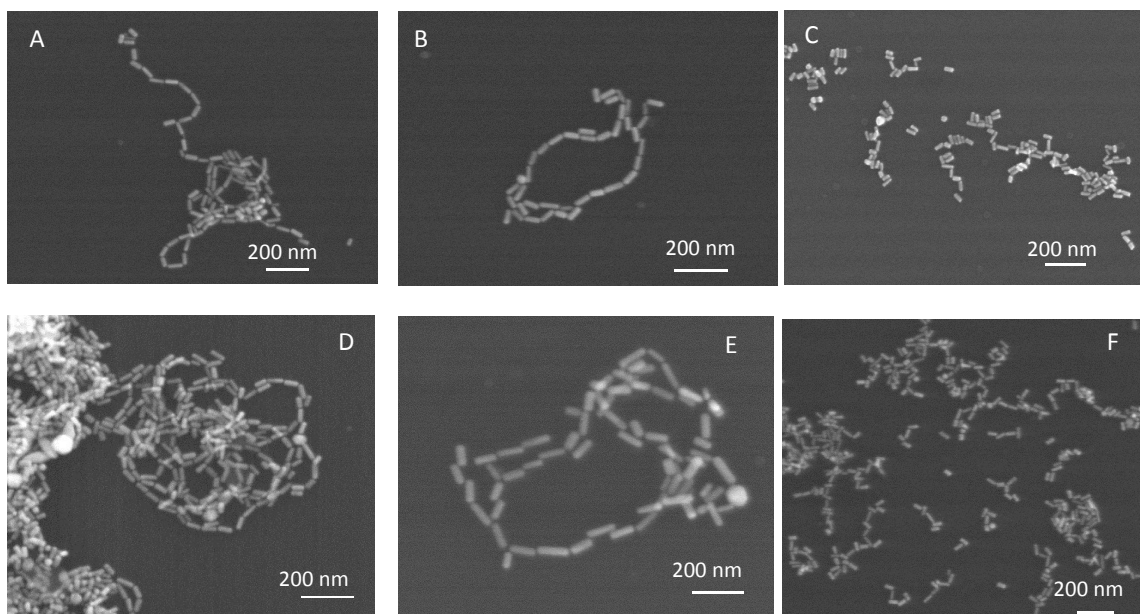
Figure S2. Representative ESEM images (low-vacuum mode) from L-Cys (uper) and D-Cys (lower) mediated collinear (A, B, D, E) and zigzag (C, F) chains,. The assembly time t = 120 min for collinear chains and t = 30 min for zigzag chains.
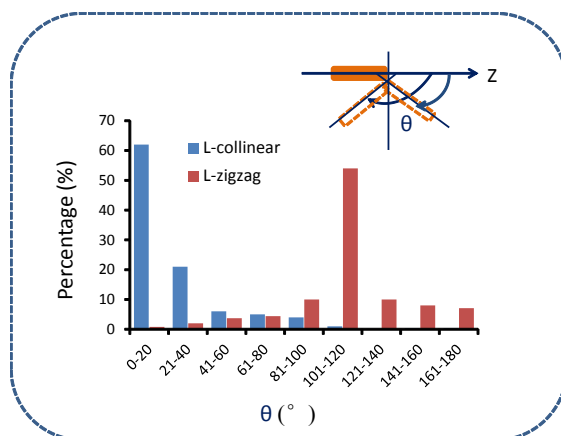

Figure S3. Statistical distribution of the bond angle in L-Cys mediated collinear (blue) and zigzag (red) chains based on the analysis from more than 500 nanorods in the ESEM micrographs (results for the case of D-Cys are in Figure 1D). Inset: Schematics for the GNR-GNR bond angle. The bond angle θ ($0 \leq \theta \leq 180°$) is defined by the angle between the long axis of the second GNR and the z-axis (along the long axis of the first GNR).

