**Electronic Supplementary Information**

**Gold Nanoparticle Self-Assembly Promoted by a Non-Covalent, Charge-Complemented Coiled-Coil Peptide**

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**Peptide Synthesis:** The peptides were synthesized by standard fluorenyl-methoxycarbonyl (Fmoc) solid-phase chemistry with the coupling reagent HBTU with DIEA on H-Rink Amide Chem Matrix resin (0.52 mmol/g). Peptides were cleaved from the resin using a mixture of TFA, thioanisole, ethanedithiol, and anisole (9:0.5:0.3:0.2 v/v) for 3 hours at room temperature. After filtration, TFA was removed in vacuo, peptides were cold ether precipitated, and purified to homogeneity by semipreparative RP-HPLC Phenomenex C-5 column (Solvent A: acetonitrile/0.1 % TFA, Solvent B: water/0.1 % TFA) 30-50 % A for GCN4-E, 30-45 % A for GCN4-X, and 25-65 % A for GCN4-p1). Purified peptides were analyzed by analytical RP-HPLC, MALDI-TOF mass spectrometry, and amino acid analysis.

<table>
<thead>
<tr>
<th>Peptide</th>
<th>RT</th>
<th>Mass Calculated</th>
<th>Mass obtained(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCN4-E:</td>
<td>35.4(a)</td>
<td>3653</td>
<td>3651</td>
</tr>
<tr>
<td>GCN4-X:</td>
<td>21.4(b)</td>
<td>3653</td>
<td>3653</td>
</tr>
<tr>
<td>GCN4-p1:</td>
<td>29.2(c)</td>
<td>3723</td>
<td>3723</td>
</tr>
</tbody>
</table>

\(a\) 30-50 % Solvent A, \(b\) 30-45 % Solvent A, \(c\) 25-65 % Solvent A, \(d\) MALDI-TOF mass spectrometry

**Amino Acid Analysis:**

**GCN4-E**

Asx (1), 1.2; Glx (11), 11.3; Gly (1), 1.1; His (1), 0.9; Ala (3), 3.0; Tyr (1), 1.0; Val (3), 2.9; Met (1), 0.8; Lys (3), 2.9; Leu (6), 5.6

**GCN4-X**

Asx (1), 0.9; Glx (11), 11.6; Gly (1), 1.1; His (1), 1.0; Ala (3), 2.9; Tyr (1), 1.2; Val (3), 3.0; Met (1), 0.9; Lys (3), 2.7; Leu (6), 5.5

**GCN4-p1**

Asx (3), 3.1; Ser (1) 1.0; Glx (7), 7.0; Gly (1), 1.0; His (1), 1.0; Arg (1), 1.1; Ala (1), 1.0; Tyr (1), 1.1; Val (3), 3.0; Met (1), 0.5; Lys (5), 4.8; Leu (6), 5.9

**Gold Nanoparticle Fabrication:**

**Synthesis of 2 nm core GNPs:** Cationic GNPs (2 nm core) were prepared according to literature procedure.1

**Synthesis of 6 nm core GNPs:** 1-Octanethiol-protected gold nanoparticles (GNP-C₈, 6 nm core) were synthesized using our previously reported procedure.2 GNP-C₈ was functionalized with the TTMA ligand (Figure 2c in manuscript) via place exchange reaction. Briefly, 30 mg of GNP-C₈ in toluene (15 mL) was mixed with 90 mg of ligand in dichloromethane (15 mL). After 30 min of purging with argon, the reaction was continued for 2 days. Functionalized nanoparticles precipitated from solution and were purified from free ligand by washing with dichloromethane (5 x 30 mL), followed by dialysis (10,000 MWCO) with water.

**CD spectroscopy:** Peptide CD spectra were recorded on a J-810 spectrophotometer (Jasco) using a 1 mm quartz cuvette at room temperature in 10 mM phosphate buffer (pH 3.4 or pH 7.4). Increasing amounts of gold nanoparticles (2 nm core-2, 4, 6, 8 μM) were added to the peptides.
(15 μM) in 150 μL. Measurements were scanned from 190-260 nm with a 1 nm bandwidth, 1 s response and 0.5 nm data pitch. Each spectrum was an average of three scans and converted to molar ellipticities (deg cm$^2$ dmol$^{-1}$). The Job titration was performed by maintaining the total peptide and gold nanoparticle concentration at 20 μM, while varying the individual concentrations. 2 nm core gold particles were used for all CD experiments due to high absorbance of the 6 nm core gold nanoparticle’s in solution.

