

## Supplemental Material

### Plasmonic Circular Dichroism of Peptide Functionalized Gold Nanoparticles

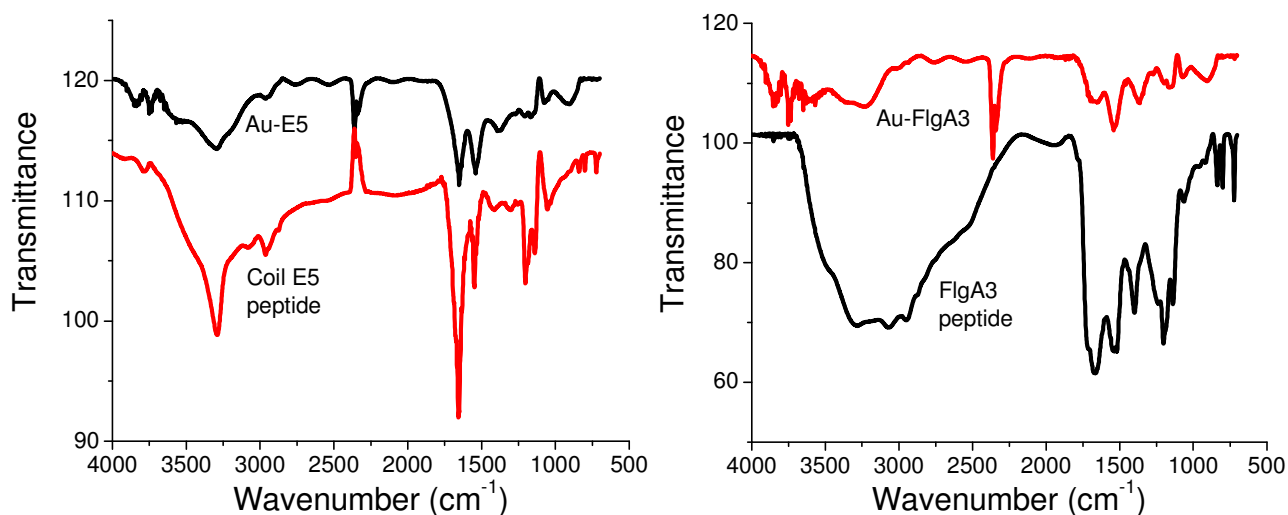
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#### Methods

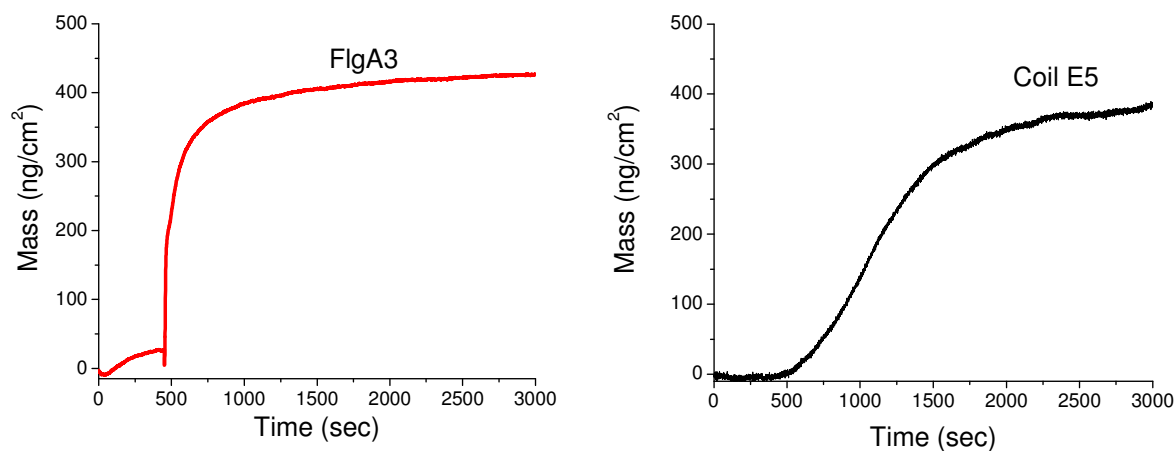
**Nanoparticle functionalization.** A3 peptide (1  $\mu$ L, 0.1 M in deionized water) or coil E5 peptide (1  $\mu$ L, 0.1 M in deionized water) was added to 500  $\mu$ L of 10 nm gold nanoparticles ( $1.14 \times 10^{13}$  particles/mL, Ted Pella) in double deionized water and incubated for 2 hours. For removal of excess peptide, peptide coated particles were centrifuged at 14,000 rpm on an Eppendorf centrifuge 5804 for 10 minutes and rinsed several times. The gold-peptide pellet was separated from supernatant and redissolved in 500  $\mu$ L of deionized water.

