# Photoinduced Formation of Stable Ag-Nanoparticles from Ternary Ligand-DNA-$Ag^+$ Complexes

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## Electronic Supporting Information (ESI)

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## 1. Materials and methods

All reagents and solvents were obtained from commercial sources and used as received. Purified water with resistivity ≥ 18 MΩ $cm^{-1}$ was used for preparation of buffered solutions and for all measurements. HEPES buffer (10 mM, pH 7.5) was used for all experiments.

Compounds **1a** (as perchlorate salt) and **1b** (as tetrafluoroborate salt) were synthesized according to published procedures.[1] $AgClO_4$ (Aldrich) was used from a stock solution in water (0.10 M).

Electronic absorption spectra were recorded using a Varian Cary 100 Bio spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorometer. Circular dichroism spectra were measured with a Chirascan CD spectrometer (Applied Photophysics). Spectrophotometric measurements were performed in thermostated quartz sample cells of 10 mm pathlength at 20 ± 1°C. Irradiations were conducted with an Atlas Photonics LUMOS 43 diode light source.

The 1:1 stoichiometry and stability constant of the complex **1a**-$Ag^+$ was determined from the spectrophotometric titration data using the SPECFIT/32 program. The data of the spectrophotometric titrations were used to determine the binding constants $K_b$ from a Scatchard plots ($r/c$ vs. $c$; $r$ = ratio of bound ligand molecules per DNA, $c$ = concentration of unbound ligand) according to the model of McGhee and von Hippel.[2]

X-rax photoelectron spectroscopy (XPS). The surface elemental composition was obtained with a SSX-100 S-probe photoelectron spectrometer using Al Kα X-ray radiation of 200W. For XPS, the sample solutions were dried on gold coated glass slides and analyzed directly (no data shown) as well as after a UV-ozone treatment to reduce the amount of DNA masking the weak silver peaks.

All elements present were identified from survey spectra (0-1200eV) with energy resolution of 1.0 eV.[3] The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. The corresponding data processing was performed using CasaXPS processing software version 2.3.16 PR 1.6. The concentrations obtained are reported as the percentage of that particular atom species (atom-%) at the surface of the sample (< 7 nm depth). The energy resolution was reduced to 0.05eV for high resolution scans. The spectra were peak fitted using Casa XPS software, and all binding energies were referenced relative to the aliphatic hydrocarbon C1s signal calibrated at 285.9eV.

Scanning electron microscopy was done using a Zeiss Ultra55 Field Emission Scanning Electron Microscope (Zeiss, Oberkochen, Germany) at an acceleration voltage of 10 kV. The sample

[1] (*a*) A. Granzhan, H. Ihmels, *ARKIVOC,* 2007, ***viii,*** 136. (*b*) M. Tian, H. Ihmels, *Chem. Commun.* 2009*,* **46**, 3175.

[2] D. E. Graves, Drug-DNA Interactions, In *Methods in Molecular Biology, Vol. 95: DNA Topoisomerase Protocols: Volume II: Enzymology and Drugs,* (Ed.: N. Osheroff and M. A. Bjornsti), Totowa, NJ: Humana Press, 2001; 161–69.

[3] (*a*) L. Shang, Y. Wang, L. Huang, and S. Dong, *Langmuir*, 2007, **23,** 7738; (*b*) A. I. Boronin, S. V. Koscheev, K. T. Murzakhmetov, V. I. Avdeev, G. M. Zhidomirov, *Appl. Sur. Sci.*, 2000, **165**, 9.

solutions have been dried onto silicon wafers and imaged without any metal coating to prevent a broadening of the nanoparticles by the metal layer. The TEM mode of the same microscope has been used for transmission electron microscopy. The sample solution has been dried onto TEM grids that were imaged at an acceleration voltage of 15 kV.

AFM measurements were carried out on a Bioscope I operated on a NanoScope IV controller (Bruker/Veeco/Digital Instruments, Santa Barbara, California). The surface morphologies were scanned in tapping mode in air using Si probes AC160TS with a nominal spring constant of 40 N/m, resonance frequency of 300 kHz and tip radius of < 10 nm (Olympus, Tokyo, Japan). Images of 1–10 µm size were acquired with 512x512 pixels at a scan rate of 1 Hz and evaluated using SPIP software (Image Metrology, Horsholm, Denmark). For imaging the sample solutions containing additionally 2 mM $NiCl_2$ have been incubated on freshly cleaved mica for 10 min, rinsed with water and dried.

