

Materials Chemistry

Peptide Conjugates for Directing the Morphology and Assembly of 1D Nanoparticle Superstructures

Chen Zhang,^[a] Chengyi Song,^[a] H. Christopher Fry,^[b] and Nathaniel L. Rosi^{*[a]}

Abstract: Designed peptide conjugates molecules are used to direct the synthesis and assembly of gold nanoparticles into complex 1D nanoparticle superstructures with various morphologies. Four peptide conjugates, each based on the gold-binding peptide (AYSSGAPMPFF; PEP_{Au}), are prepared: C₁₂H₂₃O-AYSSGAPMPPP (1), C₁₂H₂₃O-AYSSGAPMPPF (2), C₁₂H₂₃O-AYSSGAPMPFF (3), and C₁₂H₂₃O-AYSSGAPMPFFF (4). The effect that C-terminal hydrophobic F residues have on both the soft-assembly of the peptide conjugates and the resulting assembly of gold nanoparticle superstructures is examined. It is shown that the addition of two C-terminal F residues (3) leads to thick, branched 1D gold nanoparticle superstructures, whereas the addition of three C-terminal F residues (4) leads to bundling of thin 1D nanoparticle superstructures.

Inorganic nanoparticles are important structural and functional building blocks for the assembly of new advanced materials.^[1] Any given material may have a hierarchy of structural and functional domains, including, for example, nanoparticles, nanoparticle superstructures, and finally assemblies of nanoparticle superstructures. Controlling each level of this hierarchy is essential for controlling material properties and, ultimately, application. Numerous methods exist for preparing discrete nanoparticles of various size, shape, and composition,^[1a–e] and the number of viable methods for carefully assembling nanoparticles into nanoparticle superstructures is rapidly growing.^[1f–k] Ideally, nanoparticle assembly methods should permit control over each level of a material's structural hierarchy: 1) the size, shape, and composition of the nanoparticle building blocks, 2) the metrics and morphology of the nanoparticle superstructure, and 3) the co-assembly of the nanoparticle superstructures into larger-scale structures. In this Communication, we present assembly methods that address 1–3)

in the context of constructing and assembling 1D gold nanoparticle superstructures.

We have developed synthetic methods that utilize peptide conjugate molecules to direct the simultaneous synthesis and assembly of inorganic nanoparticles.^[2] The peptide conjugates consist of a peptide containing a particular sequence of amino acids for binding to a specific inorganic surface^[1f,3] and a particular organic moiety attached to the peptide N-terminus that influences peptide assembly. We demonstrated that such peptide conjugates can be used to prepare a diverse collection of complex nanoparticle assemblies containing well-defined structures with tailorable shapes, metrics, and properties.^[2] One can make numerous modifications to the peptide conjugate molecule (Scheme 1) that may affect its assembly. Much



Scheme 1. Illustration of a peptide conjugate detailing the different potential regions for modification: R = organic tail; X_m and Y_n = additional amino acids; PEP_{Au} = AYSSGAPMPFF.

of our work has focused on modifying the N-terminus with various aliphatic carbon chains or π -conjugated molecules (R in Scheme 1).^[2a,c–e,g] One can also modify the peptide sequence, provided that these modifications do not alter the peptide's inorganic recognition sequence and therefore its inorganic binding capabilities. Along these lines, we have introduced alanine residues to the N-terminus (X_m in Scheme 1) of a gold-binding peptide (PEP_{Au} = AYSSGAPMPFF)^[4] and shown how these additional amino acids influence peptide conjugate assembly and ultimately nanoparticle superstructure assembly.^[2c,e] When such conjugates are allowed to assemble in aqueous conditions, the hydrophobic organic molecule and the amino acids at the N-terminus are expected to locate in the core of the peptide assembly while the bulk of the peptide and its C-terminus are expected to locate on the surface of the assembly, exposed to the aqueous buffer solution.^[5] Based on this assembly paradigm, we predict that modifications to the C-terminus (Y_n in Scheme 1) should significantly affect conjugate assembly and possibly lead to new nanoparticle superstructures.