**UV/Vis Spectroscopy:** UV-vis spectra were recorded on Cary 300 Bio spectrophotometer in a 1 cm quartz cuvette over a 250-800 nm range. Scans were taken within 5 min after adding gold nanoparticles (6 nm core-0.1 μM) to peptides (0.3, 1, 1.5, 2.5 μM) in 10 mM phosphate buffer at pH 7.4 in 1 mL.

**Dynamic Light Scattering:** Size distributions of peptide/gold nanoparticle suspensions were recorded on a Protein Solutions Dyna Pro 99 instrument with a 1.5 mm quartz cuvette at 20°C. The stock solutions were filtered (0.45 μm pore size) and then incubated for 45 min before readings were taken of various gold nanoparticle (6 nm core-0.1 μM) to peptide (0.3, 1, 1.5, 2.5 μM) ratios in 10 mM phosphate buffer pH 7.4 in 25 μL. An average of three measurements was recorded. For the dissociation with NaCl, a 1:15 ratio of GNPs (6 nm core-0.05 μM) with GCN4-E (0.75 μM) in 5 mM phosphate buffer pH 7.4 in 25 μL was incubated for 45 min, which was followed by increasing the amounts of NaCl solution (20, 35.7, 50, 70, 100 mM) which was read after 5 min inhibition.

**Transmission Electron Microscopy:** Samples were prepared at room temperature by mixing a 1:15 ratio of gold nanoparticles (6 nm core-0.1 μM) and peptide (1.5 μM) in 10 mM phosphate buffer at pH 7.4 for 30-90 min. Final samples volume was 20 μL. Samples were placed on a 400 mesh formvar/carbon-coated copper grid for 3 min before blotting with filter paper. Samples were imaged using a Philips CM-100 TEM operated at 100 kv accelerating voltage. Images were captured on Kodak SO-163 electron image film. For the time course experiments, samples were prepared as described above except with gold nanoparticles (6 nm core-0.1 μM) and GCN4-E (1.5 μM) in 5 mM phosphate buffer at pH 7.4 in a final volume of 25 μL. Then, 2 μL were removed from the solution after 5, 30, 60, and 90 min incubation and placed on the grid for 3 min before blotting with filter paper.

**Small Angle X-ray Scattering:** SAXS experiments were performed on a formvar film. Samples consisted of gold nanoparticles (6 nm core-0.1 μM) with GCN4-E (1.5 μM) in 10 mM phosphate buffer at pH 7.4 in 400 μL total volume. Samples were applied to a SAXS film and allowed to assemble over 24 hours.

Figure S1. Circular Dichroism studies with increasing concentration of cationic GNP’s (2 nm core-2, 4, 6, and 8 μM) with GCN4-E and GCN4-X (15 μM) in 10 mM phosphate buffer at pH 7.4.

Figure S2. Enlarged TEM image of 6 nm core cationic GNPs alone.
Figure S3. Enlarged TEM image of 6 nm core cationic GNPs with added GCN4-E (1:15 ratio of GNPs to peptide with 90 minute incubation).
Figure S4. Enlarged TEM image of the zoomed in boxed region of the monolayer in Figure 4b. 6 nm core cationic GNPs with added GCN4-E (1:15 ratio of GNPs to peptide with 90 minute incubation).
Figure S5. Enlarged TEM image of 6 nm core cationic GNPs with added GCN4-X (1:15 ratio of GNPs to peptide with 90 minute incubation).
**Figure S6.** Enlarged TEM image of 6 nm core cationic GNP5s with added GCN4-p1 (1:15 ratio of GNP5s to peptide with 90 minute incubation).

**Figure S7.** SAXS profile for 6 nm core cationic GNP5s (0.1 μM) gave a q value of 0.8 nm⁻¹ (interparticle distance of 7.85 nm) and with the addition of GCN4-E (1.5 μM) in 10 mM phosphate buffer pH 7.4 gave a q value of 0.69 nm⁻¹ (interparticle distance of 9.10 nm). Interparticle distance was determined by using the following equation 2*3.14/q.
Figure S8. Monitoring the dissociation of the GNP-peptide complex with increasing concentrations of NaCl (10, 25, 50 mM) by DLS.
Figure S9. Enlarged TEM image of 6 nm core cationic GNPs with GCN4-E assembly (1:15 ratio of GNPs to peptide) for 5 minute incubation.
**Figure S10.** Enlarged TEM image of 6 nm core cationic GNPs with GCN4-E assembly (1:15 ratio of GNPs to peptide) for 30 minute incubation.
Figure S11. Enlarged TEM image of 6 nm core cationic GNPs with GCN4-E assembly (1:15 ratio of GNPs to peptide) for 60 minute incubation.
Figure S12. Enlarged TEM image of 6 nm core cationic GNPs with GCN4-E assembly (1:15 ratio of GNPs to peptide) for 90 minute incubation.