Prior to SEM, TEM and XPS studies the AgNP solutions were dialyzed against water for 24 h to remove buffer components, inorganic salts and photodegradation products of the ligand.

## 2. Synthesis of AgNP

A solution of the benzo[*b*]quinolizinium derivative **1a** ($c$ = 50 µM), $AgClO_4$ ($c$ = 0.1 mM) and ct DNA or plasmid DNA ($c$ = 120 µg/ml) in HEPES buffer (pH 7.5) was irradiated in a quartz cuvette (pathlength = 1 cm) at room temperature with $\lambda_{ex}$ = 420 nm. The AgNP formation was followed photometrically by means of the development of the surface plasmon band (SPB) at 401 nm (Figure S1).

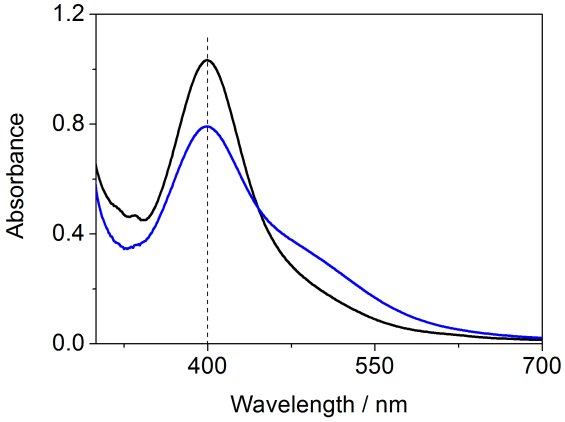



**Figure S1.** Absorption spectra of AgNP obtained by irradiation of **1a** and $Ag^+$ in the presence of ct DNA (black line) and plasmid DNA (blue line) under identical conditions: $c_{\mathbf{1a}}$ = 50 µM, $c_{Ag}$ = 0.1 mM, $c_{DNA}$ = 120 µg/ml, HEPES buffer (pH 7.5), $\lambda_{ex}$ = 420 nm), $t$ = 6.5 h.

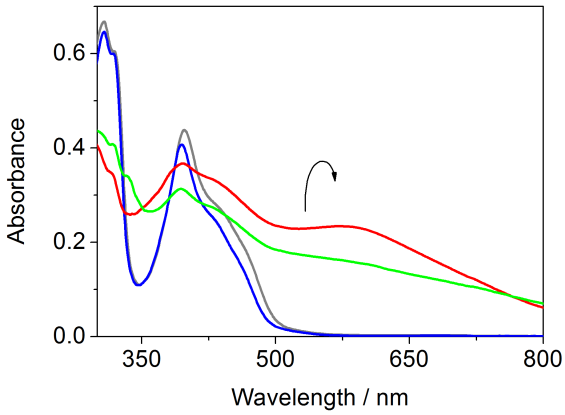



**Figure S2.** Absorption spectra of **1a** (gray), **1a**-$Ag^+$ ($c_{\mathbf{1a}}$ = 30 µM, $c_{Ag}$ = 0.1 mM) before (blue) and after irradiation with $t$ = 1 h (red) and $t$ = 3 h (green) in HEPES buffer (pH 7.5); $\lambda_{ex}$ = 420 nm.

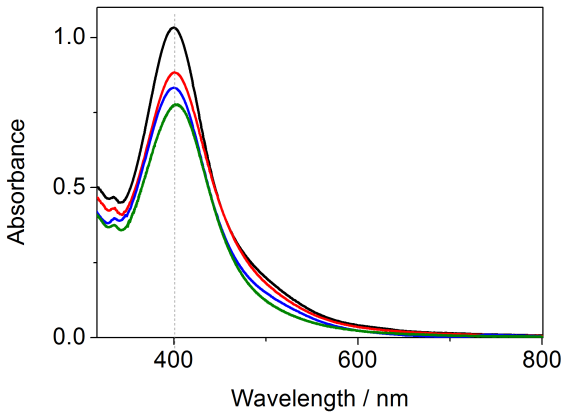



**Figure S3.** Absorption spectra of AgNP immediately after synthesis (black) and after storage in the dark at 4 °C for 6 d (red), 36 d (blue), and 9 months (green).