3．Calculations of SERS enhancement factor (EF)

Figure S4 showed the Raman spectra in the range of 600-800 cm^{-1} acquired from a Cys bulk solution (1.0 M). The ensemble-averaged SERS enhancement factors cited in the main text are derived from the Raman intensities of the C-S stretching mode by using[2]

$$EF = \frac{I_{SERS}/N_{surf}}{I_{Raman}/N_{vol}}$$

where I_{Raman} is Raman peak intensity of C-S mode for an average number of N_{vol} molecules in the scattering volume of Cys bulk solution. I_{SERS} is the SERS peak intensity of C-S mode for an estimated number of N_{surf} molecules in the GNR polymers in the same scattering volume.
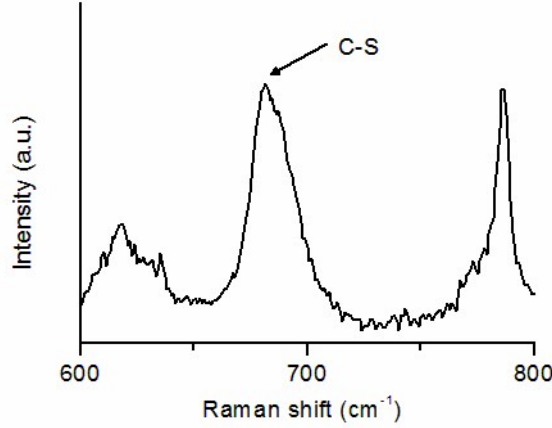

Figure S4. Raman spectrum of Cys bulk solution (1.0 M).

Side surfaces of a GNR are supposed to be fully occupied by CTAB molecules, so Cys preferentially adsorbs onto the ends of GNRs[3]. We assume that each end of a GNR is semispherical, and the total end area is $S_{end} = \frac{1}{2}\pi D^2$, where D is the diameter of the GNR. Therefore, we have

$$EF = \frac{I_{SERS}}{I_{Raman}} \cdot \frac{C_{Cys-bulk} \cdot V_{light} \cdot N_A}{n_{Cys@GNR} \cdot C_{GNR} \cdot V_{light} \cdot N_A}$$
$$= \frac{I_{SERS}}{I_{Raman}} \cdot \frac{C_{Cys-bulk}}{\frac{2S_{end}}{S_{Cys}} \cdot C_{GNR}} = \frac{I_{SERS}}{I_{Raman}} \cdot \frac{C_{Cys-bulk} \cdot S_{Cys}}{C_{GNR} \cdot \pi D^2}$$

where $C_{Cys-bulk}$ is concentration of bulk Cys solution, C_{GNR} is concentration of GNRs in the Cys-mediated GNR polymers, $n_{Cys@GNR}$ is number of Cys on each GNR, S_{Cys} is the occupation area of a Cys molecule on the GNR end, V_{light} is the illuminated volume, and N_A is Avogadro's constant. According to previous studies[4,5] on Cys molecular monolayer adsorbed on the gold surfaces, S_{Cys} for single molecule was taken as ~0.245 nm^2.

Taking L-Cys mediated GNRs polymers as an example, we calculated the EF values based on the Raman scattering intensities of the C-S stretching mode. The values of EF were estimated

as $\sim 1.9 \times 10^6$ for the collinear polymers and $\sim 1.0 \times 10^6$ for the zigzag polymers. Similar results were obtained from D-Cys mediated GNR polymers. Note that the above estimation of EF yields a lower limit of the actual value. This is because the molar ratio of Cys to GNRs used here suggests only a sub-monolayer coverage, rather than a full monlayer coverage, of Cys on the ends of GNRs[3].
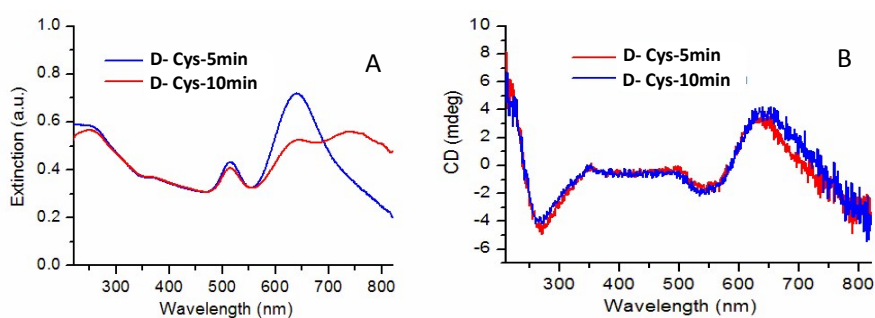
4．Dynamic extinction and CD spectra

Figure S5. Dynamic extinction (A) and CD (B) spectra collected during the formation of zigzag polymers of GNRs for the case of D-Cys within the assembly time t = 5-10 min. Cys with a concentration of 9.0 μM was used.

