Supporting Information for

Recognition of Chiral Zwitterionic Interactions at Nanoscale Interfaces by Chiroplasmonic Nanosensors

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1. Preparation of gold nanorods: preparation, Zeta potential measurement

The CTAB-coated GNRs were synthesized using a modified seed-mediated method as reported in previous study.[S1] After two rounds of purify by centrifugation (9000 rpm for 5 min), the superfluous CTAB were removed. The precipitates were collected and redisposed in deionized water. All chemicals were purchased from Sigma and used as received. Pure Milli-Q grade water was used in all sample preparations.

A qualitative control of repulsive forces between adjacent GNRs was achieved by simply tuning the concentration of CTAB in the as-prepared colloidal solution. Specifically, to 1mL of as-prepared GNRs aqueous solution, 4 to 20 μL CTAB solutions (5 mM) was used. Different repulsive forces due to different CTAB concentrations were measured by Zeta potential (ξ. in **Table S1**, pH~7). For measuring the corresponding different Zeta potential values in acidic solutions (pH ~2), 10 μL HCl solution at certain concentration was mixed with 1mL aforementioned GNRs solution. The mixture was kept at room temperature for 3 hours before Zeta potential measurement, the results can be seen in **Table S1**, pH~2.

Table S1. Zeta potential values of GNRs with different CTAB stabilizer at pH~7 and pH~2.

Concentration of added CTAB (μM)	*Zeta potential at different pH values (ξ. mV)*	
	pH ~ 7	pH ~ 2
40	42.7	41.0
60	43.7	41.9
80	47.5	46.9
100	48.8	47.4

2. Cys chiral interactions mediated GNRs assembled chains: preparation, SEM images, SERS, CD and extinction spectra

As-prepared GNR/CTAB colloidal solution (~0.9 nM, Zeta potential ξ 48.8 mV) was mixed with L-, D-, or DL-Cys solution (27×10^{-6} M) under a volume ratio of 2:1. The chiral interactions mediated GNRs assembly process was triggered by adding deionized water or HCl solutions to dilute the repulsive force between adjacent GNRs. Specifically, 100 μL deionized water or 100 μL HCl (0.01 M) solution was added into 1 mL as prepared Cys patched dispersed GNRs solution, as such the assembly process of GNRs could occur via Cys chiral interactions in neutral or in acidic solution.

At quasi-equilibrium state of the assembly process, the assembled products were capsulated by negatively charged poly (styrene sulfonic acid) sodium salt (PSS, MW 70000, 2g/L, 6×10^{-3} M NaCl) for SERS measurements. Then the as-prepared clusters preserved by PSS encapsulation were separated by natural sedimentation method, and redispersed in deionized water. Silicon substrates (with positive charges at the surfaces) were immersed in the sample solutions for 0.5-1 hour. The adsorbed samples on silicon substrates were dried for SEM structural characterization. Dynamic extinction and CD spectra were used to monitor the assembly process of GNRs. For preparing the GNRs assembled chains at different pH values, calculated volume of deionized water or HCl solutions at certain concentration was added into as-prepared Cys patched dispersed GNRs solution. As such the Cys chiral interactions mediated GNRs assembly process could be triggered within the pH range from 7 to 2.

