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Reversible modulation of plasmonic chiral signals of achiral gold nanorods using chiral supramolecular template

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Experimental

1) Gold nanorods (Au NRs) were fabricated by a seed-mediated, Ag(I)-assisted growth procedure according to the reported protocols.[1,2] The seed solution was prepared by mixing 0.25 mL of $HAuCl_4$ solution (0.01 M) and 7.5 mL of CTAB solution (0.1 M) in a test tube. Then, 0.6 mL of an ice-cold $NaBH_4$ solution (0.01 M) was added all at once, followed by rapid inversion mixing for 2 min. The resultant solution developed a pale brown-yellow color. After that, the test tube was kept in a water bath maintained at 25 ^oC to obtain stable seed solution. The growth solution was prepared by mixing 285 mL of CTAB (0.1 M), 12 mL of $HAuCl_4$ (0.1 M) and 1.8 mL of $AgNO_3$ (0.01 M) in a 500 mL reagent bottle. Another 100 mL of HCl (37 wt %) was added into the above solution. After this step, 1.92 mL of L-ascorbic acid (0.1 M) was added to the resultant solution with gentle stirring, which changed the color of the growth solution from dark yellow to colourless. Finally, 0.6 mL of seed solution was added to the resulting solution at 27-30 ^oC, and the color of the solution gradually changed within 10-20 min. The temperature of the growth medium was maintained constant at 27-30 ^oC during the whole procedure.

2) For preparation of phenylboronic acid-capped Au NRs (PBA-Au NRs), 4-mercaptophenylboronic acid (3.6 mg) was added into the above CTAB-capped Au NRs solution and incubated at 4 ^oC for 12 h. The resulting PBA-Au NRs solution was purified by centrifugation (11,000 rpm, 11 min) to remove the superfluous CTAB and then re-dispersed in deionized water. This purification procedure was repeated 2 cycles.

3) The azobenzene-glycopeptides (denoted as L-AGP and D-AGP) were synthesized according to our previous report.[3] The purity was analyzed by reverse-phase HPLC on ZORBAX Eclipse Plus C18 Column (4.6×100 mm, 3.5 μm) using 85% CH_3OH/15% H_2O as eluent. Column flow = 1.00 mL min^{-1}.

4) Supramolecular nanotwists (NTWs) were prepared by fully dissolving the L- or D-AGP molecules in water at 70 ^oC before being cooled to room temperature for self-assembly.

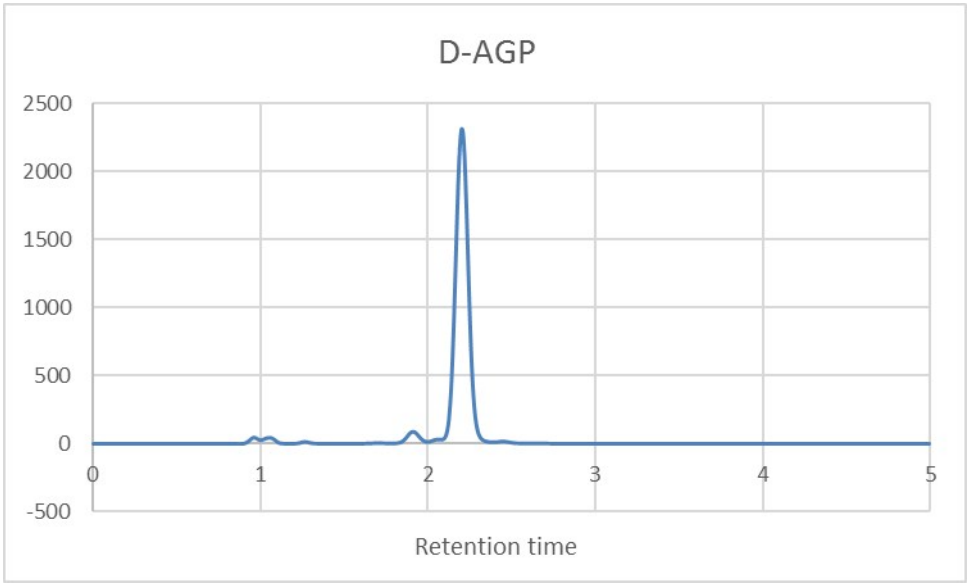
5) For preparation of chiral nanocomposites, a solution of PBA-Au NRs was added to the solution of L- or D-AGP NTWs, and then the solution pH was adjusted to 8.5 using 0.25 M NaOH solution for co-assembly.