5．Estimation of average aggregration number in the collinear GNR polymers

Concurrent with the extinction and CD measurements within the time of self-assembly (15-90 min), collection of samples for SEM imaging was conducted for monitoring the variation of the GNR polymer length with time. These SEM images (Fig. S6) allowed us to extract important information for the investigation of the influence of degree of polymerization on the plasmonic CD (PCD) intensity.
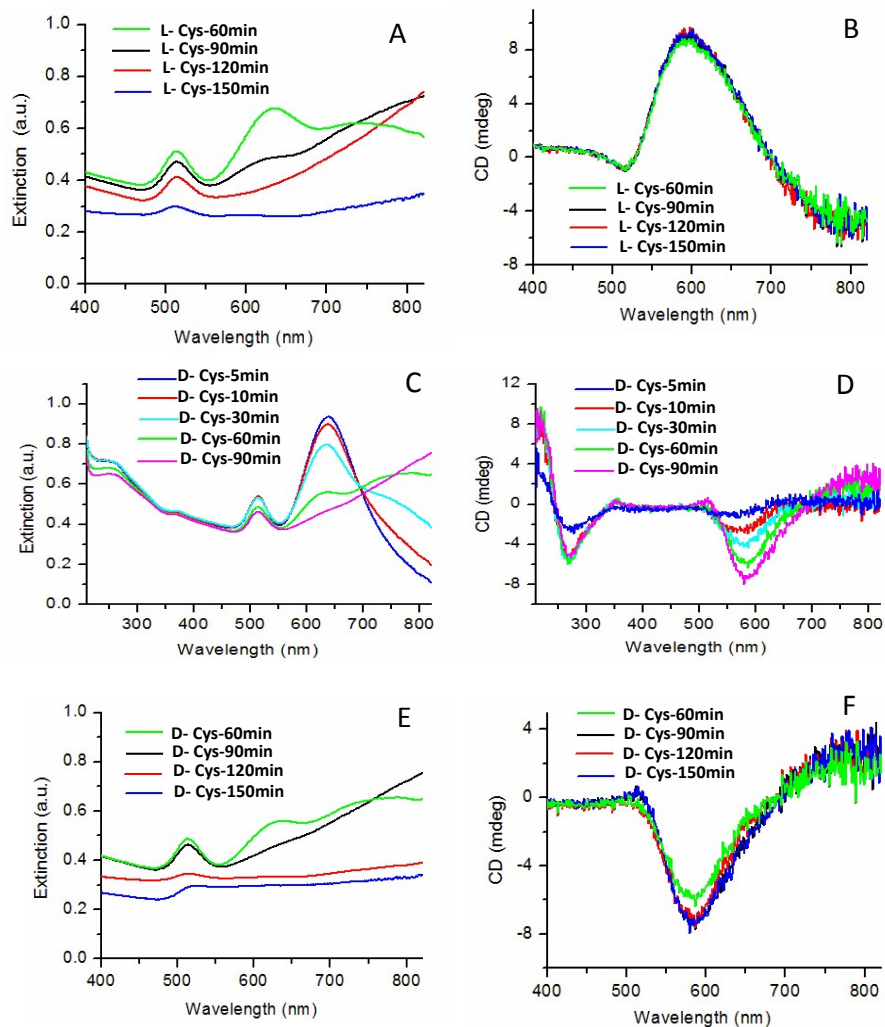
Figure S6. Dynamic extinction (A, C, E) and CD (B, D ,F) spectra collected during the formation of collinear polymers of GNRs. Upper panel: for the case of L-Cys within the assembly time t = 60-150 