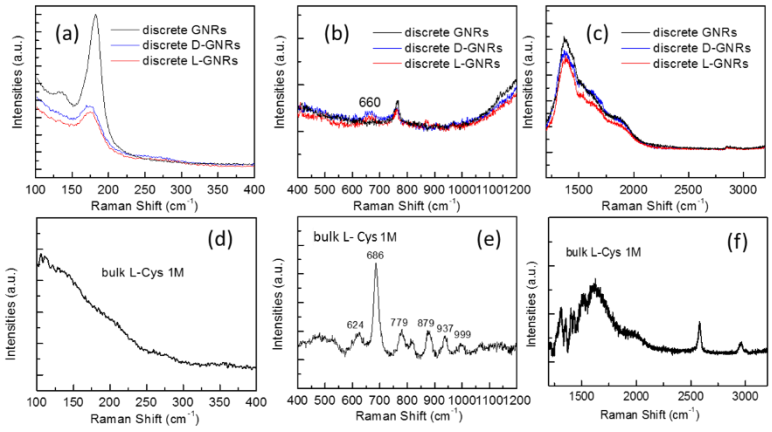

Figure S1 (a-c) SERS spectra of CTAB capped discrete GNRs (black line), discrete D-GNRs (blue line) and discrete L-GNRs (red line). (d-f) Raman spectra of bulk L-Cys (1 M).

Table S2 SERS bands of cysteine and their assignment proposed in the literature.

Raman shift (cm^{-1})			*Bands assignment[a]*
Bulk cysteine	*Cys patched discrete GNRs*	*L-GNRs assembled chains via Hb interactions*	
	280	271	$Au\text{-}S_{stretching}$
		495	$C{=}O_{deformation}$
			$CO_{twisting}$
624			$CC_{stretching}$
686	660	662	$CS_{stretching}$
779			CO_2 wagging
879			$CC_{stretching}$
937	902	893	$SH_{bending}$
999	968	973	$NCH_{bending}$
			$CC_{stretching}$

[a] The assignments are based on the references S2, S3.

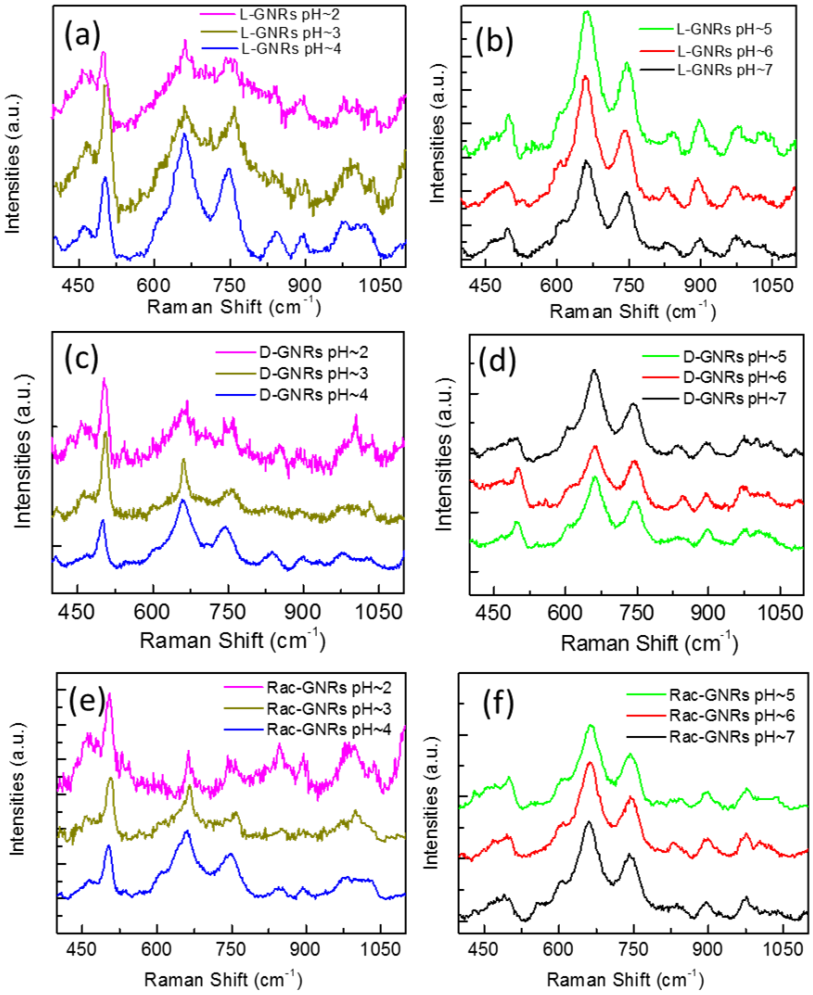

Figure S2 SERS spectra of L-GNRs (a, b), D-GNRs (c, d) and Rac-GNRs (e, f) assembled chains at different pH values.

