Electronic Supplementary Information

Mapping the nanoparticles coating monolayer with NMR pseudo-contact shifts

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(Total 13 pages including this cover page)

Table of Contents

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 ^1H. Chemical shifts are reported relative to internal Me_4Si. 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 $HAuCl_4 \cdot 3H_2O$ (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_2O (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_2O and CD_3OD.

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).

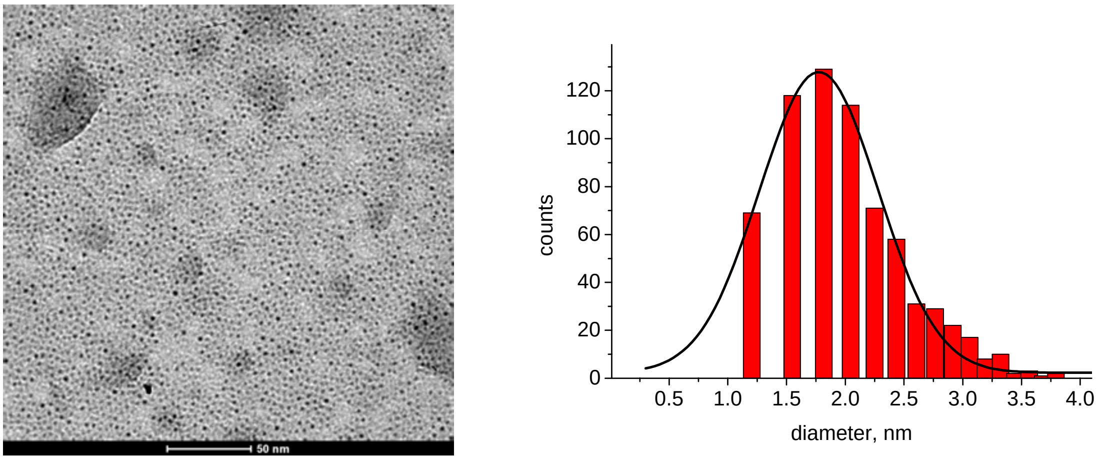

Figure S1: Sample TEM image of **1**-coated MPGN and size distribution: average diameter = 1.8 nm (σ = 0.5 nm).

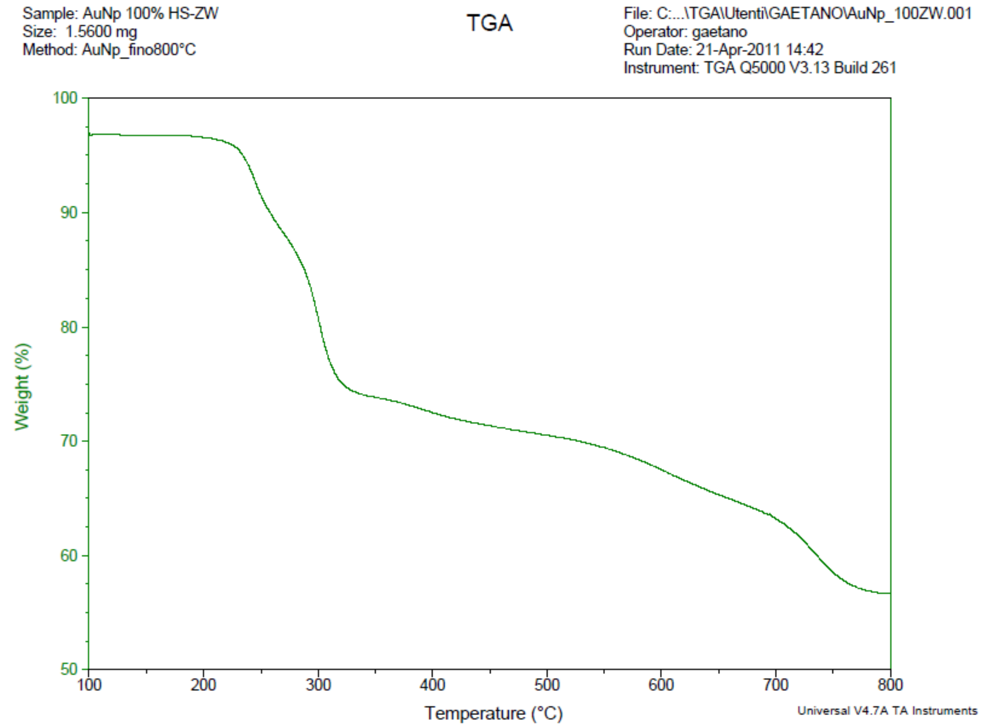

Figure S2: TGA analysis of a sample of **1**-coated MPGNs under nitrogen atmosphere.