**Nanoparticle assembly.** 2.0  $\mu$ L of  $\text{AgNO}_3$  or  $\text{K}_2\text{PdCl}_6$  (0.1 M in water) was added to 500  $\mu$ L of peptide (E5 or FlgA3) coated gold nanoparticles and incubated for 15 minutes before CD characterization. The pH of the coil E5-gold nanoparticle solution was adjusted using NaOH or HCl to a pH of ~4 or 11.

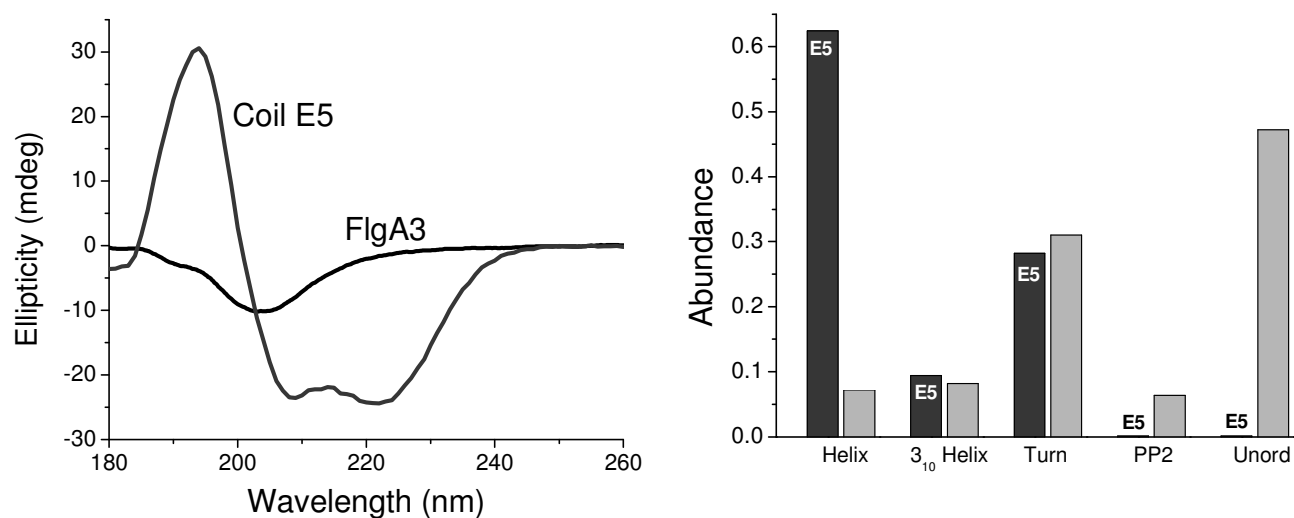
**Characterization of peptide-nanoparticle interaction.** CD spectra of the peptide-nanoparticle complexes was collected on a Jasco J-815 CD spectrometer using a quartz cuvette with a 0.5 cm pathlength from 700-190 nm at a scan rate of 20 nm/min. Absorbance spectra were collected at the simultaneously during respective CD scans on Jasco J-815 CD spectrometer. For CD scans at variable temperatures, a single position peltier cell holder was used to control temperatures from 25°C to 85°C. Peptide coated gold particles were heated at 10°C intervals for 15 minutes before collecting CD spectra.