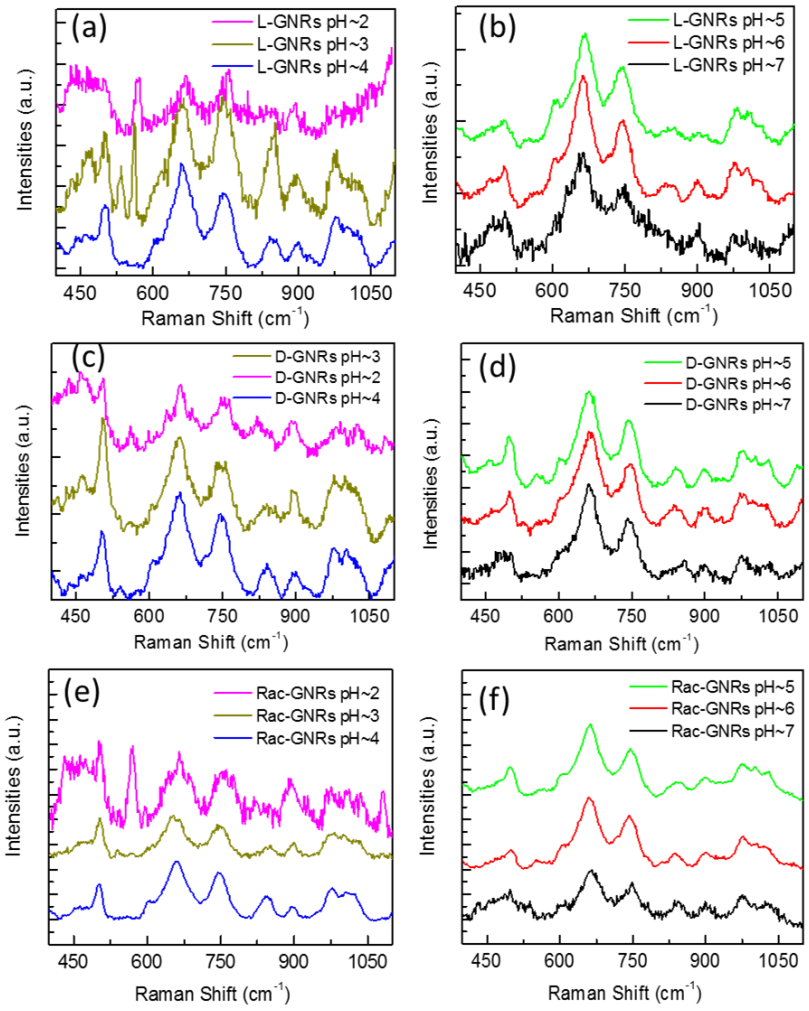

Figure S3 SERS spectra of L-GNRs (a, b), D-GNRs (c, d) and Rac-GNRs (e, f) assembled chains at different pH values.

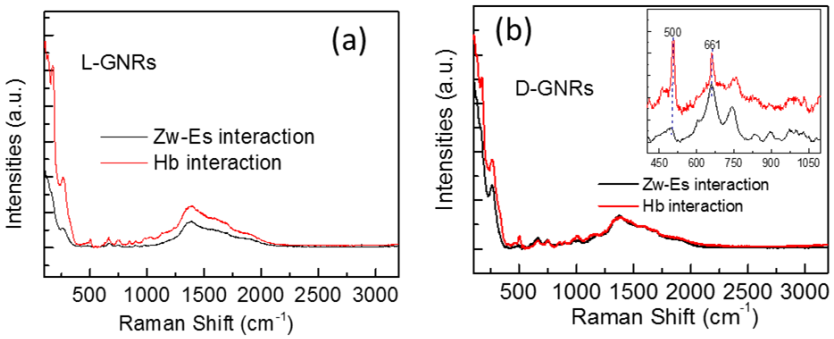

Figure S4 SERS spectra of Zw-Es (black line) and Hb interaction (red line) mediated L-GNRs (a) and D-GNRs (b) assembled chains in the range of 100-3200 cm^{-1}. Insert is the SERS spectra of D-GNRs assembled chains in the range of 400-1100 cm^{-1}.

