

Supporting Information.

# Long-pulse laser launch and ionization of tailored large neutral silver nanoparticles with atomic mass assignment

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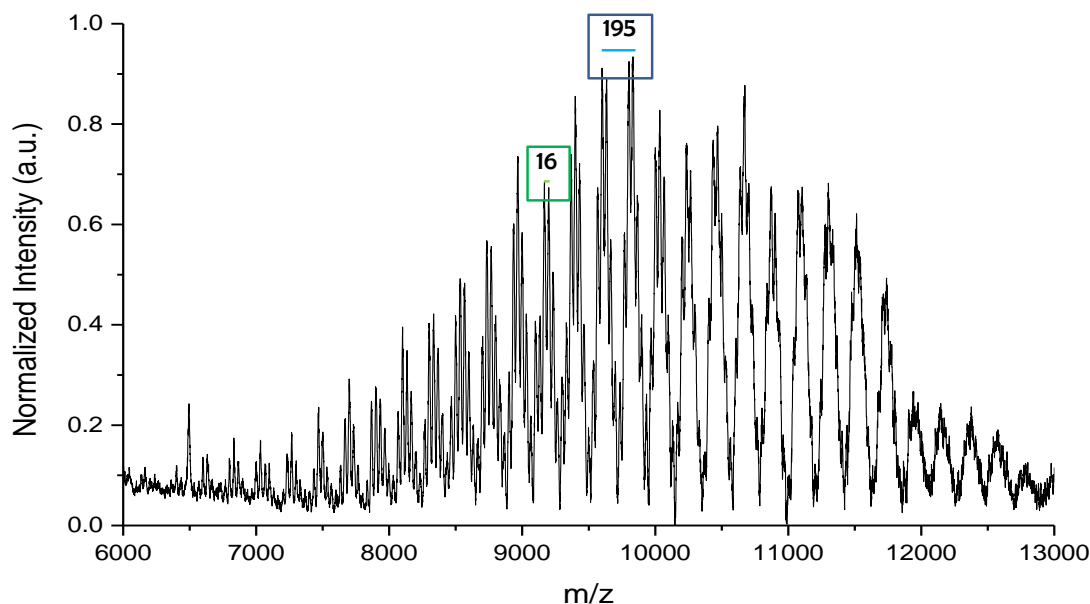
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## 1. Synthesis of the silver nanoparticles.

F<sub>9</sub>-AgNP1, F<sub>13</sub>-AgNP2, F<sub>17</sub>-AgNP3, H<sub>17</sub>-AgNP4 were synthesized by mixing AgNO<sub>3</sub> and two equivalents of the ligand (perfluorohexane-, octane- and decanethiol and octanethiol, respectively) in ethylene glycol at 160°C during 20 hours. Ethylene glycol acts here both as solvent and reducer. After purification via centrifugation-redispersion in methanol, tetrahydrofuran and diethyl ether, the particles were obtained as a yellowish-brown solid in case of the fluorinated particles and a dark brown solid in case of H<sub>17</sub>-AgNP4; with approximately 50 % yield based on thermogravimetric analysis (TGA).

## 2. Nanoparticle characterization.

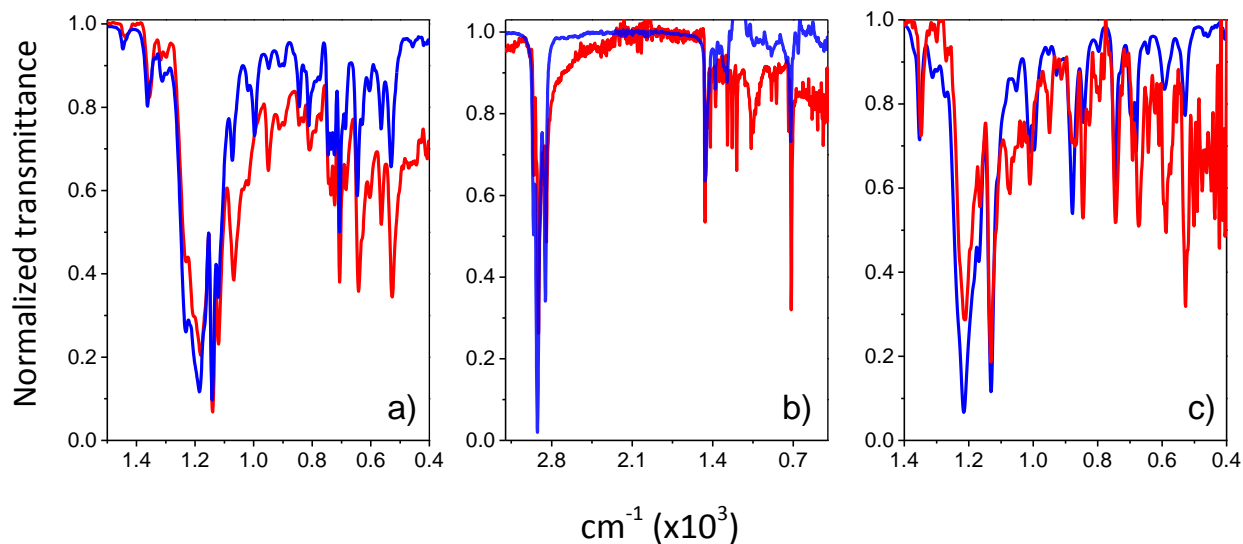
All synthesized particles (gold, platinum, silicon, silver and silver-sulfur) were characterized and analyzed by MALDI-ToF mass spectrometry. In most of the cases, low intense broad bands were detected due to fragmentations or aggregations of the particles under MALDI conditions. For platinum particles coated with 2-phenylethanethiol, a well-resolved spectrum could be obtained (Fig. S1). However, a detailed analysis revealed that C-O bond cleavage during MALDI and left only ligand-free platinum oxide clusters behind.