In our first studies in this area, we demonstrated that C₁₂-PEP_{Au} (PEP_{Au} containing a C₁₂ chain attached to its N-terminus; C₁₂ = C₁₂H₂₃O) assembles into 1D twisted fibers and directs the synthesis and assembly of left-handed gold nanoparticle double-helical superstructures.^[2a] We recently reported that these helical superstructures exhibit plasmonic circular dichro-

[a] C. Zhang, Dr. C. Song, Prof. N. L. Rosi
Department of Chemistry, University of Pittsburgh
219 Parkman Avenue, Pittsburgh, Pennsylvania 15260 (USA)
Fax: (+01)412-624-8611
E-mail: nrosi@pitt.edu

[b] Dr. H. C. Fry
Center for Nanoscale Materials, Argonne National Laboratory
9700 South Cass Avenue, Argonne, Illinois 60439 (USA)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201304074>.

ism properties,^[2f] which could ultimately be useful for the preparation of chiral metamaterials,^[6] provided that individual double helices could be aggregated together into an extended array. Our hypothesis in this work is that the addition of extra phenylalanine (F) residues to the C-terminus of C₁₂-PEP_{Au} could promote interfibril interactions in buffer that would lead to the formation of fiber bundles, which could in turn serve to direct the formation of thick linear nanoparticle superstructures or possibly even bundles of double-helical superstructures. Thus, the C-terminus might potentially be used as a handle for controlling the co-assembly of 1D nanoparticle superstructures into larger scale structures. We note that it is well-established that hydrophobic F residues can impact peptide assembly in aqueous conditions,^[7] and that F₂ alone, for example, assembles into nanotubular structures.^[8] However, it has not been demonstrated that hydrophobic F residues can direct the aggregation or bundling of linear nanoparticle superstructures. We explore this phenomenon for the first time in this report.

To explore our hypothesis, we designed the following series of peptide conjugate molecules: C₁₂-AYSSGAPPMP (1), C₁₂-AYSSGAPPMPF (2),^[2a] C₁₂-AYSSGAPPMPFF (3), and C₁₂-AYSSGAPPMPFFF (4). We first studied the assembly of these peptide conjugates in 0.1 M HEPES buffer (pH 7.3 ± 0.1; HEPES = 4-(2-hydroxyethyl)-piperazineethanesulfonic acid). We dissolved samples of conjugate 1–4 in HEPES to yield 150 μM peptide conjugate solutions, which were allowed to sit at room temperature for various specific time periods (30 min, 1, 3, and 7 days). After these time periods, we spotted TEM grids with samples from each solution, applied a phosphotungstic acid stain, and then imaged each sample by TEM to monitor the progress of assembly (Figure 1). Several general conclusions can be drawn from the microscopy data. First, after a short incubation period (30 min), no assembly is observed for conjugate 1, while conjugates 2 and 3 both assemble into spherical structures (diameter of 2 = 21.3 ± 3.4 nm, based on 100 counts; diameter of 3 = 21.0 ± 3.8 nm, based on 100 counts), and conjugate 4 assembles into 1D fibers (width = 6.5 ± 0.8 nm, based on 100 counts; see Figure S3 in the Supporting Information for distribution diagrams; note: all reported distributions are based on measurements from TEM images of multiple samples). With increasing time, conjugates 1–4 all form fibers. For each conjugate, we observe an increasing number of fibers with increased incubation time, and also with an increasing number of C-terminal F residues. Finally, we observed fiber bun-

dling for both conjugate 2 and 3 after longer incubation times in HEPES buffer. Significant bundling for conjugate 3 was first observed after one day, and many thick bundles (width = 35.7 ± 12.4 nm) were observed after one week, as observed by both TEM (Figure 1) and tapping-mode AFM studies (see Figure S4 in the Supporting Information). The AFM data reveal fiber bundles with a height of ~20 nm, which indicates that these bundles are intertwined fibers rather than thick flat sheets of individual fibers. Conjugate 2 required a longer incubation time to form bundles: significant fiber bundling was only observed after three days and after one week the bundling was not nearly as significant as conjugate 3. Conjugate 4, which contains three terminal F residues, forms fibers most rapidly, and some of these fibers bundle together; however, we observe fewer and thinner fiber bundles for 4 than 3. We reason that since conjugate 4 rapidly assembles into fibers, the fibers may precipitate from solution before having sufficient time to interact with each other during assembly to allow formation of large quantities of fiber bundles.