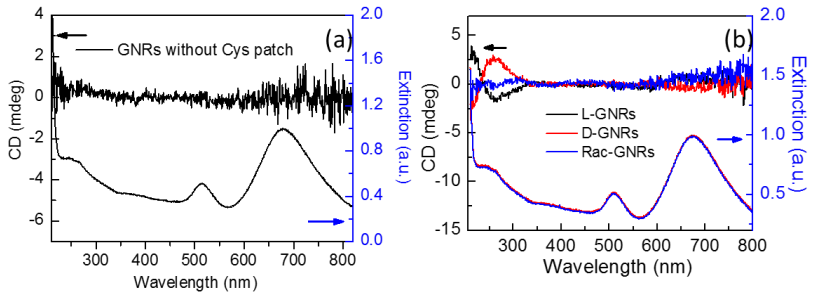

Figure S5 (a) CD and extinction spectra of discrete GNRs without Cys patches. (b) CD and extinction spectra of Cys molecules patched GNRs dispersed in neutral solution: L-GNRs (black line), D-GNRs (red line), and Rac-GNRs (blue line).

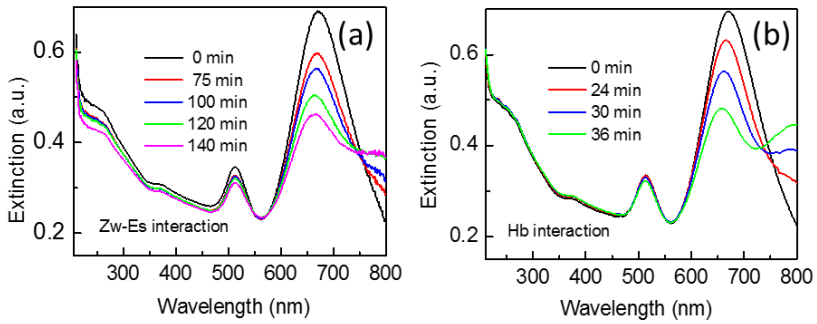

Figure S6 Dynamic extinction spectra acquired during the assembly process of L-GNRs in neutral (a) and acidic (b) solutions. The assembly time t=0 is referred to the start point at which L- GNRs assembly was initiated.

