Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Strong chiroptical activity from achiral gold nanorods assembled with proteins

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Experimental section

Materials

Tetrachloroauric(III) acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), sodium borohydride ($NaBH_4$) and Ascorbic acid were from Nacalai Tesque. Hexadecyltrimethylammonium bromide (CTAB) and silver nitrate ($AgNO_3$) were purchased from Wako Pure Chemical Industries Ltd. Pepsin, Glutathione, Trypsin and Lysozyme were purchased from Wako Pure Chemical Industries Ltd. Lactalbumin (Albumin from milk) was purchased from TCI, Inc. Ovalbumin (albumin, egg), HSA (albumin, Human, F-V lyophilized) and Globulin was purchased from Nacalai Tesque. Bovine serum albumin (albumin, Bovine Fraction V) was purchased from Sigma-Aldrich.

Measurements

The instruments used in this work were: SHIMADUZU UV-1800 (for UV-vis spectra measurements), JASCO J-820 spectrometer (for CD spectra measurements), JEOL JSM-6500F (for FE-SEM measurements), FEI Tecnai Osiris (for TEM measurements) and HORIBA SZ-100 (for Zeta potential measurements and DLS measurements).

Preparation of Au Seeds

In a typical procedure, 0.25 mL of an aqueous (0.010 M) solution of $HAuCl_4$ was added to 7.5 mL of a CTAB solution (0.10 M) in a vail. The solutions were gently mixed by the inversion. The solution appeared bright brown-yellow in color. Then, 0.60 mL of an aqueous (0.010 M) ice-cold $NaBH_4$ solution was added all at once, followed by rapid mixing for 2min. The solution color changed to pale brown-yellow. Then the vial was kept in a water bath maintained at 25 °C for 2 h.

Preparation of Au Nanorods

95 mL of CTAB (0.10 M), 4 mL of $HAuCl_4$ (0.010 M), and 0.6 mL of $AgNO_3$ solutions (0.01 M) were added in that order, one by one, to a vial, followed mixing. The solution at this stage appeared bright brown-yellow in color. Then 0.64 mL of Ascorbic acid (0.10 M) was added to it. The solution became colorless upon addition and mixing of Ascorbic acid. Finally, 0.40 mL of seed solution was added, and the reaction mixture was gently mixed for 10 s and left undisturbed for at 3 h.

Gold nanorods (100 mL) were first purified by centrifugation. The residue (20 mL) obtained after 30 min of centrifugation (12000 rpm) was dispersed in 30 mL of water.

The solutions centrifuged (12000 rpm) for 30 min. The supernatant solution was

carefully removed 30 mL, and the residue was dispersed in the remained solutions. The solution was kept at 4 °C for 2 h to remove excess CTAB. Upon cooling, excess CTAB crystallized out which was separated by filtration. The filtrate contains Au nanorods that were used directly for various studies. (concentration ~1.6 nM)

Preparation of AuNRs assemblies with HSA in 20 % MeCNaq.

AuNRs assemblies with HSA was prepared by mixing 80 µL CTABaq. (0.01 M), 40 µL MeCN, 80 µL purified gold nanorods and 0~100 µL HSAaq (0.21 mM) at room temperature.

Calculation of anisotropic factor (*g*-factor)

Anisotropic factor (g-factor) is defined as: $g = \frac{\Delta\varepsilon}{\varepsilon}$

where $\Delta\varepsilon = \varepsilon^L - \varepsilon^R$ and $\Delta\varepsilon = \varepsilon^L + \varepsilon^R$, and ε^L and ε^R are the molar extinction coefficients for left circularly polarized (LCP) and right circularly polarized (RCP) light, respectively.

Meanwhile, by applying Lambert-Beer's law

$\Delta A = \Delta\varepsilon \times c \times l$ and $A = \varepsilon \times c \times l$

Where ΔA *is the* difference between absorbance of LCP and RCP light, c (mol / L) is the concentration of the sample, *l* (cm) is the length of the cell.

The output of CD spectrometers is usually measured as ellipticity ϑ (in mdeg), related to ΔA through ϑ (mdeg)=32980ΔA.