The peptide conjugate assembly studies detailed above were performed in the absence of gold salt, which is an integral component of our nanoparticle superstructure syntheses.^[2a–f] From previous studies by us and others, we know that Au³⁺ (as well as other multivalent cations, such as Ca²⁺) can significantly accelerate and affect peptide conjugate assembly.^[2a,9] It is known from these studies that the multivalent cations shield the negatively charged regions of the peptide, preventing interpeptide electrostatic repulsions and promoting conjugate assembly.^[9] In our system, once gold salts are added to solutions of peptide conjugates in HEPES, fiber growth rapidly occurs and gold nanoparticles form and assemble along

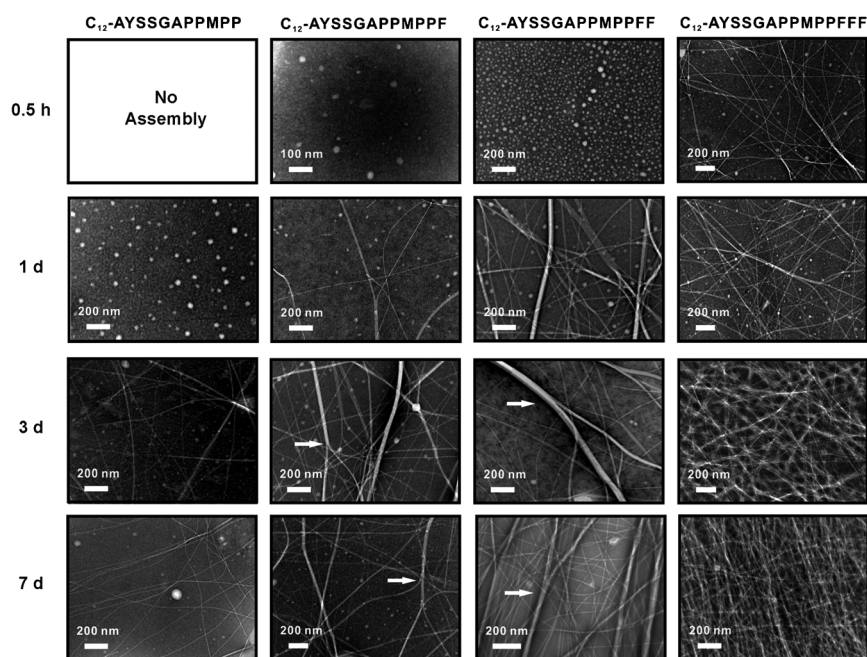


Figure 1. TEM images of soft assemblies prepared using peptide conjugates 1, 2, 3, or 4 in HEPES buffer at different time points (0.5 h, 1 d, 3 d, 7 d). White arrows indicate points where individual or thin fibers merge to form thick fiber bundles.

the fibers to yield gold nanoparticle superstructures, because HEPES can reduce Au^{3+} to Au^0 .^[4,10] The rapid formation of gold nanoparticle superstructures prevents careful observation of conjugate assembly. To study conjugate assembly under conditions that more accurately reflect the conditions used to prepare the gold nanoparticle superstructures, we investigated peptide conjugate assembly in the presence of calcium cations. Specifically, we added 0.1 M calcium chloride (1.5 μL , 0.15 μmol) to 150 μM solutions of conjugate 1–4 in 125 μL 0.1 M HEPES (Figure S5 in the Supporting Information). After incubating for 30 min at room temperature with added Ca^{2+} , conjugates 1–4 each formed fibers. The degree of fiber formation increased with an increasing number of C-terminal F residues and, again, some bundling was observed for conjugates 2 and 3, with conjugate 3 exhibiting much more significant bundling than 2. These results mirror what we observed after seven day incubation without Ca^{2+} , which suggests that increasing the ionic strength by adding Ca^{2+} accelerates the assembly process. We anticipated that assembly of conjugates 1–4 in the presence of Au^{3+} would be similar to their assembly in the presence of Ca^{2+} .