6) TEM samples were prepared as follows: 5 μL of solution sample was deposited onto a carbon-coated copper grid. The excess of the solution was quickly wicked away by a piece of filter paper, and the sample was left to dry in air. TEM imaging of the self-assembled superstructures was performed on a Thermo Scientific™ Talos™ F200S scanning/transmission electron microscope at an accelerating voltage of 200 kV.

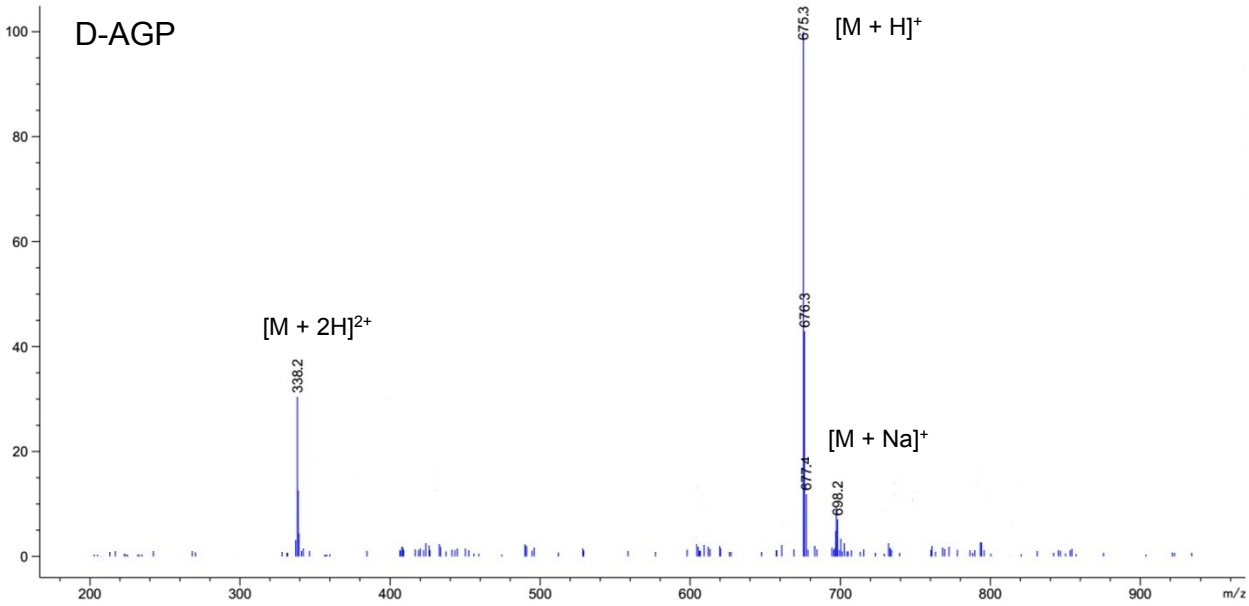
7) CD spectra of the solution samples were recorded on an Applied Photophysics Chirascan Plus spectrophotometer. In multiple cycle experiments, the PCD signal of the chiral nanocomposites was monitored at 900 nm in response to temperature, light or pH variations.

8) UV-Vis spectra of the solution samples were acquired on an Agilent CARY5000 spectrophotometer or TU-1901 spectrometer (Beijing Purkinje General Instrument Co., Ltd.).