## 3. Microscopy studies

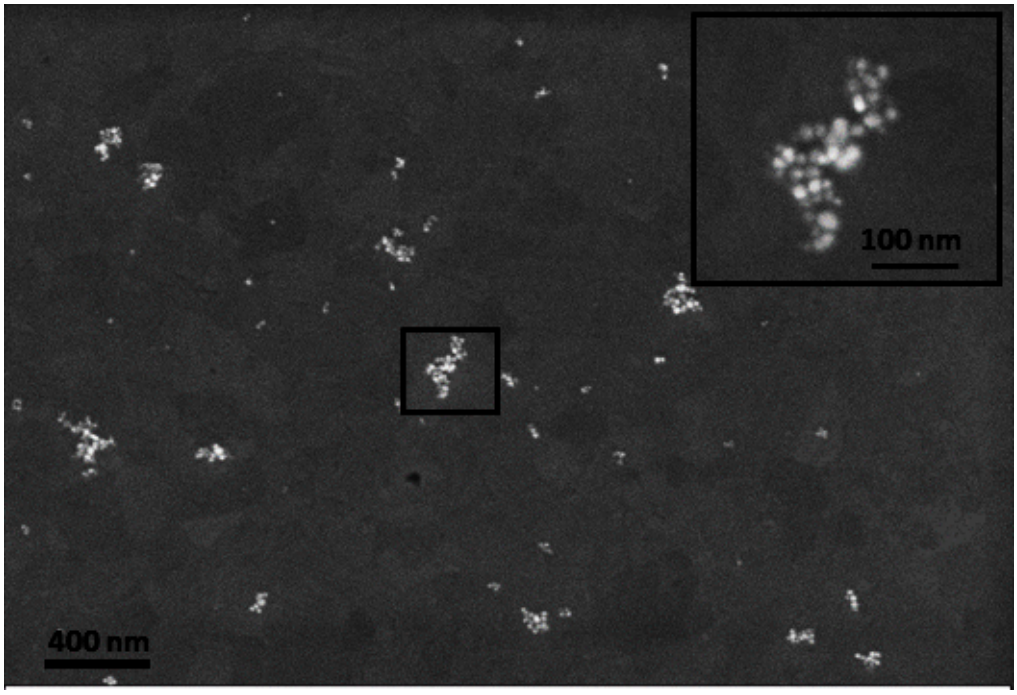



**Figure S4.** SEM images showing AgNPs that were prepared from irradiation of **1**, $Ag^+$ and plasmid pBR322 on template-stripped Au.

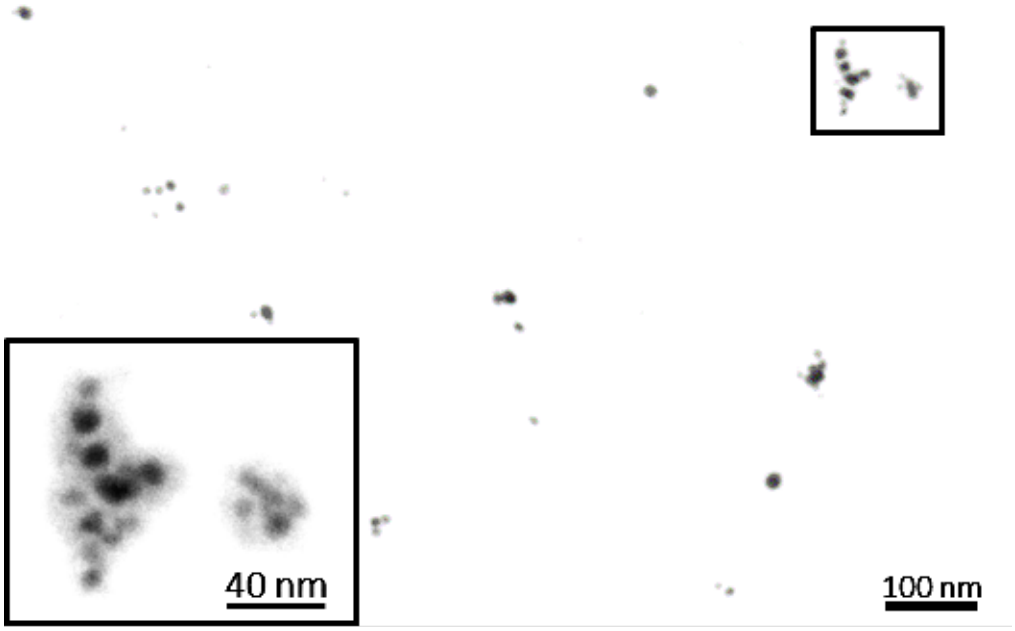



**Figure S5.** TEM images showing AgNPs that were prepared from irradiation of **1**, $Ag^+$ and ct DNA on a TEM grid. The AgNPs (dark contrast) can be differentiated from the rather thick corona comprising the ct DNA.