After having established that the addition of C-terminal F residues significantly affects fiber assembly and bundling, we next proceeded to explore the impact of these modifications on nanoparticle superstructure formation in the presence of gold salt. For these studies, we followed our established synthetic protocol.^[2a] Chloroauric acid solution (1.0 μL , 0.1 M HAuCl_4 in 1.0 M TEAA; TEAA = triethylammonium acetate) was added to a solution of peptide conjugate (1–4) in 0.1 M HEPES buffer. After incubating these solutions for one day at room temperature, the reaction products were imaged by using TEM (Figures 2, 3 and Figures S6–9 in the Supporting Information). Conjugate 1 yielded aggregates of 1D gold nanoparticle superstructures (Figures 2a, 3a, and Figure S6 in the Supporting Information, width: 24.1 ± 4.1 nm, based on 100 counts; nanoparticle diameter: 8.1 ± 1.3 nm, based on 100 counts), while conjugate 2 yielded well-defined gold nanoparticle double

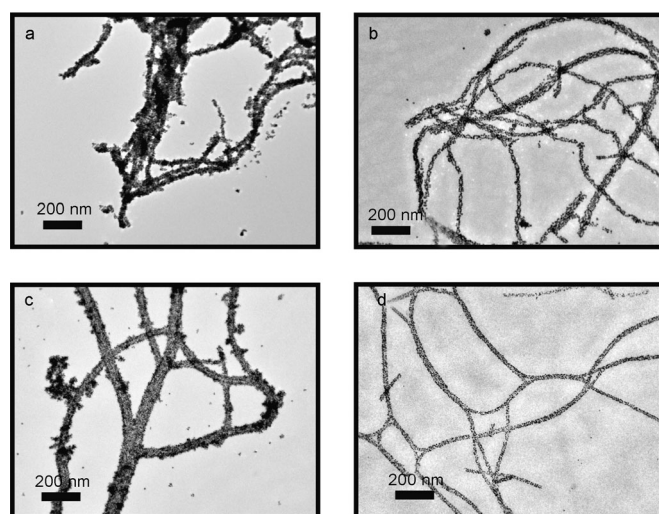


Figure 2. TEM images of nanoparticle superstructures formed using peptide conjugates 1 (a), 2 (b), 3 (c), and 4 (d).

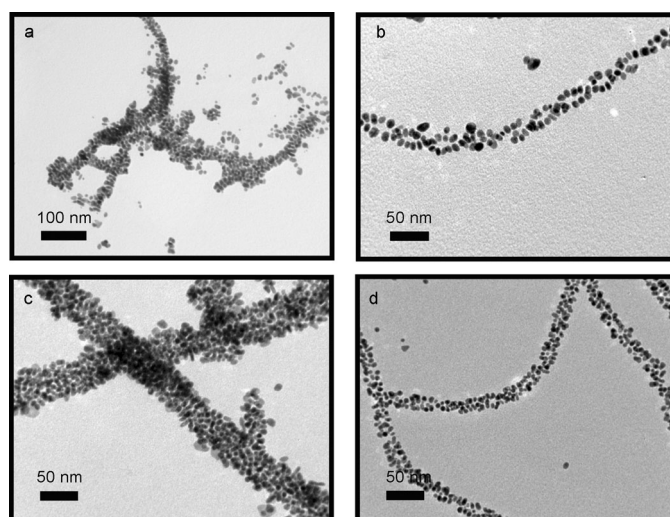
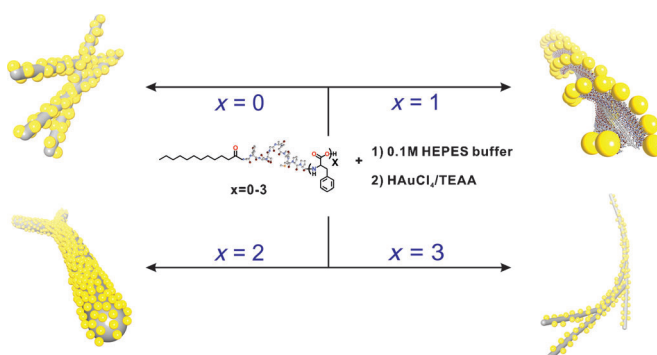