min. Middle and Lower panels: for the case of D-Cys within the assembly time t = 5-150 min. L- or D-Cys with a concentration of 9.0 μM was used.
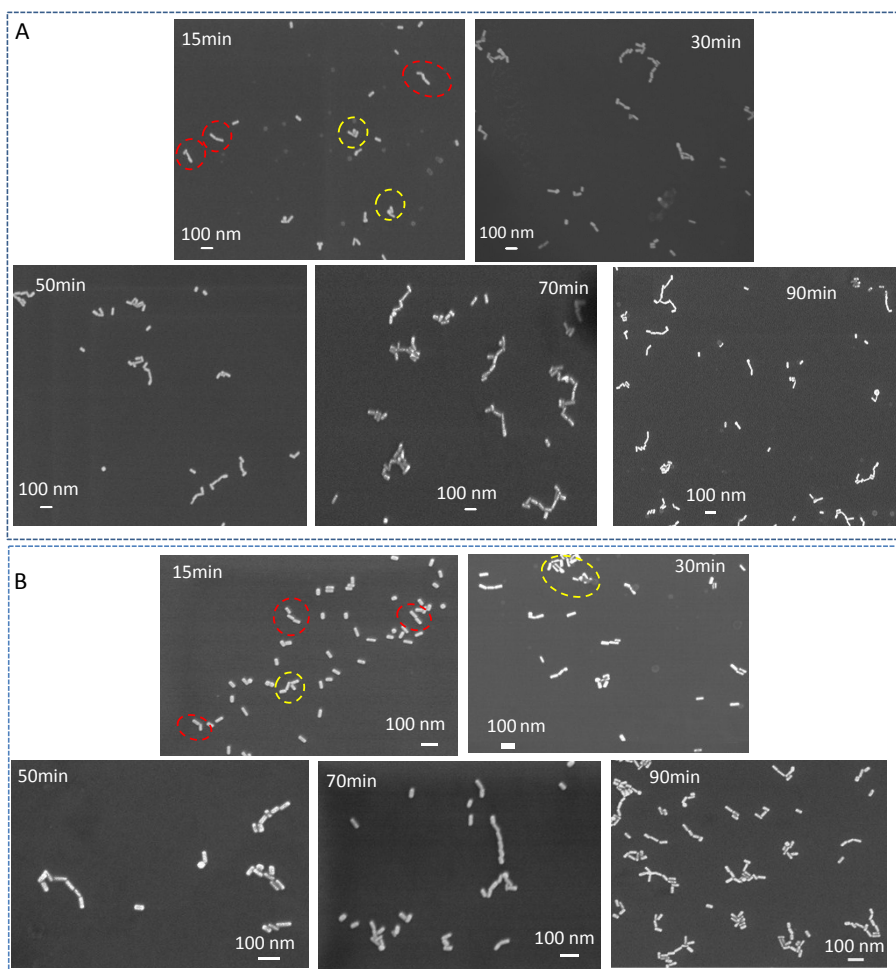
Figure S7. Representative SEM images of the collinear chains of GNRs at different self-assembly time: 15 min, 30 min, 50 min, 70 min, 90 min. (A) with L-Cys (9.0 µM) as linkers; (B) with D-Cys (9.0 µM) as linkers. For clarity, red and yellow circles are used to denote the linear chains and disorder aggregates, respectively.
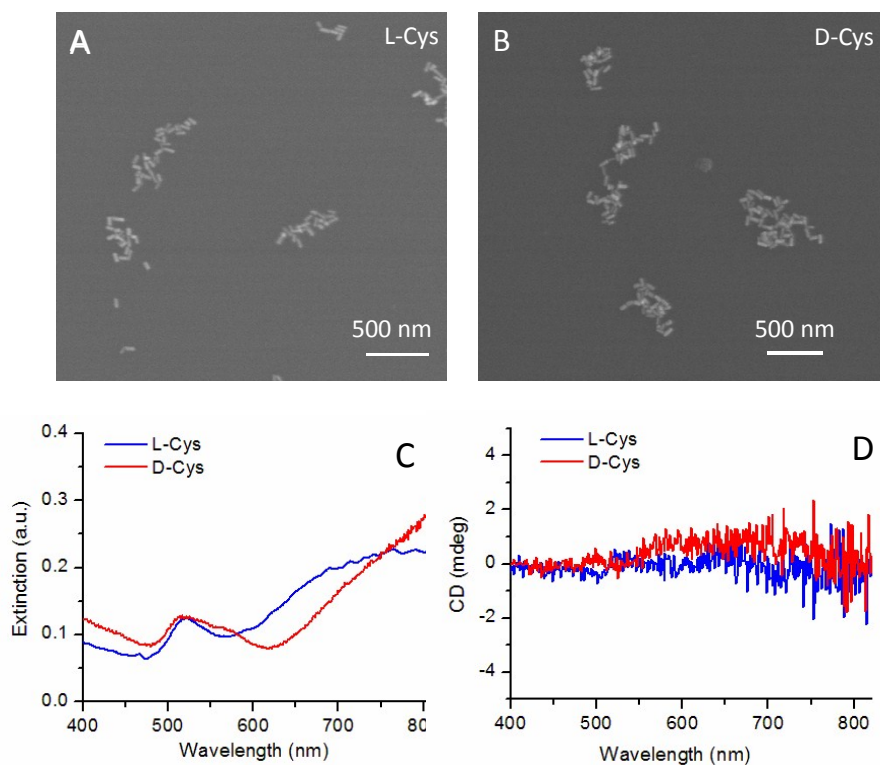
Figure S8. Representative SEM images of disordered aggregates of GNRs mediated by L-Cys (A) or D-Cys (B) and the corresponding extinction (C) and CD (D) spectra.