Results



Analytical reverse-phase HPLC of D-AGP



Electrospray ionization mass spectrometry of D-AGP

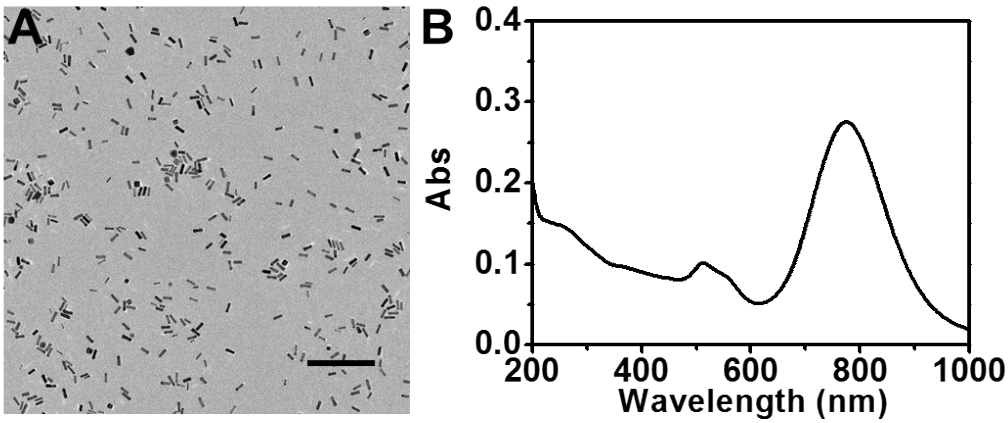


Fig. S1 (A) Representative TEM image of PBA-Au NRs. The scale bar is 500 nm. (B) UV-Vis spectrum of PBA-Au NRs solution.

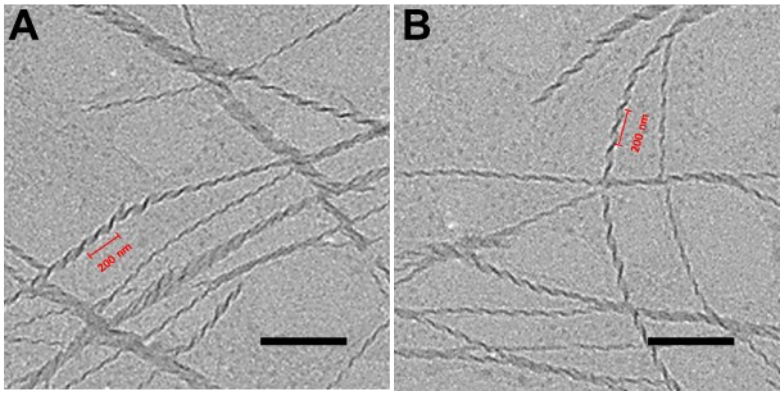


Fig. S2 Higher resolution TEM images of left- (A) and right-handed (B) supramolecular NTWs assembled from L-AGP and D-AGP, respectively. The pitch is ~200 nm. The scale bars represent 500 nm.

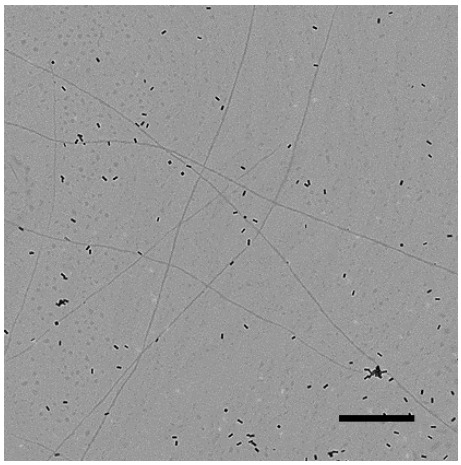


Fig. S3 Representative TEM image of the mixture of CTAB-capped Au NRs (0.48 nM) and L-AGP NTWs (0.09 mM) at pH 8.5. The scale bar is 1 μm.

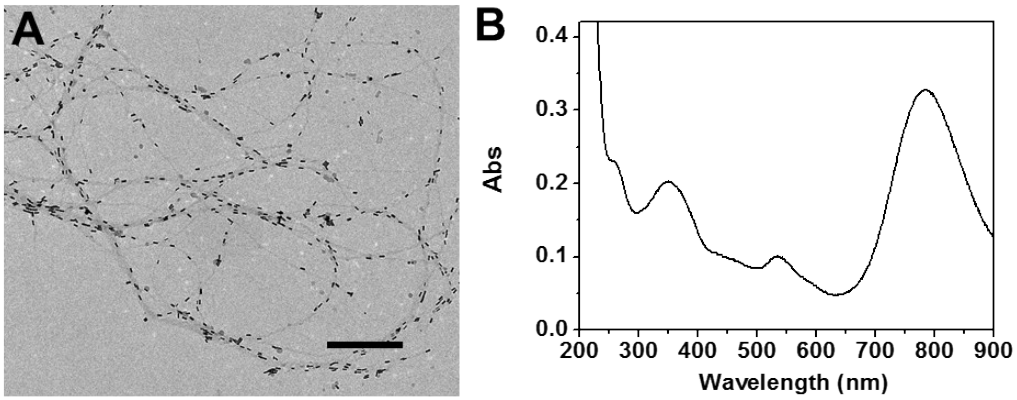


Fig. S4 Representative TEM image (A) and UV-Vis spectrum (B) of D-AGP NTWs/PBA-Au NRs (0.09 mM/0.48 nM). The scale bar is 1 μm.