Figure 3. Magnified TEM images of nanoparticle superstructures formed using peptide conjugates 1 (a), 2 (b), 3 (c), and 4 (d).

helices, as previously reported (Figure 2b, 3b, and Figure S7 in the Supporting Information, width: 20.1 ± 1.8 nm, based on 100 counts; nanoparticle diameter: 7.3 ± 1.4 nm, based on 100 counts). Conjugate 3 yielded thick, branched 1D nanoparticle superstructures (Figure 2c, 3c and Figure S8 in the Supporting Information, width: 61.4 ± 15.7 nm, based on 100 counts; nanoparticle diameter: 6.3 ± 1.2 nm, based on 100 counts). Conjugate 4 resulted in thin intertwined 1D nanoparticle superstructures (Figure 2d, 3d, and Figure S9 in the Supporting Information, width: 20.5 ± 4.9 nm, based on 100 counts; nanoparticle diameter: 6.0 ± 1.1 nm, based on 100 counts). These results are illustrated and summarized in Scheme 2.

The results from these studies are generally consistent with our peptide conjugate assembly studies. Superstructures formed by using conjugate 1 are linear, yet very irregular (Figure 2a and Figure S6 in the Supporting Information). We note that in this case, the terminal F residue of PEP_{Au} has been deleted; this may negatively affect the formation of discrete nanoparticles and lead to irregular or aggregated nanoparti-



Scheme 2. The number of F_x residues ($x=0-3$) at the C-terminus of C_{12} -AYSSGAPPMPF $_x$ determines the structure of 1D gold nanoparticle superstructures. $x=0$: aggregated 1D structures; $x=1$: double helices; $x=2$: thick, branched 1D structures; $x=3$: thin, intertwined structures.

cles. In fact, previous studies have demonstrated that the terminal F residue of PEP_{Au} is important for binding to the Au surface.^[11] Conjugate **3** predominantly forms thick bundles of fibers, which leads to the formation of thicker 1D nanoparticle assemblies (Figure 2c and Figure S8 in the Supporting Information). In this case, we collected images of superstructure formation after 50 min of reaction (see Figure S10 in the Supporting Information). It is clear that multiple individual fibers bundle together to form thick fibers, and we can observe nanoparticle growth on these thick bundles. At this stage, it is unclear why the nanoparticles only decorate the fiber bundles rather than individual fibers; we are currently investigating the mechanism of superstructure formation using conjugate **3**, which may provide insight into this observation.

We observe some important similarities between the nanoparticle superstructure products of conjugate **2** and **4** (Figure 2b, d, and Figures S7 and S9 in the Supporting Information). Consistent with our previous studies,^[2a,b,f] conjugate **2** predominantly assembles into nonaggregated fibers, which lead ultimately to the formation of isolated double-helical nanoparticle assemblies as the major product and some bundled and intertwined double helices. Conjugate **4** forms a mixture of fibers and fiber bundles, which leads to the formation of some isolated yet a majority of intertwined 1D nanoparticle superstructures. The widths of these thin nanoparticle superstructures (**2**: 20.1 ± 1.8 nm; and **4**: 20.5 ± 4.9 nm) are consistent with having a single fiber (**2**: 6.7 ± 0.9 nm; and **4**: 6.5 ± 0.8 nm) decorated with nanoparticles (**2**: 7.3 ± 1.4 nm; and **4**: 6.0 ± 1.1 nm). The nanoparticle arrangement in the superstructures formed with conjugate **4** is difficult to discern, although we can identify some regions of the structure that appear to exhibit a helical arrangement of the nanoparticles (arrows in Figure S9, Supporting Information). Superstructures from conjugate **4** assemble together to form larger-scale structures with diameters ranging from ~20 to ~60 nm (see Figure S9 in the Supporting Information). These data indicate that the addition of F residues (in the case of conjugate **4**) provides a way to assemble helical nanoparticle assemblies into larger-scale structures.