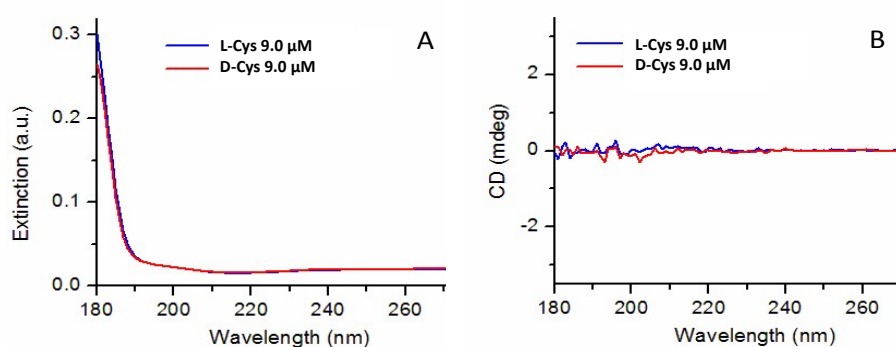## 6．**Estimation of CD amplification factor (AF)**

Figure S9. (A) Extinction and (B) CD spectra from pure L- and D-cys bulk solutions (9.0 μM).

Herein we introduce an amplification factor (AF) similar to that in SERS[2] to estimate the amplification of the native CD of Cys by plasmonic CD response of the GNR polymers.

$$AF = (I_{PCD}/N_{surf})/(I_{ECD}/N_{vol}) = \frac{I_{PCD}}{I_{ECD}} \cdot \frac{C_{Cys-bulk} \cdot V_{light} \cdot N_A}{n_{Cys@GNR} \cdot C_{GNR} \cdot V_{light} \cdot N_A}$$

where I_{PCD} is the peak plasmonic CD value from Cys mediated GNR polymers, I_{ECD} is CD from bulk Cys solution at 203 nm, N_{vol} is number of Cys molecules in bulk Cys solution illuminated by the incident light, N_{surf} is number of Cys molecules at hot spots in the same illuminated volume, $C_{Cys-bulk}$ is concentration of bulk Cys solution, C_{GNR} is concentration of GNRs in the Cys mediated GNR polymers, $n_{Cys@GNR}$ is number of Cys on each GNR.

