

Supplementary information

Binding and templation of nanoparticle receptors to peptide α -helices through surface recognition

Partha S. Ghosh, Ayush Verma and Vincent M. Rotello*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003, USA.; Tel: (+1) 413-545-2058; E-mail: rotello@chem.umass.edu.

General: All the reagents were purchased from Aldrich and used as received. All the recognition experiments were carried out in miliQ water of pH 11. Concentrations of the peptide and particle stock solutions were measured by UV.

Synthesis of ligands: Both the thiol ligands, teghydroxy (TOH) and tegtrimethyl ammonium (TTMA), were synthesized according to the literature procedure.^{1,2}

Synthesis of MMPC 1 - 3: 1-pentanethiol-capped gold nanoparticles were dissolved in dichloromethane (DCM) and the ligands were dissolved in DCM alone (for MMPC **1**) or 1:1 DCM-methanol mixture (for MMPC **2** and **3**). Both the solutions of particles and ligands were purged with argon separately for 30 min. Then two solutions were admixed and stirred at room temperature for ~ 48 h. MMPC **1** was precipitated out from the solution, while MMPC **2** and **3** remain in solution. In order to remove free ligands, MMPC **1** was washed five times with DCM by centrifugation, and MMPC **2** and **3** were dialyzed in distilled water for a day. The particles were dried and dissolved in D₂O to acquire NMR spectra. The percentage of cationic charge was calculated by NMR end group analysis.

Synthesis of peptide: The tetraaspartate peptide, **TAP**, was synthesized using the Fmoc chemistry-based solid-phase peptide synthesis technique. The crude peptide was purified by reverse-phase HPLC, and subsequently characterized by ESI mass spectrometry (M.W. = 1672.6).

Circular dichroism: 15 μ M of peptide with various concentrations of nanoparticles were taken in a quartz cuvette with a 1-mm path length and placed on a Jasco 720 spectrophotometer. After 5 min of equilibration at 23 °C, CD spectra were acquired by scanning from 250 nm to 190 nm. Average of five scans was recorded at a rate of 20 nm/min with interval of 0.1 nm and 8 sec response. The final spectra were obtained by subtracting the blank one and it was fitted into secondary structure algorithm CDSSTR (protein ref. set 7 comprising of 49 proteins) using DICHROWEB (<http://www.cryst.bbk.ac.uk/cdweb/html/home.html>). Neutral (TEG-OH) nanoparticle was used for the control experiment.

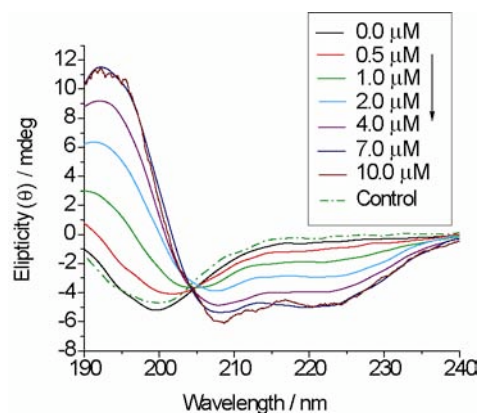


Fig. S1 CD spectra of 15 μM peptide solution with several concentrations of MMPC **1**.

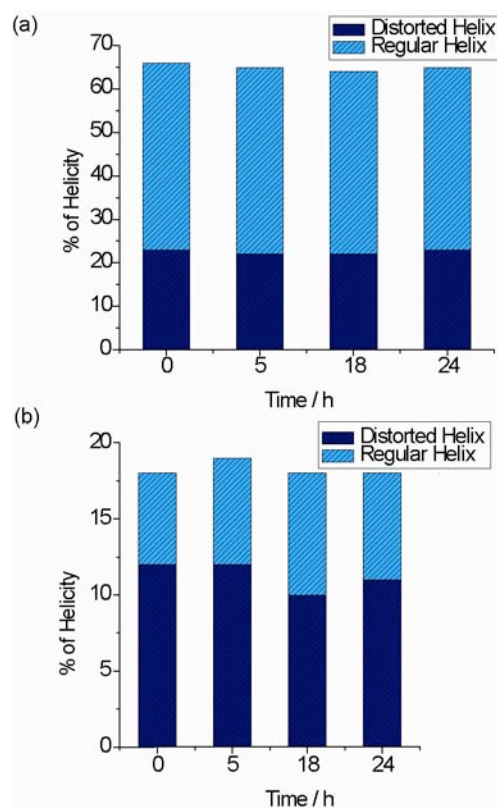


Fig. S2 Calculated overall helicity of the peptide (15 μM) at different time interval on incubation with (a) MMPC **1** and (b) MMPC **3**.

Fluorescence experiments: Fluorescence spectra were measured in a 1 cm quartz cuvette on a Shimadzu RF-5301 PC spectrofluorophotometer at 30 °C. Trp fluorescence was monitored at 355 nm wavelength by exciting at 295 nm. 2 μM of peptide solution was titrated with MMPC **1** – **3** in miliQ water of pH 11. The quenching of Trp fluorescence by neutral MMPC **4** was measured to cancel the effect of absorption of nanoparticles. The corrected intensities were plotted against the nanoparticle

concentration and fitted into a nonlinear least-squares curve-fitting equation³ using Origin 7.0 program (OriginLab Co., Northampton, USA).

DLS study: The experiments were performed on a MALVERN Zetasizer Nano Zs instrument in water (pH = 11). The stock solutions of nanoparticle and peptide were filtered with 0.2 μm filter (Fisher Sci.). The average of three measurements was reported. The sizes of MMPC **1** and MMPC **1**-peptide adducts were determined to be 8.7 ± 0.4 nm and 8.4 ± 0.2 nm, respectively.

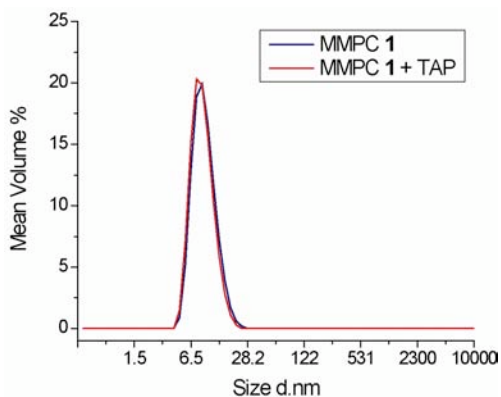


Fig. S3 Size distribution of MMPC **1** (1.0 μM) and MMPC **1**-peptide complex (1 μM MMPC **1** + 5 μM TAP) in water of pH 11.

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- 1 C. Palegrosdemange, E. S. Simon, K. L. Prime, G. M. Whitesides, *J. Am. Chem. Soc.*, 1991, **113**, 12.
 - 2 H. Bayraktar, P. S. Ghosh, V. M. Rotello, M. J. Knapp, *Chem. Commun.*, 2006, 1390.
 - 3 C. C. You, M. De, G. Han, V. M. Rotello, *J. Am. Chem. Soc.*, 2005, **127**, 12873.