To investigate whether C-terminal F residues are important for fiber formation and fiber bundling, we studied the assembly of $\text{C}_{12}\text{-PEP}_{\text{Au}}\text{-E}$ (**5**; $\text{C}_{12}\text{-AYSSGAPPMPPE}$). E, glutamic acid, is hydrophilic. Solutions of **5** ($150 \mu\text{M}$ in 0.1 M HEPES buffer) were allowed to stand for one week. Negatively stained TEM images of the assembly product revealed only spherical assemblies (see Figure S11 in the Supporting Information). In addition, only spherical assemblies were observed after 30 min incubation in the presence of Ca^{2+} (see Figure S12 in the Supporting Information). These data suggest that C-terminal hydrophobicity may be important for directing fiber formation and bundling.

In this study we investigated the impact that modifications to the C-terminus of $\text{C}_{12}\text{-PEP}_{\text{Au}}$ have on the soft assembly of peptide conjugates and the structure and assembly of 1D nanoparticle superstructures. We discovered that the addition of hydrophobic F residues can lead to fiber bundling that in turn leads to the formation of thick or intertwined 1D nanopar-

ticle superstructures. These results indicate that C-terminal modifications to peptide conjugates represent another category of synthetically addressable features that can be carefully tuned to impact the structure of nanoparticle superstructures and the co-assembly of these structures. Finally, these studies, when grouped with our previous studies on these systems,^[2] demonstrate that peptide conjugates are a highly tailorable class of molecules whose structures and compositions can be carefully programmed to direct the synthesis and assembly of a diverse array of complex hierarchical nanoparticle-based structures.

Experimental Section

Materials and methods

All solvents and chemicals were obtained from commercial sources and used without further purification. 0.1 M HEPES Buffer (HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) was made by directly diluting 1.0 M HEPES buffer (pH 7.3 ± 0.1 ; Fisher Scientific) with water (NANOpure, Barnstead DiamondTM System; 18.2 M Ω). Peptides with sequences of AYSSGAPPMP, AYSSGAPPMPPE, AYSSGAPPMPFF, and AYSSGAPPMPFFF were synthesized and purified by New England Peptide with final purity of 99%. AYSSGAPPMPPE was prepared by Argonne National Laboratory with final purity of 99%. Reverse-phase HPLC was performed at ambient temperature with an Agilent 1200 liquid chromatographic system equipped with diode array and multiple wavelength detectors using a Grace Vydac protein C4 column (214TP1010, 1.0 cm \times 25 cm). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an Applied Biosystem Voyager System 6174 MALDI-TOF mass spectrometer using α -cyano-4-hydroxy cinnamic acid (CHCA) as the matrix. TEM samples were prepared by pipetting one drop of solution onto a 3 mm-diameter copper grid coated with carbon film; 2% aqueous phosphotungstic acid was used for negative staining. TEM was conducted on either a JEOL 200CX instrument operated at 200 kV and equipped with a Gatan CCD image system or FEI Morgagni TEM operated at 80 kV and equipped with an AMT side mount CCD camera system. Samples for atomic force microscopy (AFM) were prepared on freshly peeled MICA substrates. Tapping-mode AFM was performed on a Veeco Dimension V SPM.

Preparation of *N*-hydroxyl-succinimide ester and peptide conjugates

***N*-Hydroxyl-succinimide ester:** Dodecanoic acid (696 mg, 6 mmol) and *N*-hydroxysuccinimide (725 mg, 6.3 mmol) were dissolved in dry ethyl acetate (30 mL) under an argon atmosphere. After addition of dicyclohexyl carbodiimide (DCC) (1341 mg, 6.5 mmol) at 0°C, the solution was stirred overnight at room temperature. The reaction mixture was processed by removing the precipitate by filtration. The solvent was removed under reduced pressure and the crystalline residue recrystallized from isopropanol (*i*PrOH) to yield the *N*-hydroxyl-succinimide ester (211 mg, 1 mmol, 17%).