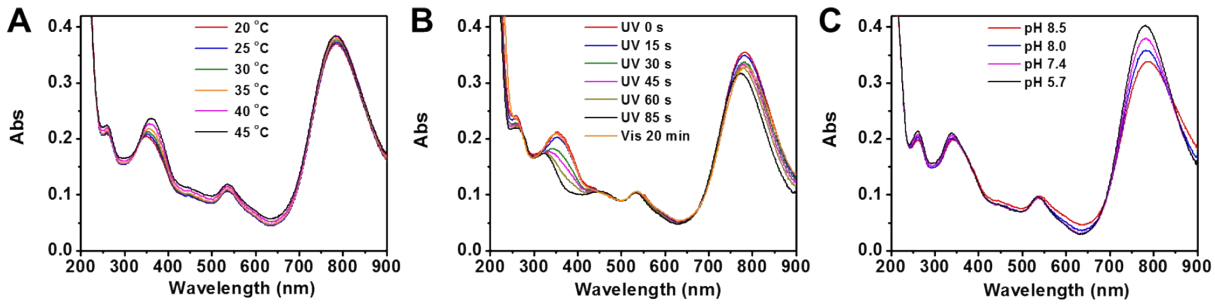


Fig. S5 UV-Vis spectra of L-AGP NTWs/PBA-Au NRs (0.09 mM/0.48 nM) in response to different stimuli (temperature, light or pH).