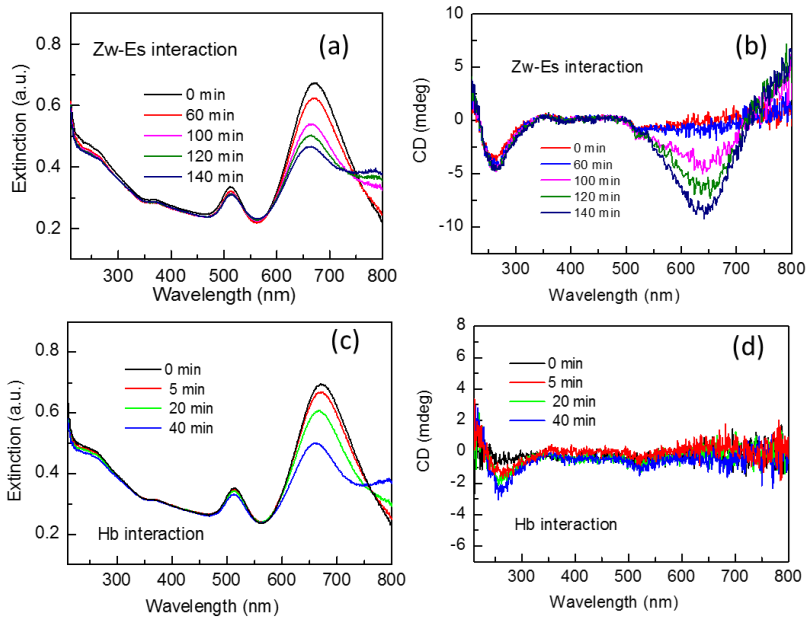

Figure S7. Dynamic extinction (a, c) and CD (b, d) spectra acquired during the assembly process of D-GNRs in neutral (a, b) and acidic (c, d) solutions. The assembly time t=0 is referred to the start point at which D- GNRs assembly was initiated.

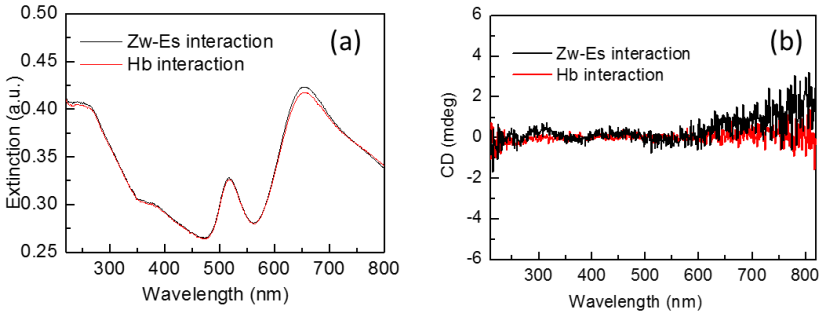

Figure S8. Extinction (a) and CD (b) spectra of Rac-GNRs assembled chains via Zw-Es (black line) and Hb (red line) interactions at quasi-equilibrium stage.