Peptide conjugates: Peptide conjugates (**1–5**) were synthesized and purified by using established methods.^[2a] Briefly, for conjugate **1**, AYSSGAPPMP (1.20 mg, 8.80×10^{-7} mol) was dissolved in DMF (60 μL). After the addition of dodecanoic *N*-hydroxyl-succinimide ester (0.6 mg, 2.81×10^{-6} mol) in DMF (60 μL) and Et_3N (1 μL) under stirring, the solution was stirred at room temperature for 16 h. Pure peptide conjugate **1** was obtained by conducting reversed-

phase HPLC (see Figure S1 in the Supporting Information) eluting with a linear gradient of 0.05% formic acid in CH₃CN and 0.1% formic acid in water (5:95 to 95:5 over 30 min). The molecular weight for each peptide conjugate was confirmed by MALDI-TOF mass spectrometry (see Figure S2 in the Supporting Information). Concentration of the peptide was determined spectrophotometrically in water/acetonitrile (1:1) using the molar extinction coefficient of tyrosine (1280 M⁻¹ cm⁻¹) at 280 nm.

Note: Peptide conjugates **2**, **3**, **4**, and **5** were prepared, purified and characterized in a similar fashion.

Peptide conjugate soft assembly: Lyophilized peptide conjugate **1** (~3.74×10⁻⁸ mol) was completely dissolved in 0.1 M HEPES buffer (250 µL) in a plastic vial. The vial was capped and sealed with parafilm to prevent/minimize evaporation of solvent. The above solution was incubated at room temperature and negatively stained TEM samples were prepared at different time points (0.5 h, 1 d, 3 d, and 7 d).

Note: Soft assembly of peptide conjugates **2**, **3**, **4**, and **5** were studied in a similar fashion.

Preparation of gold nanoparticle superstructures: A gold ion precursor solution was prepared: 0.1 M chloroauric acid (HAuCl₄) in 1.0 M triethylammonium acetate (TEAA; pH 7.0) buffer was incubated for 10 min at room temperature. Thereafter, this mixture was centrifuged (10 min., 5 K rpm). Lyophilized peptide conjugate **1** (~3.74×10⁻⁸ mol) was completely dissolved in 0.1 M HEPES buffer (250 µL) in a plastic vial. After 30 min, 2 µL of the supernatant of the centrifuged gold ion precursor solution was added to the peptide conjugate solution. The mixture was vortexed for a few seconds and then left undisturbed at room temperature for one day and TEM samples were prepared.

Note: When peptide conjugates **2**, **3**, **4**, and **5** were used, similar reaction conditions were employed.

Acknowledgements

Support for this work was provided in part by the National Science Foundation (DMR-0954380, N.L.R.) and in part by the Air Force Office of Scientific Research (FA9550-11-1-0275, N.L.R.). A portion of the peptide synthesis was performed at the Center for Nanoscale Materials, a U. S. Department of Energy, Office of Science, and Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357. The authors thank the Peterson NCF, the MEMS Department and Department of Biological Sciences for provision of access to TEM.