**Fig. S1:** MALDI-MS spectra of the platinum NPs stabilized with 2- phenylethanethiol with peak distances of 195 (blue) and 16 (green) Da, indicative of the carbon-oxygen cleavage under MALDI conditions.

## 2.1. Fourier transform - infrared spectroscopy

FT-IR characterizes the intramolecular bonds. We find only a small shift between the vibrational peaks of the free ligands in comparison to those bound to the silver nanoparticles even after chemical purification (Fig. S1). This is good indication for their binding to the nanoparticles.



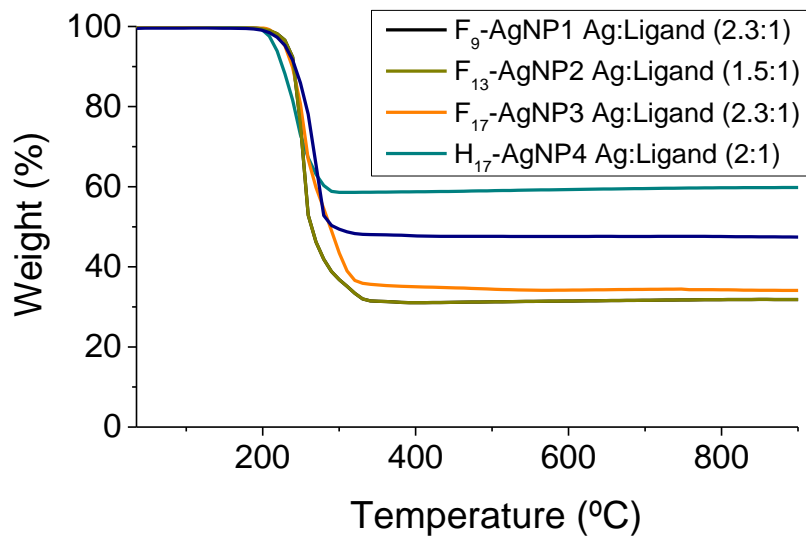
**Fig. S2:** Fourier-Transform infrared spectra of free ligands (blue lines) and the silver nanoparticles a) F<sub>9</sub>-AgNP1, b) F<sub>13</sub>-AgNP2 and c) H<sub>17</sub>-AgNP4 (red lines).

When the Brust-Schiffrin method is employed to synthesize the particles, the same FT-IR spectroscopy does not show any ligand bands, indicating the absence of ligands on the metal cores. Only the polyol method results in the desired ligand-capped nanoparticles.

## 2.2. Thermogravimetric analysis

TGA reveals a silver-ligand ratio of 2.3, 1.5, 2.3 for F<sub>9</sub>-AgNP1, F<sub>13</sub>-AgNP2 and F<sub>17</sub>-AgNP3 and a ratio of 2.0 for H<sub>17</sub>-AgNP4. It was performed by Annika Büttner on a Mettler Toledo TGA/SDTA851e. The samples were heated from 0 °C to 900 °C with a heating rate of 10 °C/minute. All samples show similar weight loss curves (Fig. S2). Decomposition starts at around 240 °C and reaches a plateau at 320 °C.