3. Cys mediated GNRs assembled chains at different Zeta potential values: CD and extinction spectra

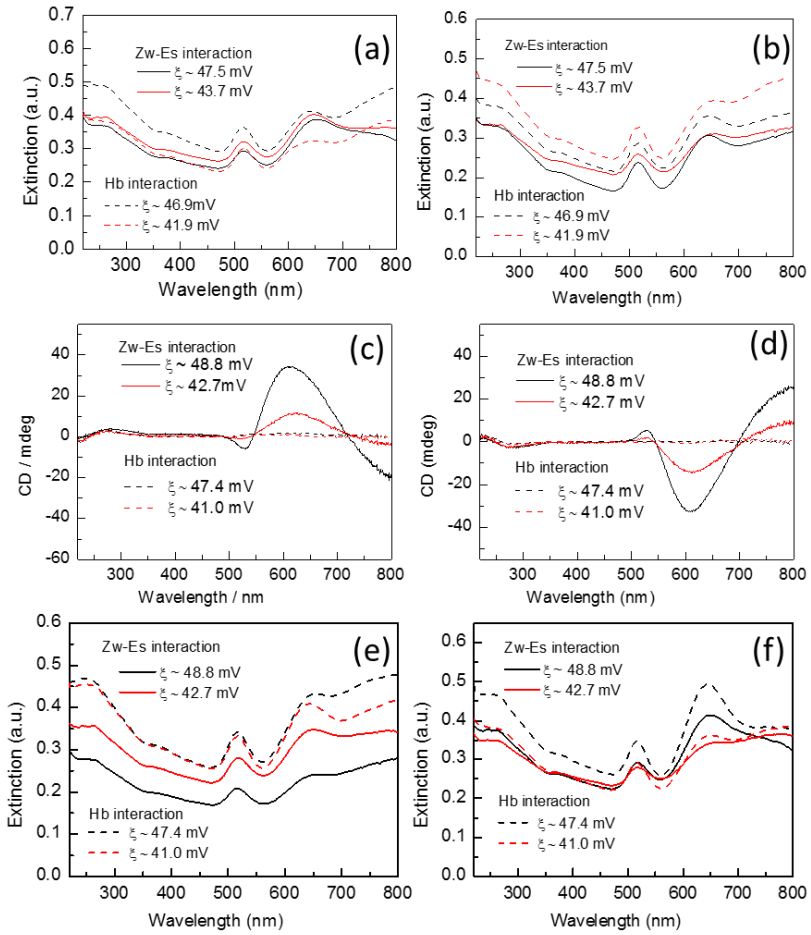

Figure S9. Extinction and CD spectra of L-GNRs (a, c, e) and D-GNRs (b, d, f) assembled chains via Cys Zw-Es (solid lines) or Hb interactions (dash lines) with different Zeta potential values: (a, b) Extinction spectra with Zeta potential values: 43.7 mV/47.5 mV for Zw-Es interaction (solid lines) and 41.9 mV/46.9 mV for Hb interaction (dash lines), (c, d, e, f) CD (c, d) and extinction (e, f) spectra with different Zeta potential values: 42.7 mV/48.8 mV for Zw-Es interaction (solid lines) and 41.0 mV/47.4 mV for Hb interaction (dash lines).

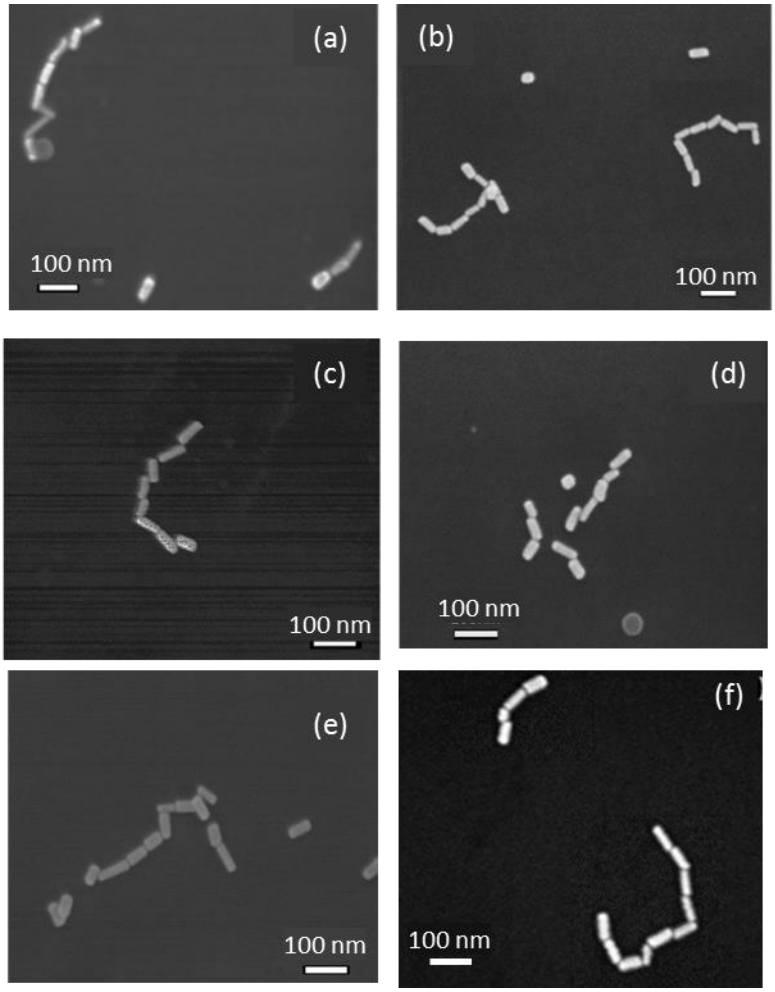

Figure S10. Typical SEM images of L- (a, b), D- (c, d) and Rac- (e, f) GNRs assembled chains formed via Zw-Es (a, c, e) and Hb (b, d, f) interactions.