Keywords: gold • nanoparticles • peptides • self-assembly • superstructures

- [1] a) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293–346; b) C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025–1102; c) M. B. Cortie, A. M. McDonagh, *Chem. Rev.* **2011**, *111*, 3713–3735; d) P. C. Ray, *Chem. Rev.* **2010**, *110*, 5332–5365; e) M. R. Buck, J. F. Bondi, R. E. Schaak, *Nat. Chem.* **2012**, *4*, 37–44; f) C.-L. Chen, N. L. Rosi, *Angew. Chem.* **2010**, *122*, 1968–1986; *Angew. Chem. Int. Ed.* **2010**, *49*, 1924–1942; g) M. R. Jones, K. D. Osberg, R. J. Macfarlane, M. R. Langille, C. A. Mirkin, *Chem. Rev.* **2011**, *111*, 3736–3827; h) Y. Ofir, B. Samanta, V. M. Rotello, *Chem. Soc. Rev.* **2008**, *37*, 1814–1825; i) N. A. Kotov, F. Stellacci, *Adv. Mater.* **2008**, *20*, 4221–4222; j) Z. Nie, A. Petukhova, E. Kumacheva, *Nat. Nanotechnol.* **2010**, *5*, 15–25; k) M. Rubio-Martínez, J. Puigmartí-Luis, I. Imaz, P. S. Dittrich, D. Maspoch, *Small* **2013**, DOI: 10.1002/sml.201301338.
- [2] a) C. L. Chen, P. Zhang, N. L. Rosi, *J. Am. Chem. Soc.* **2008**, *130*, 13555–13557; b) C. L. Chen, N. L. Rosi, *J. Am. Chem. Soc.* **2010**, *132*, 6902–6903; c) C. Song, G. Zhao, P. Zhang, N. L. Rosi, *J. Am. Chem. Soc.* **2010**, *132*, 14033–14035; d) L. Hwang, C.-L. Chen, N. L. Rosi, *Chem. Commun.* **2011**, *47*, 185–187; e) L. Hwang, G. Zhao, P. Zhang, N. L. Rosi, *Small* **2011**, *7*, 1939–1942; f) C. Song, M. G. Blaber, G. Zhao, P. Zhang, H. C. Fry, G. C. Schatz, N. L. Rosi, *Nano Lett.* **2013**, *13*, 3256–3261; g) C. Song, Y. Wang, N. L. Rosi, *Angew. Chem.* **2013**, *125*, 4085–4087; *Angew. Chem. Int. Ed.* **2013**, *52*, 3993–3995.
- [3] M. B. Dickerson, K. H. Sandhage, R. R. Naik, *Chem. Rev.* **2008**, *108*, 4935–4978.
- [4] J. M. Slocik, M. O. Stone, R. R. Naik, *Small* **2005**, *1*, 1048–1052.
- [5] a) J. D. Hartgerink, E. Beniash, S. I. Stupp, *Science* **2001**, *294*, 1684–1688; b) O. S. Lee, S. I. Stupp, G. C. Schatz, *J. Am. Chem. Soc.* **2011**, *133*, 3677–3683; c) H. C. Fry, J. M. Garcia, M. J. Medina, U. M. Ricoy, D. J. Gosztola, M. P. Nikiforov, L. C. Palmer, S. I. Stupp, *J. Am. Chem. Soc.* **2012**, *134*, 14646–14649; d) T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, *335*, 813–817; e) S. E. Paramonov, H. W. Jun, J. D. Hartgerink, *J. Am. Chem. Soc.* **2006**, *128*, 7291–7298.
- [6] a) C. M. Soukoulis, M. Wegener, *Nat. Photonics* **2011**, *5*, 523–530; b) J. B. Pendry, *Science* **2004**, *306*, 1353–1355.
- [7] a) S. Aravinda, N. Shamala, C. Das, A. Sriranjini, I. L. Karle, P. Balaram, *J. Am. Chem. Soc.* **2003**, *125*, 5308–5315; b) K. Kar, S. Ibrar, V. Nanda, T. M. Getz, S. P. Kunapuli, B. Brodsky, *Biochemistry* **2009**, *48*, 7959–7968.
- [8] M. Reches, E. Gazit, *Science* **2003**, *300*, 625–627.
- [9] a) J. C. Stendahl, M. S. Rao, M. O. Guler, S. I. Stupp, *Adv. Funct. Mater.* **2006**, *16*, 499–508; b) S. N. Dublin, V. P. Conticello, *J. Am. Chem. Soc.* **2008**, *130*, 49–51; c) R. I. Kühnle, H. G. Börner, *Angew. Chem.* **2011**, *123*, 4592–4595; *Angew. Chem. Int. Ed.* **2011**, *50*, 4499–4502.
- [10] J. Xie, J. Y. Lee, D. I. C. Wang, *Chem. Mater.* **2007**, *19*, 2823–2830.
- [11] a) H. Heinz, B. L. Farmer, R. B. Pandey, J. M. Slocik, S. S. Patnaik, R. Pachter, R. R. Naik, *J. Am. Chem. Soc.* **2009**, *131*, 9704–9714; b) J. Yu, M. L. Becker, G. A. Carri, *Small* **2010**, *6*, 2242–2245.

Received: October 17, 2013

Published online on December 16, 2013