Electron Transfer in Peptides: On the Formation of Silver Nanoparticles**

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Equipment

The peptides were synthesized on a Multisyntech Syro I according to general procedures of solid phase peptide synthesis via Fmoc-strategy. A Fmoc-L-Tyr(tBu)-Rinkamide MBHA or A Fmoc-L-Phe(tBu)-Rinkamide MBHA resin was used, received from Iris Biotech. The amino acids Fmoc-L-Pro-OH, Fmoc-Aib-OH, Fmoc-L-His(Trt)-OH and Fmoc-L-Ser(tBu)-OH were also received from Iris Biotech. All coupling reagents, further reagents and peptide grade solvents HCTU (Novabiochem), NEt3, acetic acid anhydride p.a., piperidine 99% (Acros), DIPEA, NMP, DMF, dichloromethane and diethyl ether (Iris Biotech) were used as received.

The laser experiment was performed with a XeCl-excimer laser (λ=308 nm and E=100-130 mJ). Laser flashes of 20 ns were shot at the sample (2.5 mM in aqueous solution under argon gas) and the UV-vis spectra were recorded after 80 ns.

The irradiation experiments were performed on a Thermo Oriel irradiation bank with an Osram Hg-lamp HBO® 500 W/2. The UV-vis spectra were recorded on a Perkin-Elmer UV-spectrometer Lambda40.

The powder diffractograms were recorded on a Stoe STADIP equipped with a Mythen 1K detector and Cu-λ (1.54056 Å), measurement was done in transmission mode.

The TEM images were taken from samples deposited on carbon coated TEM grids (Electron Microscopy Sciences, CF 300-Cu, Carbon Film on 300 Square Mesh Copper Grids). EDX-TEM analysis was performed with a JEOL-2010 transmission electron microscope equipped with an energy dispersive spectrometer system, operated at 300 kV. The maps, 267 x 275 pixels, were acquired with a beam size of 15 nm. Other TEM images were acquired with a FEI/Philips CM-100 Biotwin Transmission Electron Microscope, operated at 80 kV in bright field mode.

SLS analysis was performed on an ALV/DLS/SLS-5000F monomode fiber compact goniometer system with an ALV-5001 fast correlator. As light source a Coherent COMPASS 315M-100 Laser was employed operating at 532 nm (100 mW). For static light scattering analysis, angular-dependent measurements between 30 ° to 150 ° (steps of 10 °) were performed. The measurement times for each angle were 100 s with three repetitions to calculate the average scattering intensities as a function of the scattering angle. Guinier Plots were analyzed using the ALV-Stat software.
Figure S1. NMR titration of peptide Boc-L-His-L-Pro-Aib-L-Tyr-OMe with AgNO₃ in d₆-DMSO.

Figure S2. Laser flash photolysis of A) 2.5 mM peptide 1 in water, 1 to 186 shots, after 80 ns; B) 2.5 mM tyrosine in water, pH=10, 1 to 171 shots, after 80 ns.
**Figure S3.** Determination of the first order reaction kinetics: A) Formation of NP-3 at the isosbestic wavelength; B) Transformation NP-3 into NP-4 at the maximum of NP-4.

**Figure S4:** SLS measurements (Guinier plot) of the AgCl particles from Ag⁺-peptide 1 (72 μM) with A) 12 eq. NaCl, pH 8.5; B) 1 eq. NaCl, pH 12.5. The Guinier Plot in B) showed no linear correlation, necessary to calculate an average diameter, which is due to the polydispersity of the mixture.
Figure S5. Irradiation of the phenyl-peptide 2 (1.25 mM peptide, 0.33 eq. AgNO₃, 0.33 eq. NaCl, pH=8.5, 1 h).

Figure S6: Analytical TEM of Ag⁺-peptide 1 with 1 eq. NaCl (pH=12.5) after 30 s irradiation: A) transmission image with EDX scans for B) silver; C) chloride; D) oxygen. The maps, 267 x 275 pixels, were acquired with a beam size of 15 nm.
**Figure S7:** Powder X-ray diffractogram of the isolated particles derived after irradiation until isosbestic point of Ag⁺-peptide 2 with 1 eq. NaCl and 3 eq. tyrosine (pH=8.5).

**Figure S8:** SLS measurements (Guinier plot) of the particles formed by Ag⁺-peptide 1 without irradiation and after 30 s irradiation: A) $C_{1a} = 0.7$ mM, 1 eq. NaCl, pH=12.5; B) $C_{1a} = 75 \mu$M, 12 eq. NaCl, pH=8.5.