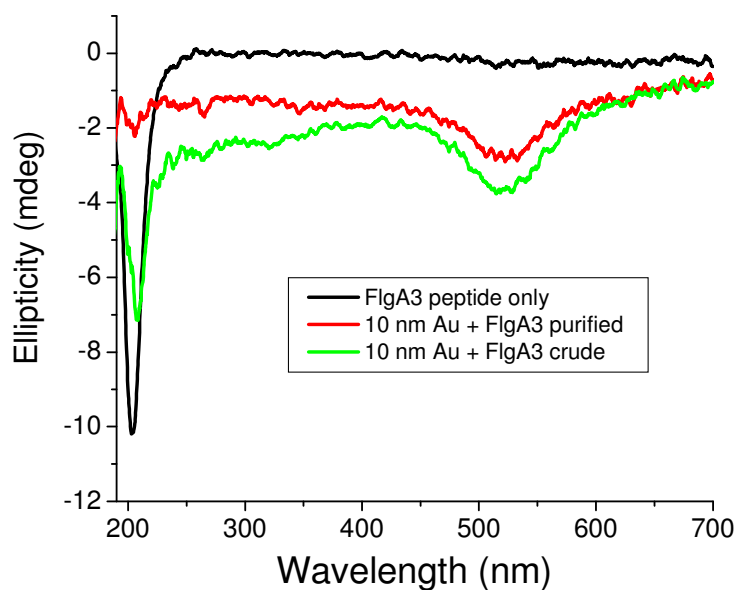
**Figure S1.** FT-IR spectra of free peptide and peptide coated gold nanoparticles for E5 and FlgA3 peptides. Spectra were collected on a Perkin-Elmer FT-IR microscope and averaged over a 1000 scans. Samples were prepared by depositing 1  $\mu\text{L}$  of respective peptide or nanoparticle solution onto a double sided polished silicon wafer and air dried.



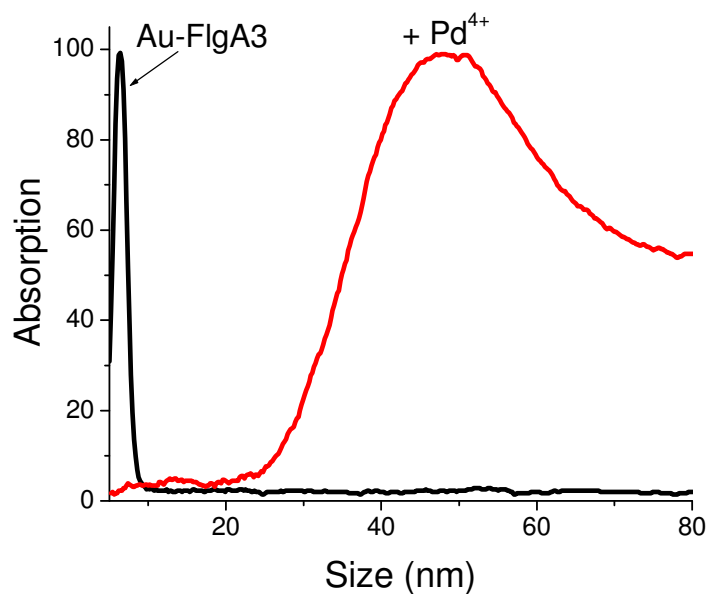
**Figure S2.** QCM binding plot of FlgA3 and coil E5 peptides (5  $\mu\text{g/mL}$  in deionized water) on a gold coated quartz crystal sensor (QSX-301, Q-Sense) at a flow rate of 0.17 mL/min using a Q-Sense E4 QCM-D system. The gold sensors were cleaned by UV ozone treatment for 10 minutes followed by heating in a 5:1:1 water/ammonia/ $\text{H}_2\text{O}_2$  solution for 10 minutes, and then thorough rinsing with deionized water. Mass was calculated using the third overtone frequency and Sauerbrey equation.



