Electronic Supplementary Information

Mapping the nanoparticles coating monolayer with NMR pseudo-contact shifts

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1. **Experimental Procedures.**

**General:** Solvents were purified by standard methods. All commercially available reagents and substrates were used as received. NMR spectra were recorded using a Bruker AV300 spectrometer equipped with a 5 mm BBO z gradient probe operating at 300 MHz for $^1$H. Chemical shifts are reported relative to internal Me$_4$Si. Multiplicity is given as follow: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, br = broad peak. UV-Visible spectra were recorded on Perkin Elmer Lambda 45 spectrophotometer equipped with a thermostated cell holder. O-(decylphosphoryl)choline (1), methylbenzoate (2), potassium p-toluenesulphonate (3), potassium tetrakis(4-chlorophenyl)borate (5), trimethyloctylammonium bromide (6) were Aldrich products used as received. O-(11-mercapto-decylphosphoryl)choline (1) were prepared as reported.$^1$

2. **Synthesis and characterization of monolayer protected gold nanoparticles (MPGN)**

Monolayer protected gold nanoparticles (MPGN) were prepared according to a previously reported two-step procedure.$^2,^3$ All the glassware used in the MPGN preparation were washed with aqua regia and rinsed with distilled water. HAuCl$_4$ is strongly hygroscopic and was weighted within a dry-box.

A solution of HAuCl$_4$·3H$_2$O (100 mg, 0.254 mmol) in water (4 mL) was extracted with a solution of tetraoctylammonium bromide (5 g, 9.14 mmol) in N$_2$ purged toluene (250 mL divided in 3 portions). To the resulting reddish-orange organic solution, dioctylamine (3.36 g, 13.92 mmol) is added (the amount of dioctylamine was calculated$^2$ in order to obtain 2 nm nanoparticles). The mixture is vigorously stirred under N$_2$ for 30 min. During this period of time the color of the mixture fades. A solution of NaBH$_4$ (93.0 mg, 2.46 mmol) in H$_2$O (2 mL) is then rapidly added. The color of the solution turns rapidly to black due to nanoparticles formation. After 2 hours of
stirring, the aqueous layer is removed. To the above nanoparticle solution, thiol 1 (0.254 mmol) dissolved in 3 mL of isopropanol is rapidly added.

The reaction mixture is evaporated and the resulting crude is dissolved in methanol and purified by gel permeation chromatography with Sephadex LH-20 resin. 1-coated nanoparticles are soluble in D$_2$O and CD$_3$OD.

TEM analysis of the different samples (one example in Figure S1) yields an average diameter for the MPGN of 1.8±0.5 nm.

General formula is Au$_{180}$RS$_{67}$, as calculated on the basis of TGA analysis (Figure S2) using the spherical approximation,$^4$ where RS indicate the thiol molecules forming the protecting monolayer.

This value well compare with that of Au$_{201}$RS$_{71}$ calculated by Murray and co-workers for 1.74 nm diameter nanoparticles with an ideal truncoctahedron core structure.$^5$

Size analysis is confirmed by UV-Vis spectra (one example is in Figure S3), were no plasmonic band is detected as expected for gold nanoparticles with diameter below 3 nm.

NMR analysis (Figure S4) indicates monolayer formation (broadening of all bands), as confirmed by diffusion-filtered experiments (not shown).

Figure S1: Sample TEM image of 1-coated MPGN and size distribution: average diameter = 1.8 nm ($\sigma$ = 0.5 nm).
Figure S2: TGA analysis of a sample of 1-coated MPGNs under nitrogen atmosphere.

Figure S3: UV-Vis spectrum of a sample of 1-coated MPGN (0.1 mg/mL) at 25°C in water.
Figure S4: $^1$H-NMR (300 MHz) spectrum of the 1-coated MPGN in D$_2$O.
3. Additional NMRtitrations of MPGNs

Figure S5. $^1$H-NMR spectra of a D$_2$O solution of thiol 1-coated gold nanoparticles recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([1] = 5 mM, the intense signal at 4.6 ppm is residual water).

Figure 6. $^1$H-NMR spectra of a D$_2$O solution of thiol 1-coated gold nanoparticles recorded upon addition of increasing amounts of an acetonitrile solution of Yb(CF$_3$SO$_3$)$_3$. ([1] = 5 mM, the intense signal at 4.6 ppm is residual water).
Figure S7. $^1$H-NMR spectra of a D$_2$O solution of 2 recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([2] = 5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).

Figure S8. $^1$H-NMR spectra of a D$_2$O solution of 2 recorded upon addition of increasing amounts of an acetonitrile solution of Yb(CF$_3$SO$_3$)$_3$. ([2] = 5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).
Figure S9. $^1$H-NMR spectra of a D$_2$O solution of 3 recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([3] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).

Figure S10. $^1$H-NMR spectra of 1-coated gold nanoparticles in D$_2$O ([1] = 5 mM) recorded upon addition of increasing amounts of a CD$_3$CN solution of Tb(CF$_3$SO$_3$)$_3$ in the presence of 3 ([3] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).
**Figure S11.** $^1$H-NMR spectra of a D$_2$O solution of 4 recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([4] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).

**Figure S12.** $^1$H-NMR spectra of 1-coated gold nanoparticles in D$_2$O ([1] = 5 mM) recorded upon addition of increasing amounts of a CD$_3$CN solution of Tb(CF$_3$SO$_3$)$_3$ in the presence of 4 ([4] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).
Figure S13. $^1$H-NMR spectra of a D$_2$O solution of 5 recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([5] = 0.5 mM, the intense signal at 4.6 ppm is residual water, increasing signal at 2.05 ppm is CH$_3$CN).

Figure S14. $^1$H-NMR spectra of 1-coated gold nanoparticles in D$_2$O ([1] = 5 mM) recorded upon addition of increasing amounts of a CD$_3$CN solution of Tb(CF$_3$SO$_3$)$_3$ in the presence of 5 ([5] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).
**Figure S15.** $^1$H-NMR spectra of a D$_2$O solution of 6 recorded upon addition of increasing amounts of an acetonitrile solution of Tb(CF$_3$SO$_3$)$_3$. ([6] = 0.5 mM, the intense signal at 4.6 ppm is residual water, increasing signal at 2.05 ppm is CH$_3$CN).

**Figure S16.** $^1$H-NMR spectra of 1-coated gold nanoparticles in D$_2$O ([1] = 5 mM) recorded upon addition of increasing amounts of a CD$_3$CN solution of Tb(CF$_3$SO$_3$)$_3$ in the presence of 6 ([6] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH$_3$CN).
Figure S17. Diffusion filtered $^1$H-NMR (300 MHz) spectra of a solution of 1-coated gold nanoparticles and 6 in D$_2$O. [1] = 5 mM, [6] = 0.5 mM, mixing time 0.3 sec, T = 28 °C. Note the complete cancellation of the water peak at 4.6 ppm.

Figure S18. Diffusion filtered $^1$H-NMR (300 MHz) spectra of a solution of 6 in D$_2$O. [6] = 0.5 mM, mixing time 0.3 sec, T = 28 °C. Note the complete cancellation of the water peak at 4.6 ppm.


3) G. Guarino, F. Rastrelli, P. Scrimin and F. Mancin, *submitted*.