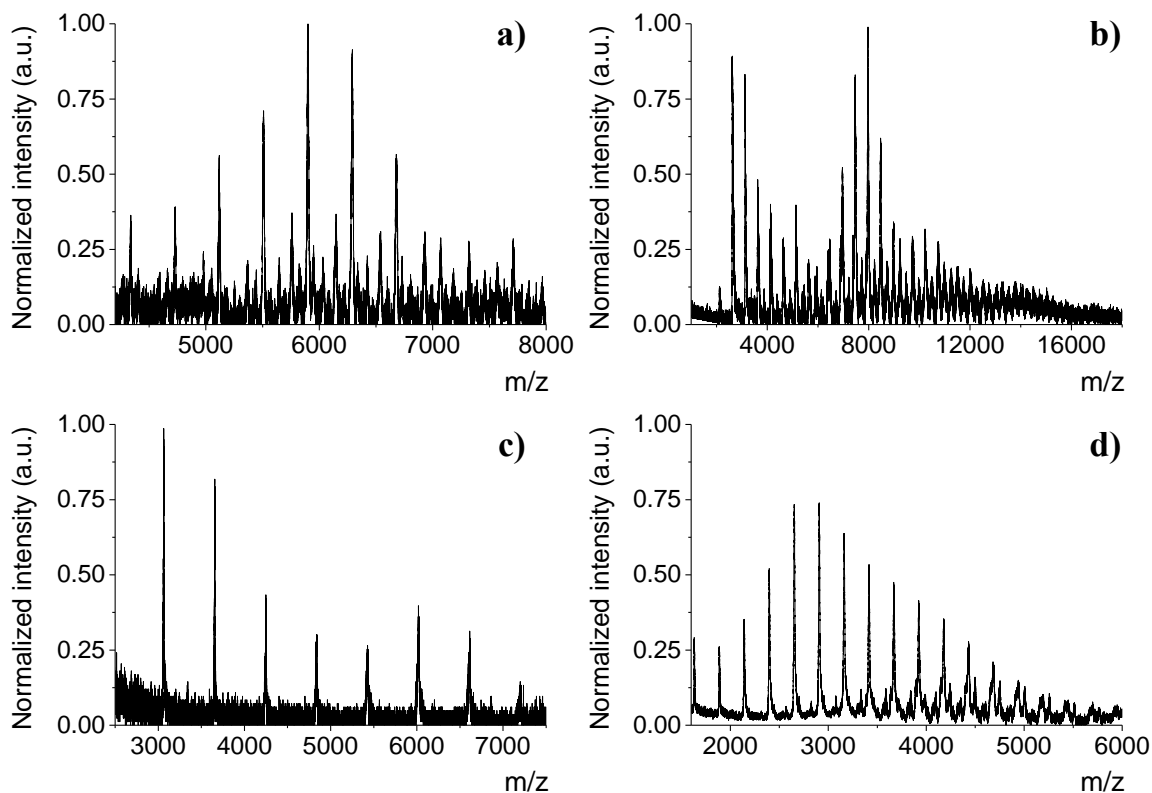
The weight loss is attributed to the decomposition and removal of the organic shell from the nanoparticle surface and the plateau is interpreted as the end of this process, when all the organic coating has been removed. The remaining substances are attributed to the residual silver.



**Fig. S3:** Thermogravimetric analysis of the silver nanoparticles.

### 2.3. MALDI ToF measurements.

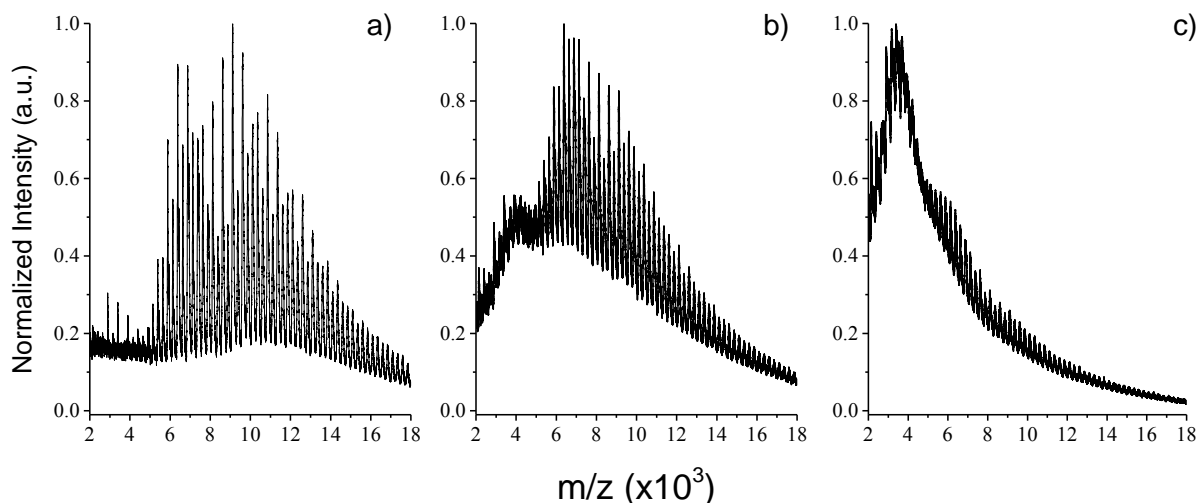
Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was performed using a Bruker microflex time-of-flight mass spectrometer with 20-50% laser intensity and 3056 V of lineal detector voltage. The spectrum was calibrated using CsI<sub>3</sub> clusters up to 10005 Da and *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene] malononitrile (DCTB) as the matrix. Typically, 0.5 mg of the matrix and 1 mg of the analyte stock solution were mixed in 100  $\mu$ L of THF and sonicated for 10 minutes. 10  $\mu$ L of the solution was applied to the steel plate and then air-dried. The high sample-to-matrix concentration and the insolubility of the particles usually led to a thick layer of agglomerates. Focusing the laser to areas of high concentration of the analyte usually results in a better signal to noise ratio. The spectrum was integrated over 500 shots at 30 Hz.