4. GNRs assembled chains mediated by Pen chiral interactions: extinction and SERS, spectra

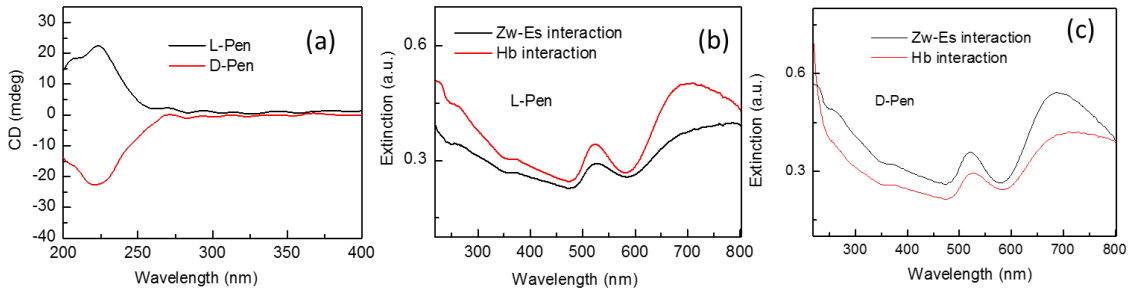

Figure S11. (a) CD spectra of pure L-/D-Pen (1 mM). (b, c) Extinction spectra of L-/D-Pen Zw-Es (black line) and Hb (red line) chiral interactions mediated GNRs assembled chains.

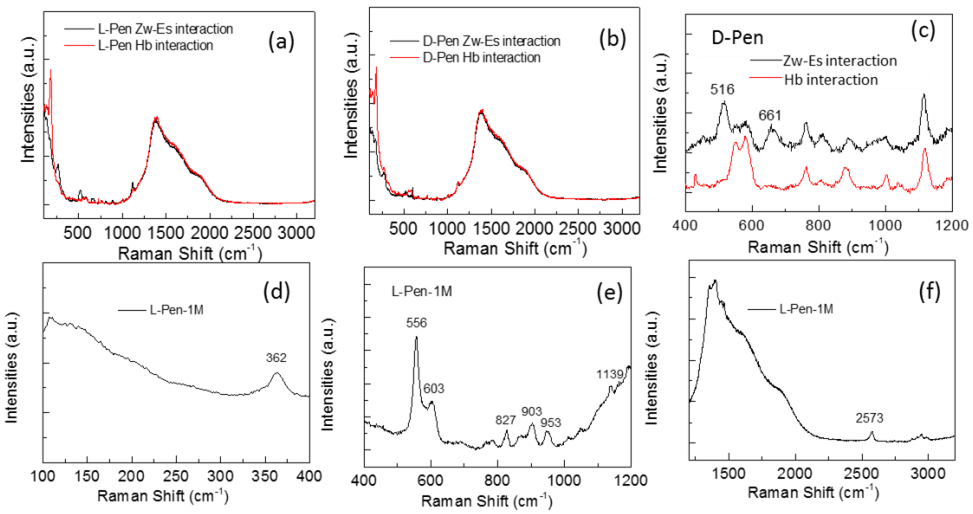

Figure S12. (a, b) SERS spectra of L-/D-Pen Zw-Es and Hb interactions mediated GNRs assembled chains in the range of 100-3200 cm-1. (c) SERS spectra of D-Pen mediated GNRs assembled chains via Zw-Es (black line) and Hb interactions (red line) in the range of 400-1200 cm^{-1}. (d-f) Raman spectra of bulk L-penicillin (1 M) in the range of 100-3200 cm^{-1}

Table S3. SERS bands of Pen and their assignment proposed in the literature.

Raman shift (cm^{-1})		*Bands assignment[a]*
Bulk Pen	*L-Pen assembled GNRs chains via Zw-Es interactions*	
362		$CCC_{bending}$
		$CCS_{bending}$
556	521	$COO_{rocking}$
		$CS_{stretching}$
	659	$OCO_{bending}$
903	891	CH_3 rocking
1139	1117	$CN_{stretching}$
2573		$SH_{stretching}$

[a] The assignments are based on the reference S4.