Therefore, *g*-factor can be calculated by

$$g = \frac{\theta\ (\mathrm{mdeg})}{32980 \times A}$$

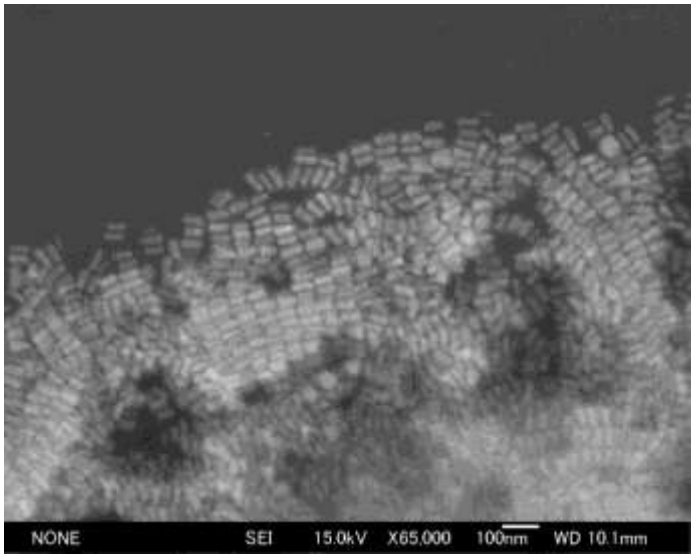

Fig. S1 FE-SEM image of as-prepared AuNRs.

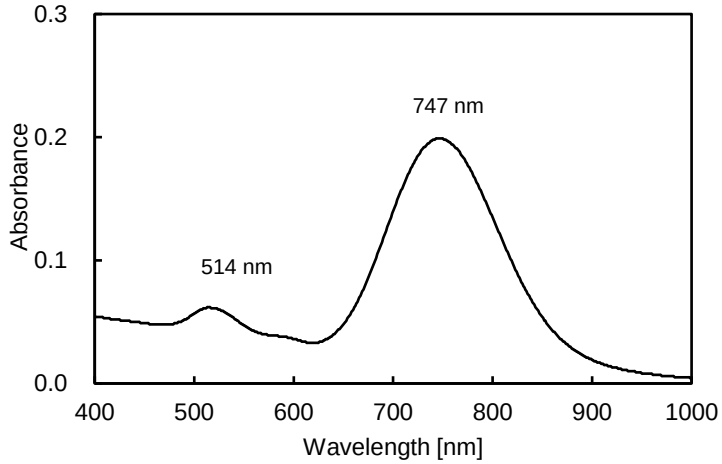

Fig. S2 UV-vis-NIR spectra of as-prepared AuNRs in water.

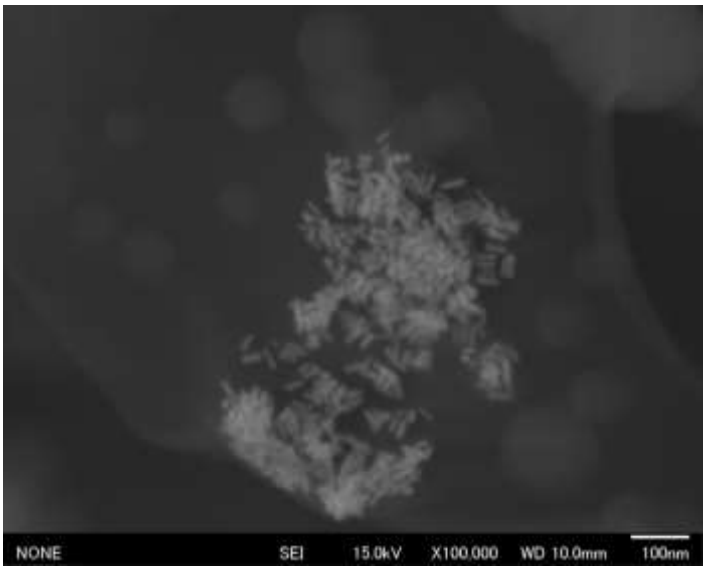

Fig. S3 FE-SEM image of AuNRs assembly with HSA in the 20 % MeCNaq. The concentration of HSA and AuNRs is set to 100 µM and 0.60 nM, respectively. The FE-SEM sample was prepared by freeze-drying process.