**Fig. S4:** MALDI mass spectra of the unprocessed samples a) F<sub>9</sub>-AgNP1, b) F<sub>13</sub>-AgNP2, c) F<sub>17</sub>-AgNP3 and d) H<sub>17</sub>-AgNP4. Equidistant peaks are separated in units of one silver atom and one molecular ligand (AgL with L<sup>(1-4)</sup>, respectively).

#### 2.4. VUV ionization post-volatilization measurements.

All nanoparticles were tested under the same sublimation conditions. Only the post ionization laser intensity was adapted to maximize the high-mass ion signal. Best signals were obtained at  $I_{\text{ion}} = 8.5(4) \times 10^5$  W/cm<sup>2</sup> for F<sub>9</sub>-AgNP1 and  $I_{\text{ion}} = 5.8(4) \times 10^5$  W/cm<sup>2</sup> for F<sub>13</sub>-AgNP2. Higher VUV laser intensities lead to enhanced dissociation rather than ionization (see Fig. S5).

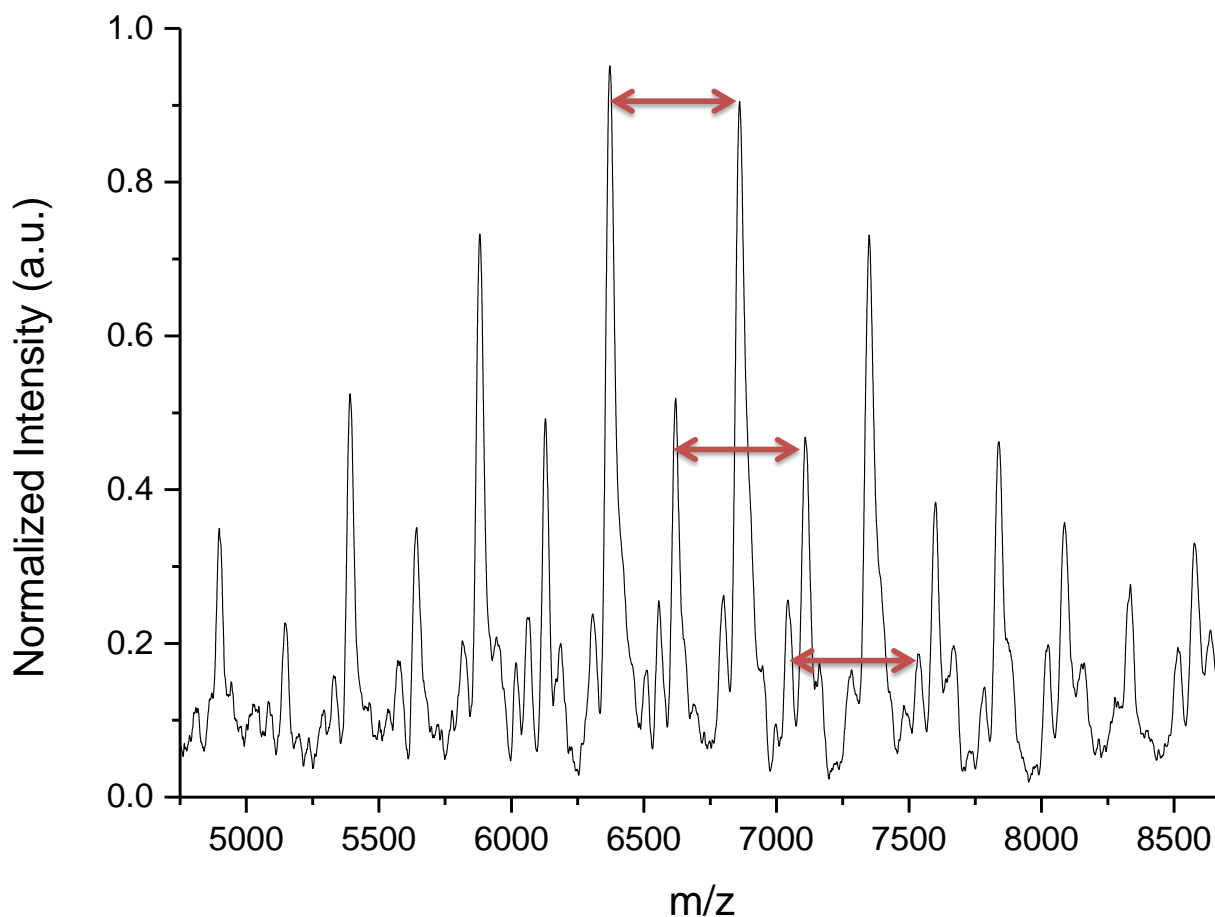


**Fig. S5:** Photofragmentation of perfluoro-alkyl capped silver nanoparticles. The ionization laser intensity changes the shape of the  $F_{13}$ -AgNP2 mass spectrum, an indication of laser-induced dissociation of the originally intact nanoparticle. From left to right the 157 nm laser intensity is changed. a)  $I=8.5(4) \times 10^5$  W/cm<sup>2</sup>. b)  $I=2.5(1)$  MW/cm<sup>2</sup>. c)  $I=4.0(1)$  MW/cm<sup>2</sup>.

In all desorption studies, we suspended 30 mg of nanoparticles in 1 mL THF and ultrasonicated the sample for 10 min. The sample was deposited on a stainless steel plate and placed on a translation stage underneath the mass spectrometer. The stage was moved to expose a fresh sample to every laser shot. The beam of a blue (445 nm) continuous diode laser is focused on to the sample plate to a final focus spot size of about 2 mm. Controlling the diode laser current we generated long optical pulses of 10 ms length. The nanoparticle desorption is followed by ionization in a short- pulse VUV laser beam ( $\tau=10$  ns, wavelength of 157.6 nm) 500  $\mu$ s later, and 4 cm above the target plate. The ionization intensity is varied by varying the voltage of the gas discharge