As in the SERS case, we have

$$AF = \frac{I_{PCD}}{I_{ECD}} \cdot \frac{C_{Cys-bulk}}{n_{Cys@GNR} \cdot C_{GNR}}$$

$$= \frac{I_{PCD}}{I_{ECD}} \cdot \frac{C_{Cys-bulk}}{\frac{2S_{end}}{S_{Cys}} \cdot C_{GNR}} = \frac{I_{PCD}}{I_{ECD}} \cdot \frac{C_{Cys-bulk} \cdot S_{Cys}}{C_{GNR} \cdot \pi D^2}$$

This estimation of AF also yields a lower limit of the actual value.

Table S1. AF of Cys by using collinear GNR polymers from five independent measurements.

For L-Cys	For D-Cys
137	122
99	70
87	80
143	115
133	174

Table S2. AF of Cys by using zigzag GNR polymers from five independent measurements.

For L-Cys	For D-Cys
14	13
10	7
6	6
20	19
13	12

7. Detection and characterization of Cysteine molecular chirality by CD responsive collinear polymers of GNRs
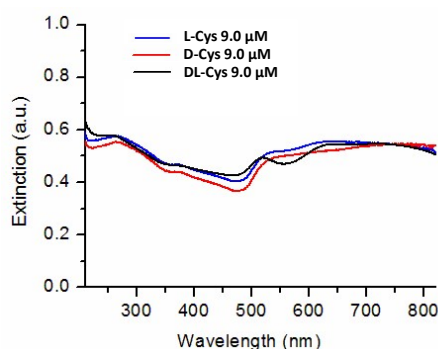
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Figure S10. Extinction spectra of the collinear GNR polymers with L- (blue line), D- (red line), and D,L-Cys (black line) as linkers, respectively.
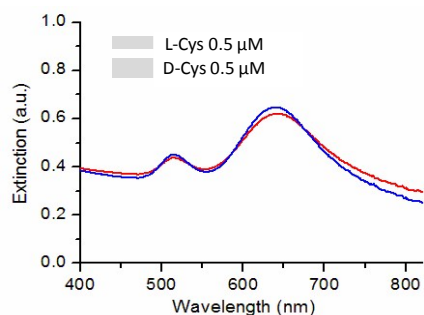

Figure S11. Extinction spectra of the collinear GNR polymers with L-Cys (blue line) and D-Cys (red line) as linkers. The concentration of Cys is 0.5 μM.
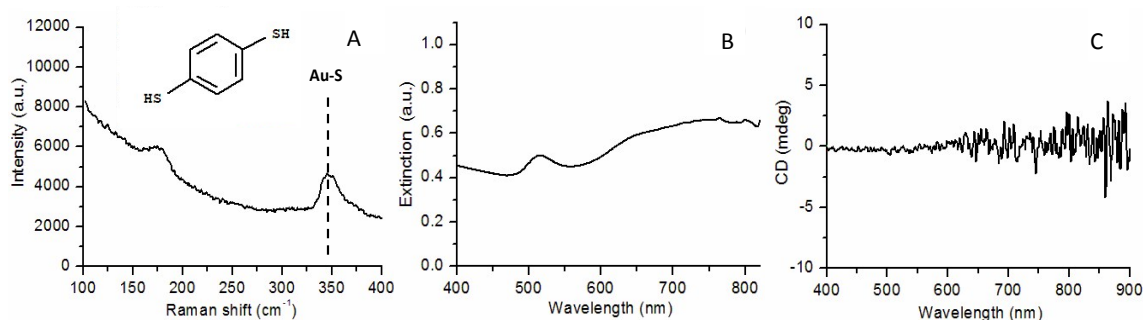

Figure S12. (A) SERS, (B) Extinction and (C) CD spectra from 1,4-Benzenedithiol (9.0 μM, inset in (A)) mediated GNR polymers.

8. Enantiomer excess determinations by CD responsive collinear GNRs polymers

For sample preparations, total concentration of the added Cys is 9.0 μM, in which the fraction ratio of L-Cys to D-Cys is changed from 100% L, 20%L:80%D, 40%L:60%D, 50%L:50%D, 60%L:40%D, 80%L:20%D, to 100% D. The extinction and CD measurements were conducted

immediately after mixing Cys solution with GNRs colloidal solution. In the main text, we showed the changes of the sign and the plasmon-induced CD signal as a function of the enantiome excess of the added Cys molecules for collinear GNR polymers.

References

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