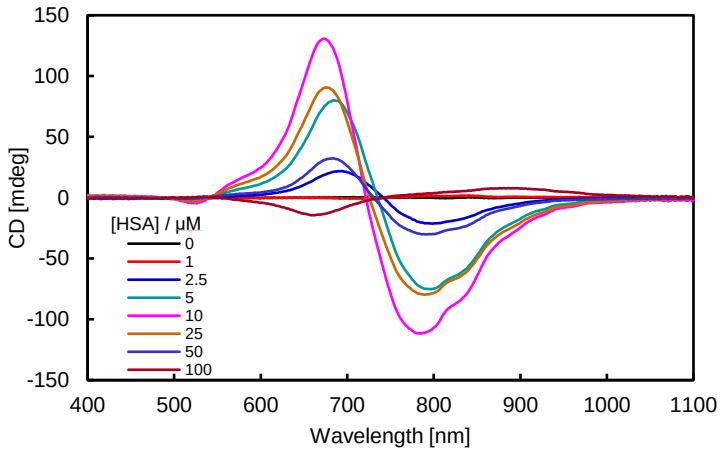

Fig. S4 CD spectra of AuNRs assemblies with HSA in 20 % MeCNaq. Cell length: 1mm. The concentration of HSA and AuNRs is set to 0−100 µM and 0.60 nM, respectively.

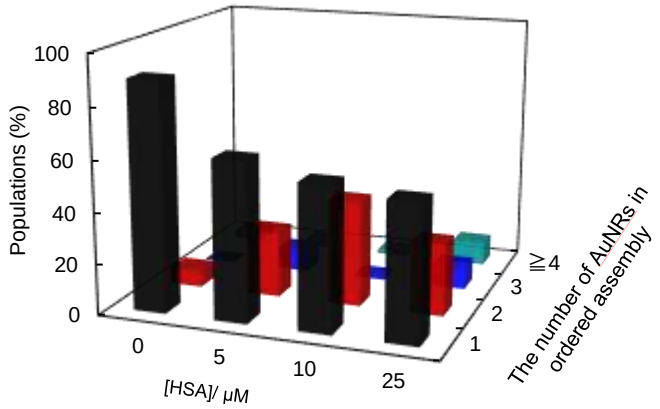

Fig. S5 Yields of AuNRs assemblies with HSA in 20% MeCNaq, determined by FE-SEM. The concentration of HSA and AuNRs is set to 0-25 μM and 0.60 nM, respectively.

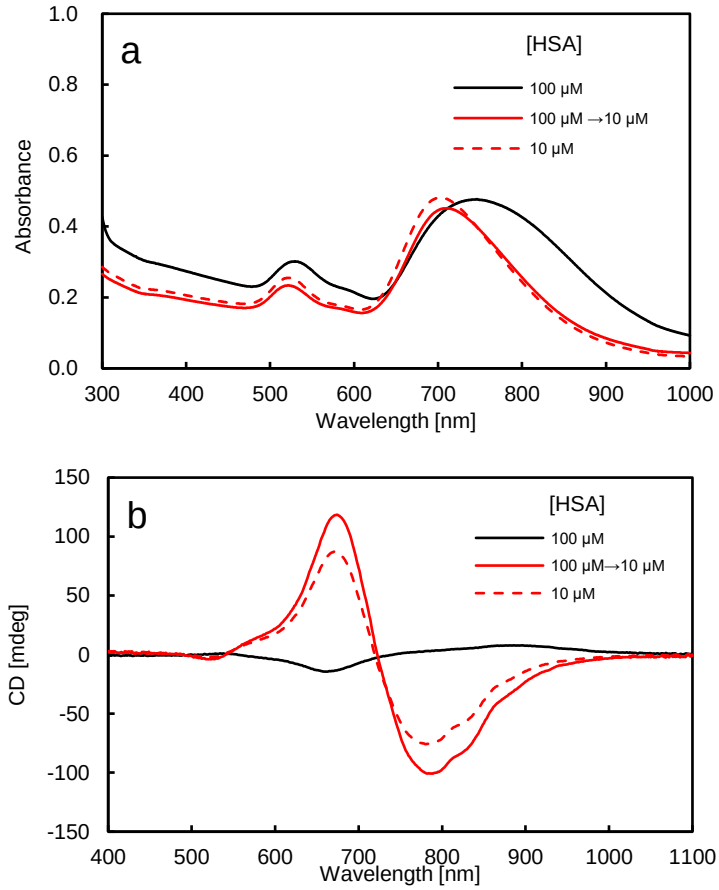

Fig. S6 (a) UV-vis-NIR spectra and (b) CD spectra of AuNRs assemblies with 10 μM and 100 μM HSA and reconstructed AuNRs assemblies by adjusting the HSA concentration from 100 μM to 10 μM. Cell length: 1mm. The concentration of AuNRs is set to 0.60 nM.