5. Cys mediated GNRs assembled chains with different pH values: CD and extinction spectra

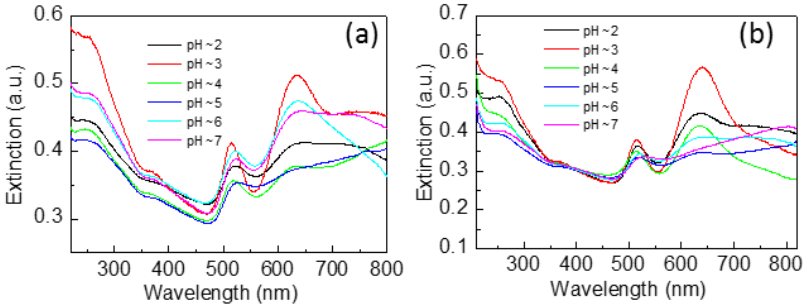

Figure S13. Corresponding extinction spectra of L-GNRs (a) and D-GNRs (b) assembled chains at different pH values.

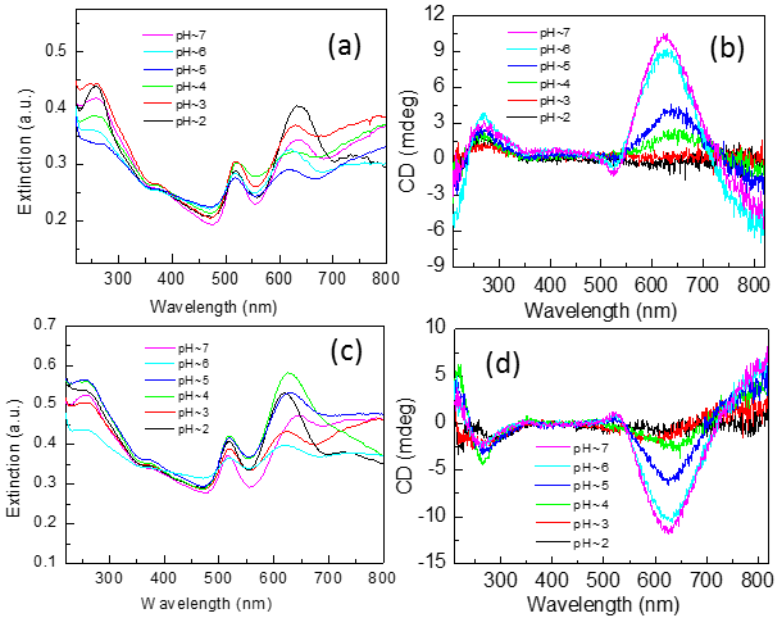

Figure S14. Extinction (a, c) and CD (b, d) spectra of L-GNRs (a, b) and D-GNRs (c, d) assembled chains at different pH values.

References

(S1) Zhang, W.; Ji, Y.; Meng, J.; Wu, X.; Xu, H. Probing the Behaviors of Gold Nanorods in Metastatic Breast Cancer Cells Based on Uv-Vis-Nir Absorption Spectroscopy. *PLoS One* **2012**, *7*, e31957.

(S2) Podstawka, E.; Ozaki, Y.; Proniewicz, L. M. Part III: Surface-Enhanced Raman Scattering of Amino Acids and Their Homodipeptide Monolayers Deposited onto Colloidal Gold Surface. *Appl. Spectrosc.* **2005**, *59*, 1516–1526.

(S3) Jing, C.; Fang, Y. Experimental (SERS) and Theoretical (DFT) Studies on the Adsorption Behaviors of L-Cysteine on Gold/silver Nanoparticles. *Chem. Phys.* **2007**, *332*, 27–32.

(S4) Howard-Lock, H. E.; Lyne Lock, C. J.; Smalley, P. S. The Crystal Structure of Racemicdl-Penicillamine and a Spectroscopic Study Of d-Penicillamine. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 333–353.