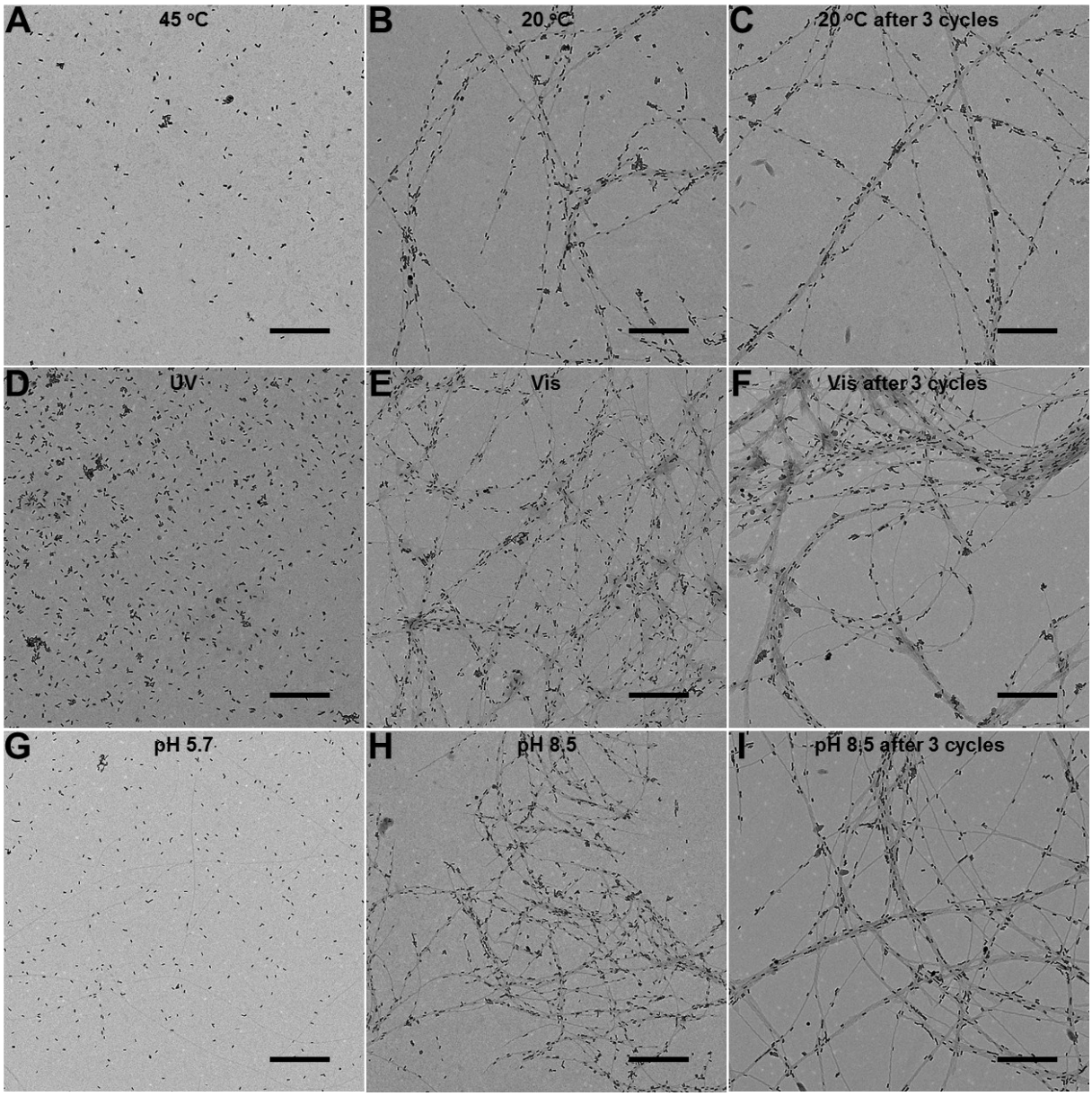


Fig. S6 Representative TEM images of L-AGP NTWs/PBA-Au NRs (0.09 mM/0.48 nM) in response to different stimuli (temperature, light or pH). The scale bars represent 1 μm.

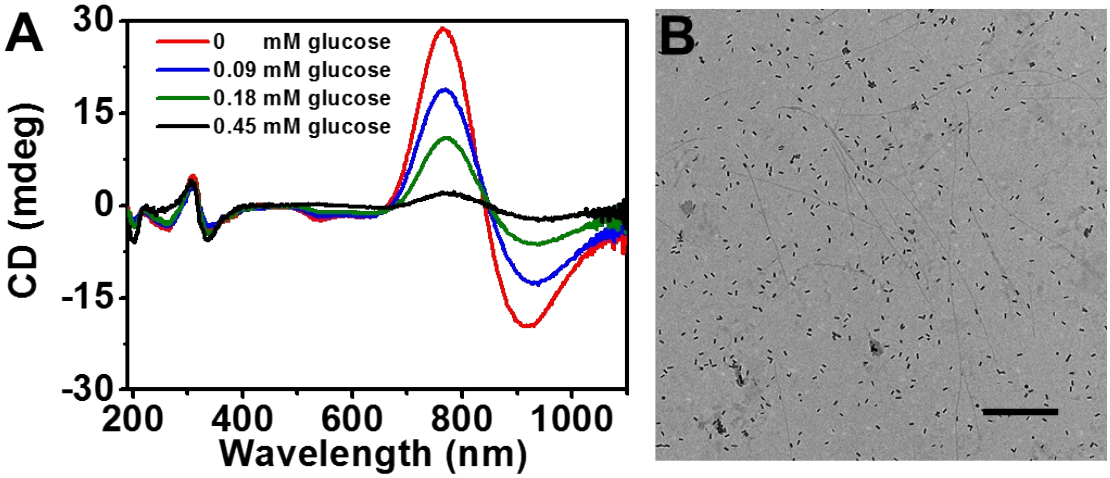


Fig. S7 (A) CD spectra of L-AGP NTWs/PBA-Au NRs (0.09 mM/0.48 nM) in the presence of various concentrations of glucose. (B) Representative TEM image of L-AGP NTWs/PBA-Au NRs (0.09 mM/0.48 nM) after the addition of 0.45 mM glucose. The scale bar is 1 μm.

References

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2 C. J. Orendorff and C. J. Murphy, *J. Phys. Chem. B*, 2006, **110**, 3990–3994.

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