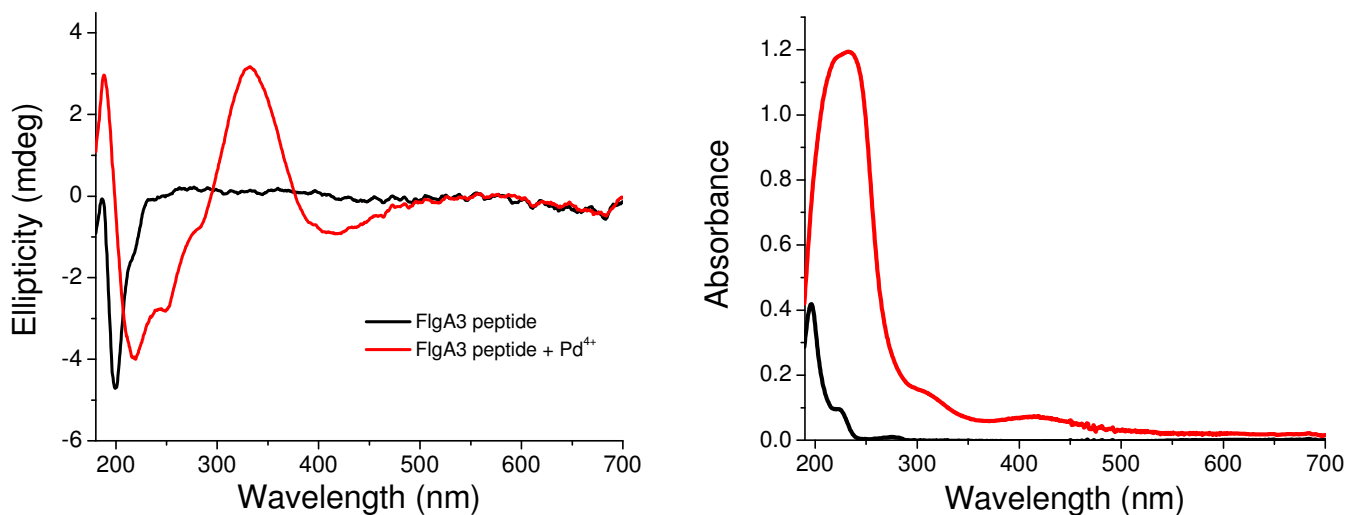
**Figure S3.** (A) CD spectra of free FlgA3 peptide (8.6  $\mu\text{M}$  in water) and E5 peptide (5.0  $\mu\text{M}$  in water) in a 0.5 cm path length quartz cuvette. (B) Analysis of secondary structure of E5 (black) and FlgA3 (grey) using CDPPro software.



**Figure S4.** CD spectra of FlgA3 coated gold particles before and after excess peptide was removed. Excess FlgA3 peptide was removed by centrifugation at 14000 rpm for 10 minutes, separation of gold pellet from supernatant, and dissolution in 500  $\mu\text{L}$  of deionized water.



**Figure S5.** Particle size distribution of Au-FlgA3 NPs and upon addition of  $\text{Pd}^{4+}$  ions using CPS particle size analyzer. Calibrated against 377 nm polystyrene particles.

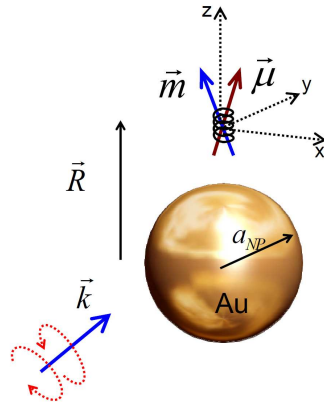


**Figure S6.** CD and absorbance spectra of FlgA3 peptide (8  $\mu\text{M}$ ) in water and after the addition of  $\text{Pd}^{4+}$  (200  $\mu\text{M}$ ) with a 0.5 cm pathlength.