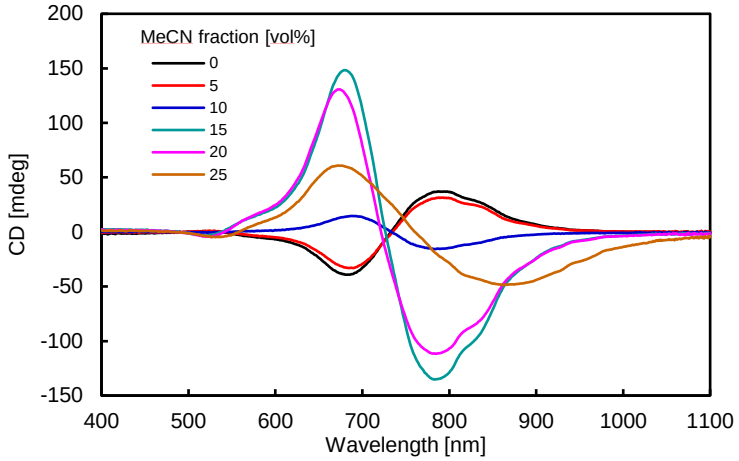

Fig. S7 CD spectra of AuNRs assemblies with HSA in the MeCN/water mixture. Cell length: 1mm. The concentration of HSA and AuNRs is set to 10 μM and 0.60 nM, respectively.

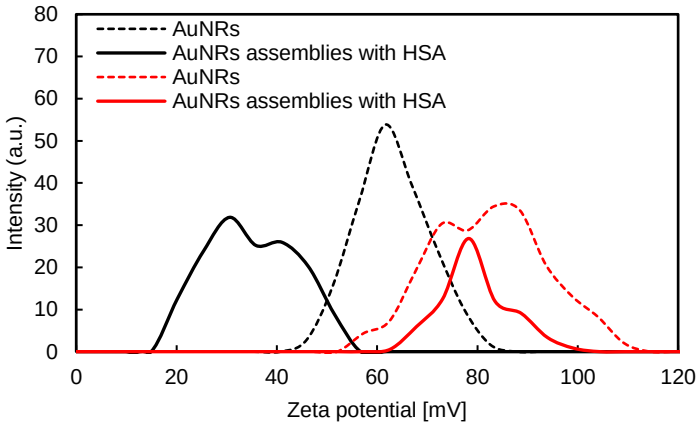

Fig. S8 Zeta potentials of AuNRs and AuNRs assemblies with HSA in 20 % (black) and 0 % (red) MeCNaq. The concentration of HSA and AuNRs is set to 10 μM and 0.60 nM, respectively.

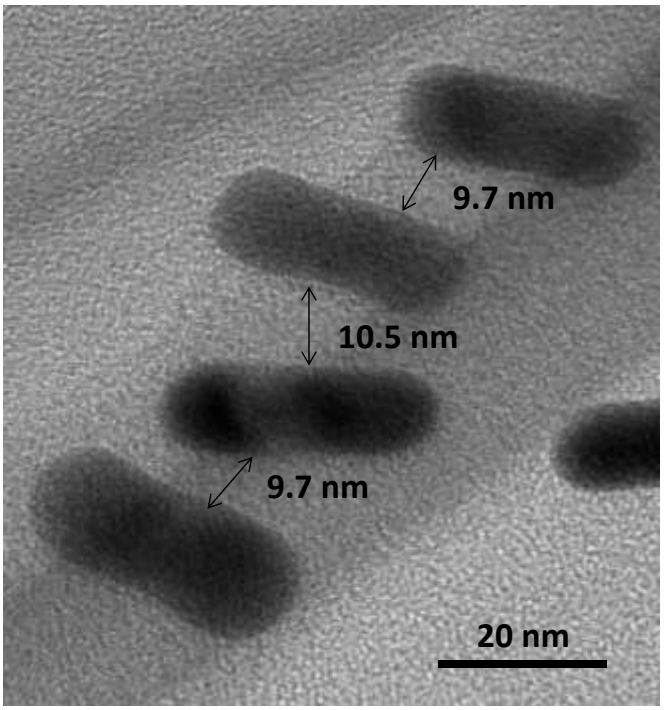

Fig. S9 TEM image of AuNRs assemblies with HSA in 20 % MeCNaq.