### Study of a mixture of particles.

In order to distinguish the volatilization of (almost) intact nanoparticles from a speculative fragmentation-aggregation model (see main text) we prepared a mixture of  $F_9$ -AgNP1 and  $F_{13}$ -AgNP2 particles and analyzed it under the same experimental conditions as before. Fig. S6 shows a pattern exclusively with peak distances around 490 Da, corresponding to the mass spectrum and ligands of  $F_{13}$ -AgNP2.



**Fig. S6:** Mass spectra of the mixture of  $F_9$ -AgNP1 and  $F_{13}$ -AgNP2 particles, showing three libraries of the  $F_{13}$ -AgNP2 clusters with equidistant peaks of  $\sim 490$  Da.

## 2.5. TEM and EDX analysis.

We carried out two separate TEM studies. First, we dissolved the 'as synthesized' nanoparticles in THF with a concentration of 1 mg/mL. Then we put a few drops onto the suspended monolayer graphene on the TEM grid. This was investigated on a Philips CM100 transmission electron microscope at 80 kV using copper grids (Cu-400HD) from Pacific Grid Tech. The mean particle diameters and their standard deviation are a) F<sub>9</sub>-AgNP1 d = (0.7±0.3) nm, b) F<sub>13</sub>-AgNP2 d = (0.5±0.2) nm, c) F<sub>17</sub>-AgNP3 d = (0.7±0.3) nm and d) H<sub>17</sub>-AgNP4 d = (1±0.4) nm. TEM imaging can only detect the metal core and not the ligand shell but in spite of comparable synthesis protocols we find a considerable variation in the NP size. As the length and chemical nature of the ligand is the only variable, these size variations seem to emerge from particular features of the ligand under investigation.

In SEM experiments, we designed a grid holder, which we placed into the ion extraction region of the ToF-MS. A fresh TEM grid was inserted to collect the volatilized nanoparticles. 200 shots of the blue laser were directed onto the sample to transfer a sufficient amount of nanoparticles through high vacuum onto the grid. These samples were imaged in SEM microscopy and also analyzed with EDX.