**Theoretical details.** The plasmon-enhancement factor for a molecule in the vicinity of a metal nanoparticle is given by the matrix:

$$\hat{P} = \begin{pmatrix} P_x & 0 & 0 \\ 0 & P_y & 0 \\ 0 & 0 & P_z \end{pmatrix} = \begin{pmatrix} (1 - \frac{\beta}{R^3}) & 0 & 0 \\ 0 & (1 - \frac{\beta}{R^3}) & 0 \\ 0 & 0 & (1 + \frac{2\beta}{R^3}) \end{pmatrix},$$

where  $\beta = a_{NP}^3 \frac{\epsilon_{NP} - \epsilon_0}{(\epsilon_{NP} + 2\epsilon_0)}$  is the polarizability of nanoparticle. The system of coordinates is such that the center of molecular dipole is located at the z-axis coming through the metal nanoparticle center (Figure S6).



**Figure S7.** Model and geometry of a system comprising a chiral molecule and metal nanoparticle.

The full equation for the CD signal for a spherical nanoparticle is given by [S1]:

$$\begin{aligned}
CD_{molecule-NP} &= CD_{molecule} + CD_{NP}, \\
CD_{molecule} &= E_0^2 \frac{8}{3} \sqrt{\epsilon_0} \omega \cdot \frac{\Gamma_{12}}{\left| (\hbar\omega - \hbar\omega_0 + i\Gamma_{12} - G_\omega) \right|^2} \text{Im} \left[ (\hat{P} \cdot \vec{\mu}_{12}) \cdot \vec{m}_{21} \right], \\
CD_{NP} &= \frac{8E_0^2}{9} \left| \frac{3\epsilon_0}{\epsilon_{NP} + 2\epsilon_0} \right|^2 \frac{a_{NP}^3}{\sqrt{\epsilon_0} R^3} \omega \text{Im}[\epsilon_{NP}] \times \left( \text{Im} \left[ \frac{\mu_{12x} \cdot m_{21x} + \mu_{12y} \cdot m_{21y} - 2\mu_{12z} \cdot m_{21z}}{\hbar\omega - \hbar\omega_0 + i\Gamma_{12} - G_\omega} \right] \right), \\
\vec{m}_{21} &= -\frac{|e|}{2mc} \langle 2 | [\vec{r} \times \vec{p}] | 1 \rangle, \quad \vec{\mu}_{21} = -|e| \langle 2 | \vec{r} | 1 \rangle,
\end{aligned}$$

where  $E_0$  is the amplitude of incident electromagnetic wave. The function  $G_\omega$  describes the broadening of the molecular resonance in the presence of a metal nanoparticle [S1]. The coefficient  $A$  used in the main text is

$$A = \frac{8E_0^2}{9}.$$

Extinctions in the standard units ( $cm^{-1} \cdot M^{-1}$ ) can be calculated from the above equations:

$$\Delta\epsilon_{CD} = \Delta\epsilon_{CD,molecule} + \Delta\epsilon_{CD,NP} = \frac{2\pi}{c_0 \sqrt{\epsilon_0} E_0^2} \frac{N_A \cdot 10^{-4}}{0.23} (CD_{molecule} + CD_{NP}),$$

where the CD absorption rates ( $CD_{molecule}$  and  $CD_{NP}$ ) are now in the cgs units. In our calculations (Fig. 5 in the main text), we used typical parameters for the matrix elements  $\mu_{12}$  and  $m_{21}$ , resulting in a typical magnitude of molecular CD in the UV range. We also considered a particular case when an electric dipole moment of a molecule is normal to the nanoparticle surface.

[S1] Govorov, A. O.; Fan, Z.; Hernandez, P.; Slocik, J. M.; Naik, R. R. Nano Lett. 2010, 10, 1374-1382.