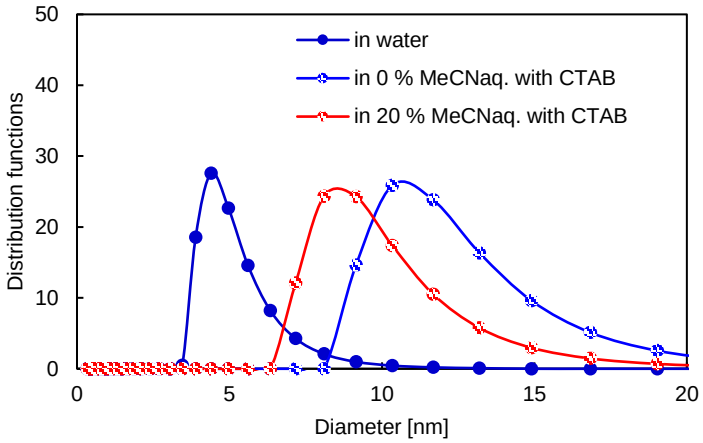

Fig. S10 DLS measurements of 0.1 mM HSA in the absence and presence (40 mM) of CTAB in water and 20 % MeCNaq.

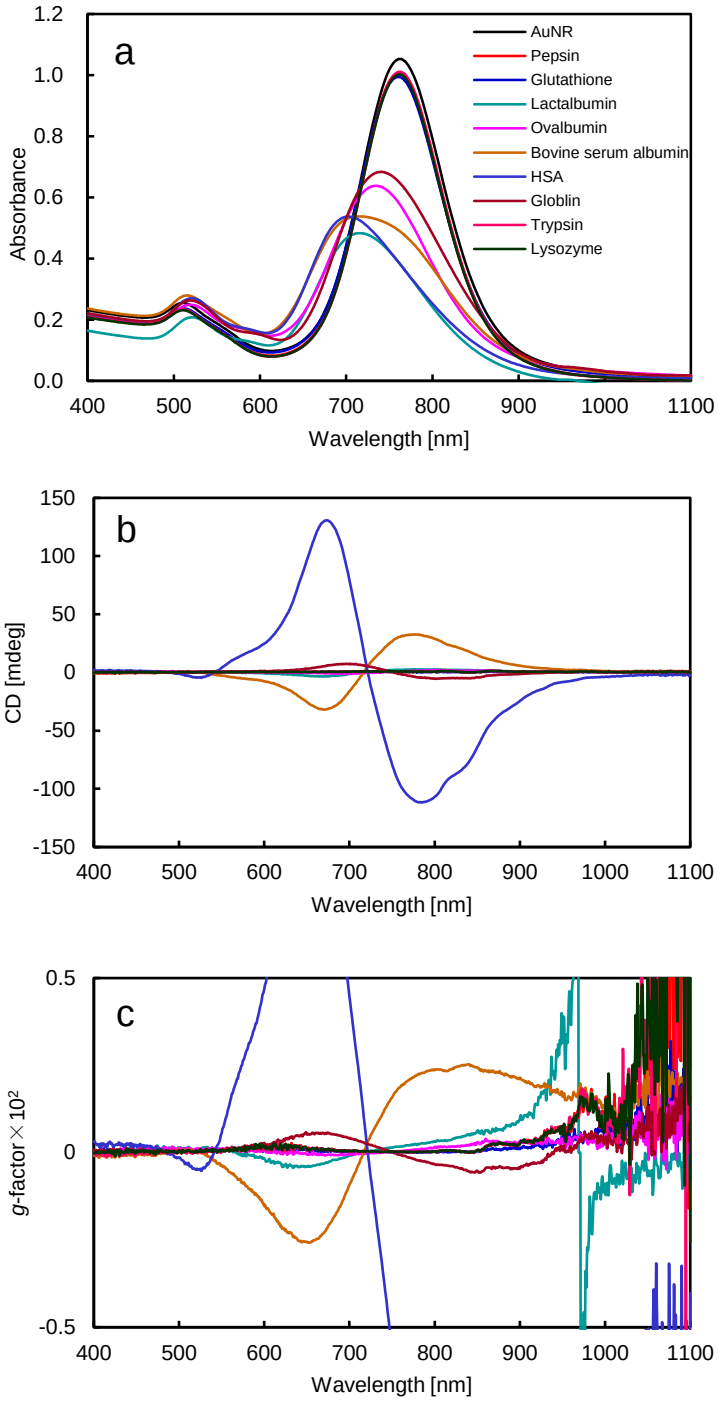

Fig. S11 (a) UV-vis-NIR spectra, (b) CD spectra and (c) *g*-factor of AuNRs assemblies with 10 μM various proteins in 20 % MeCNaq. Cell length: 1mm. The concentration of Proteins and AuNRs is set to 10 μM and 0.60 nM, respectively.