Supporting Information

Role of the capping agent in the interaction of hydrophilic Ag nanoparticles with DMPC as model biomembrane

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Figure S1. $^1$H NMR spectrum of MBA acquired right after solution preparation. Solvent: CCl$_3$D, 400.13 MHz (some drops of DMSO-d$_6$ were added to enhance solubility). [MBA] = 63 mM.

Figure S2. $^{13}$C NMR spectrum of MBA acquired right after solution preparation. Solvent: CCl$_3$D (some drops of DMSO-d$_6$ were added to enhance solubility), 100.03 MHz. [MBA] = 63 mM.
Figure S3. $^1$H NMR spectrum of sodium citrate. Solvent: D$_2$O, 400.13 MHz. [sodium citrate] = 43 mM.

Figure S4. $^{13}$C NMR spectrum of sodium citrate. Solvent: D$_2$O, 100.03 MHz. [sodium citrate] = 43 mM.
**UV-vis spectra of CIT-AgNPs and MBA-AgNPs**

The quality of AgNPs before and after immersion in the Langmuir trough was checked by their UV-vis spectra in the 200–700 nm wavelength range. The wavelength where the maximum absorbance occurs is located at 400 cm$^{-1}$. It corresponds to plasmon resonance absorption and is typically found for AgNPs with diameters up to 30 nm, whereas for larger nanoparticles or agglomerates a red shift is predicted.$^1$

![UV-vis spectra](image)

**Figure S5.** UV-vis spectra of (a) CIT-AgNPs and (b) MBA-AgNPs. Green lines correspond to freshly prepared nanoparticles in phosphate buffer solution at pH 7.2. Pink lines are spectra taken from a solution extracted from the Langmuir trough after 2 h of interaction of the nanoparticles with the DMPC monolayer packed at 5 mN/m.

**Estimation of the quantitative ratio MBA/CIT on MBA-AgNPs**

We can estimate CIT/MBA molecular ratio on MBA-AgNPs surface from our XPS data shown in Table 1 and discussed in the underlying paragraph of the main text of the manuscript as follows:
In MBA-AgNPs the atomic ratio COO$_{\text{tot}}$/Ag is 0.75 and S/Ag is 0.51. From the molecular formula of MBA (one sulfur atom per carboxylic group) one should expect COO$_{\text{tot}}$/Ag of 0.51. The difference 0.75-0.51: 0.24 would correspond to carboxylic groups of citrate that are not displaced by MBA during the synthesis procedure (see experimental section). Given that there are three carboxylic groups per citrate molecule the ratio CIT/Ag is 0.08 (0.24/3) whereas MBA/Ag is 0.51. In conclusion the surface of silver nanoparticles is covered by both species in a molecular ratio MBA/CIT$\approx$ 6.
Estimation of the contribution of different planes on AgNPs

**Figure S6.** This figure shows a particle of an arbitrary fcc structure, according to Marks model. Using this model, it could be verified that the (1 1 1) surface has 104 atoms. So, in the figure of the right 521 atoms can be seen. In addition, the (1 1 1̅) plane and the contiguous (1 1 1̅) plane have 70 atoms. The total number of atoms lying over {111} faces is 1392. Meanwhile, the (100) plane contains 48 atoms. So, all the {1 0 0} faces have 240 atoms. For this reason, the fraction of atoms lying on {1 1 1} faces is: 1392/(1392+240). In other words, in this structure more than 85% of the atoms are over the {1 1 1} faces. Taking into account the lattice parameter of Ag, the main diameter of this particle is 5.1 nm. For larger particles, the ratio of {1 1 1} faces over the total amount of other families’ faces decreases. However, for mean diameters close to 8.2 nm, the ratio is still higher than 73%. The figure shows a smaller particle size than the mean size of particles in order to avoid confusion with the facets. The bigger the particle, the less pronounced the faces of the Marks decahedron.
**Figure S7.** Adsorption isotherms of CIT-AgNPs in the absence (turquoise) and in the presence of a DMPC monolayer initially packed at $\pi_0^{\text{DMPC}} \approx 5\text{mN/m}$ (violet), 10 mN/m (blue) and 30 mN/m (fuchsia). The arrows indicate the moment when AgNPs are injected.

**Figure S8.** Compression isotherms obtained for a DMPC layer initially packed at 5 mN/m after 2 hour interaction with (a) citrate (0.75 mM) and (b) 4-mercaptobenzoic acid (1 mM) dissolved in buffer subphase (red). Isotherm of pure DMPC (violet).
Figure S9. Molecular structure of DMPC. The polar terminal group consists of a positive quaternary ammonium moiety (light blue), a negative phosphate group (light red). The hydrophobic part of the molecule is colored in yellow.

Figure S10. Time sequence of BAM images taken for a DMPC monolayer film at 5 mN/m in contact with phosphate buffer solution at pH 7.2 containing MBA-AgNPs.
Figure S11. (a) Top view and (b) lateral/side view of the $\sqrt{3}\times 4$ MBA lattice on Ag(111) (adapted from J. Phys.Chem.C 2013, 117, 24967-24974). Dark brown: C, Red: O, White: H. The surface unit cell in a) is indicated by a black line.

Bibliography