## 3. X-ray photoelectron spectroscopy (XPS) characterization

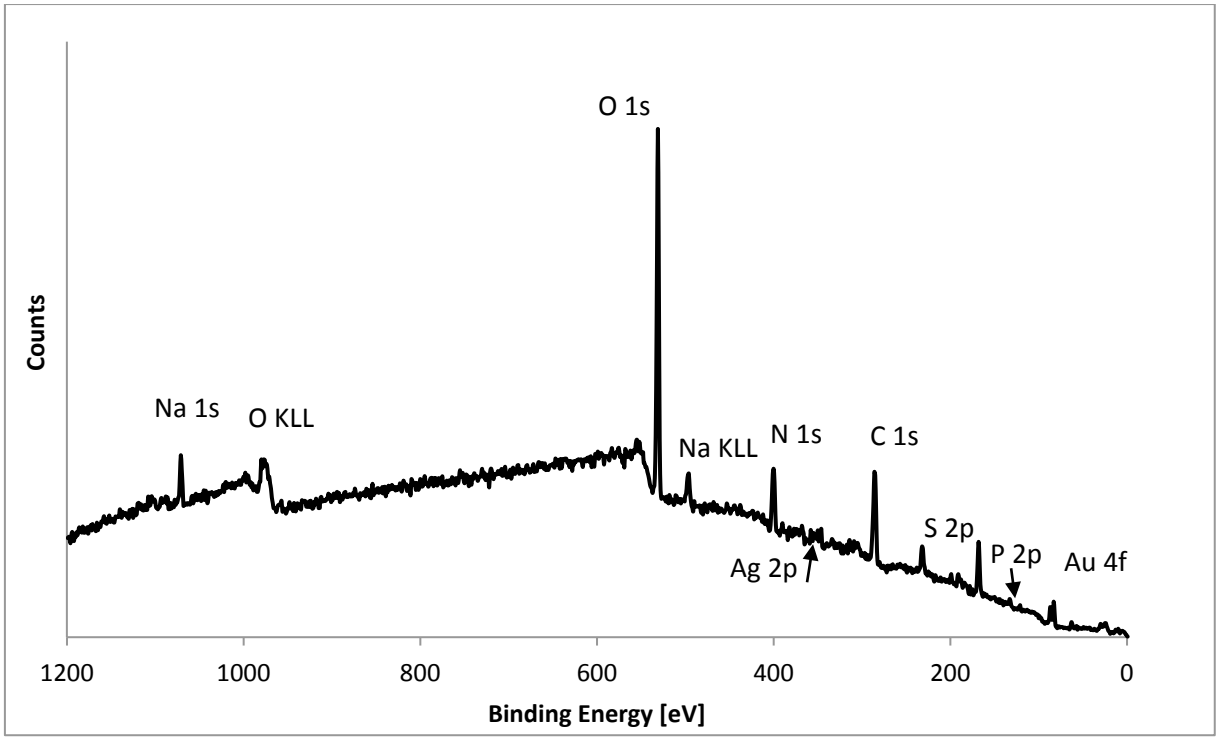
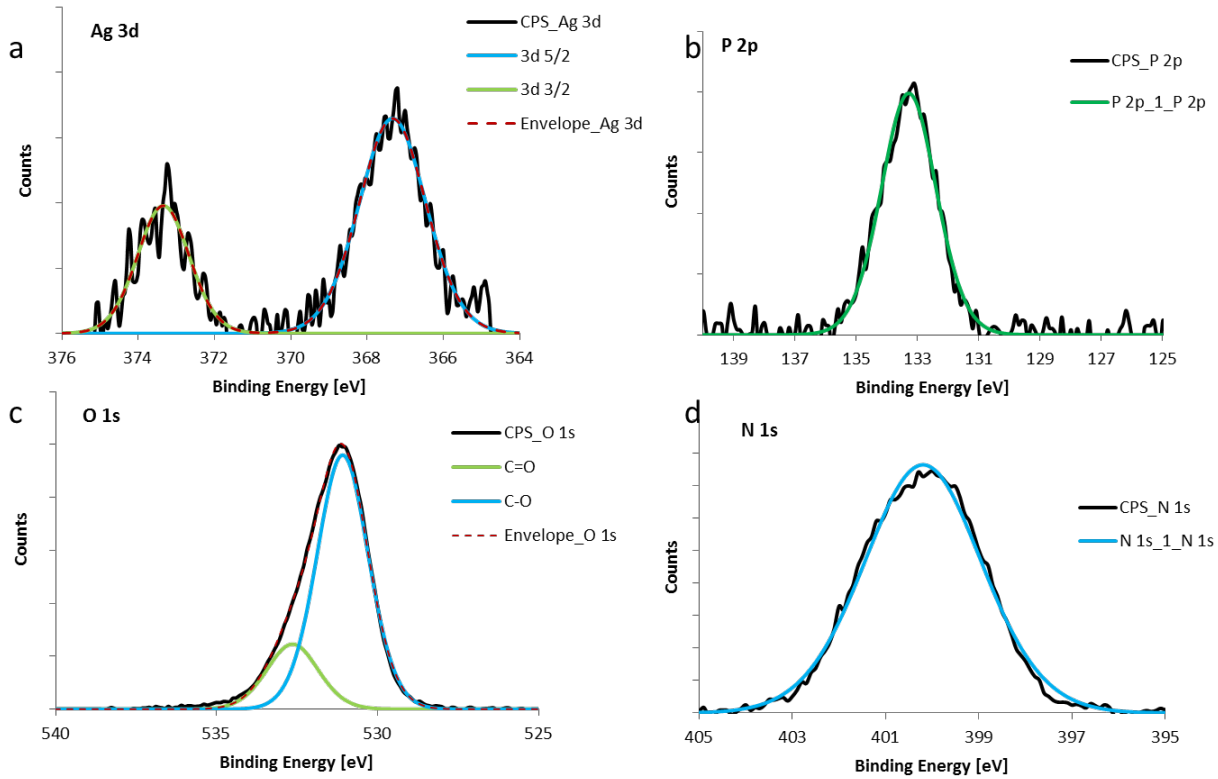



**Figure S6.** XPS survey scan of the AgNPs / ct DNA composite that was (*i*) dialyzed to remove salt from the buffer used (residual traces of Na and S originate from the buffer, the Au signal from the underlying substrate) and (*ii*) treated with UV-ozone to partially remove the thick ct DNA corona that prevented the detection of Ag signals from the deeply embedded AgNPs by XPS (cf. Figure S5). The presence of all expected elements of DNA plus the Ag fully confirms the interpretation of AgNP formation.

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| element | assignment | peak position | concentration atom-% |
|---|---|---|---|
| P | 2p | 133.29 | 1.53 |
| C | 1s, O-C=O | 288.67 | 3.52 |
| C | 1s, C-C aromatic | 284.47 | 14.7 |
| C | 1s, C-C aliphatic | 285.9 | 16.2 |
| C | 1s, C-O, C-N | 287.37 | 6.37 |
| C | 1s, π-satellite | 292.24 | 0.91 |
| Ag | 3d 5/2 | 367.34 | 0.10 |
| Ag | 3d 3/2 | 373.37 | 0.05 |
| N | 1s | 400.19 | 12.9 |
| O | 1s, C=O | 532.64 | 8.90 |
| O | 1s, C-O | 531.09 | 34.7 |

**Figure S7.** High resolution XPS element scans of UV ozone treated AgNPs / ct DNA (black lines) and corresponding fits (colored lines, see panels for legend) for: (a) Ag 3d, (b) P 2p, (c) O 1s, (d) N 1s, (e) C 1s, and (f) table with peak positions and concentrations.

## 5. Determination of the binding constant of the complex 1a-$Ag^+$

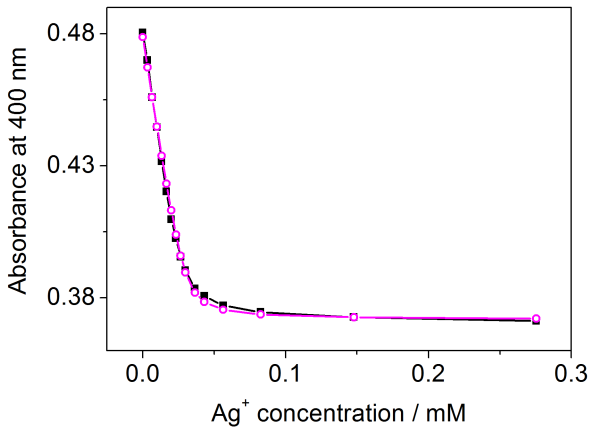


**Figure S8.** The titration curve for the complex **1a**-$Ag^+$ obtained from the spectrophotometric titration data using the SPECFIT/32 program: experimental curve (black), fitting curve (pink).