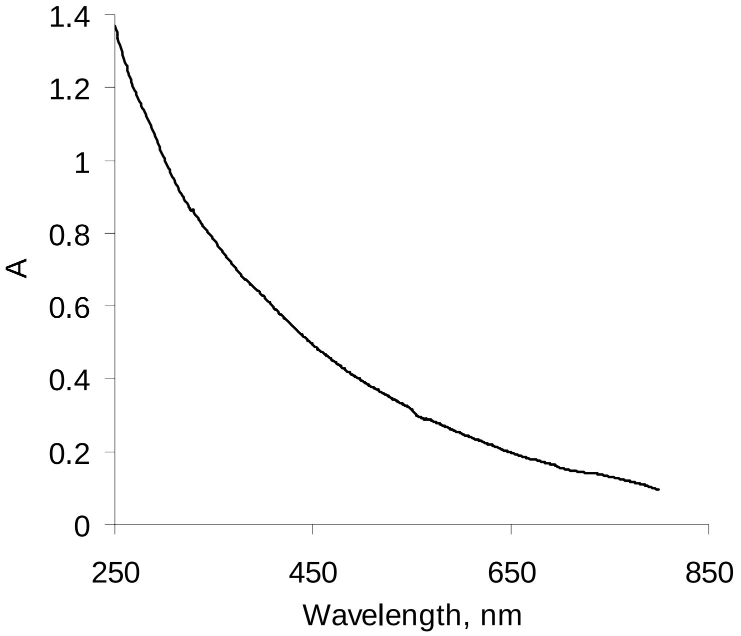

Figure S3: UV-Vis spectrum of a sample of **1**-coated MPGN (0.1 mg/mL) at 25°C in water.

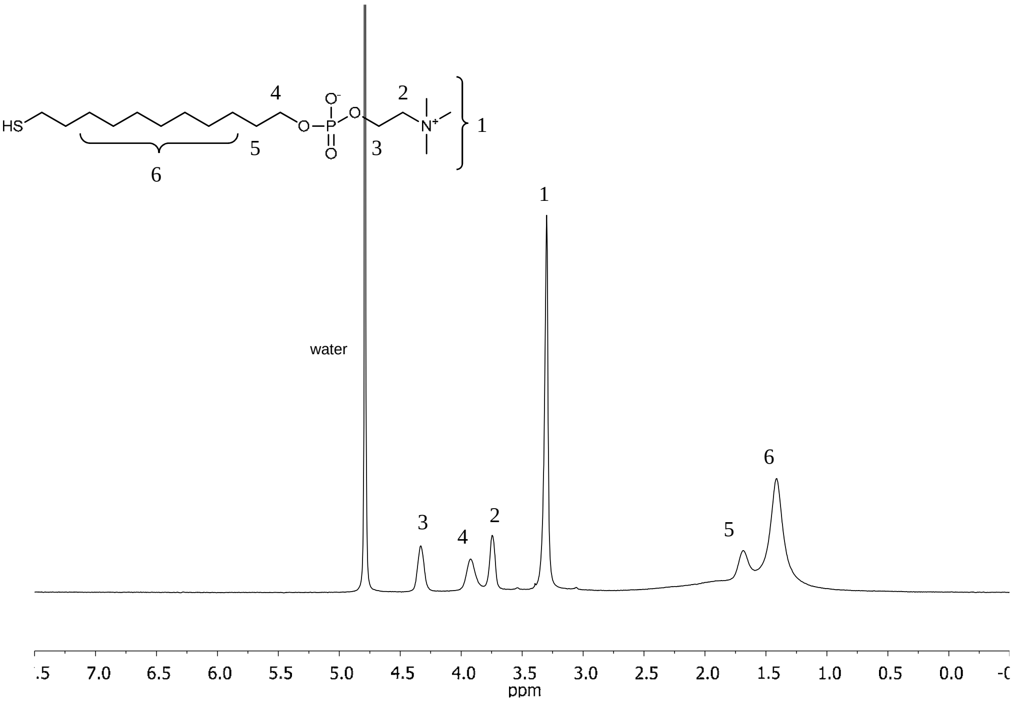

Figure S4: ^{1}H-NMR (300 MHz) spectrum of the **1**-coated MPGN in D_2O.

3. Additional NMRtitrations of MPGNs

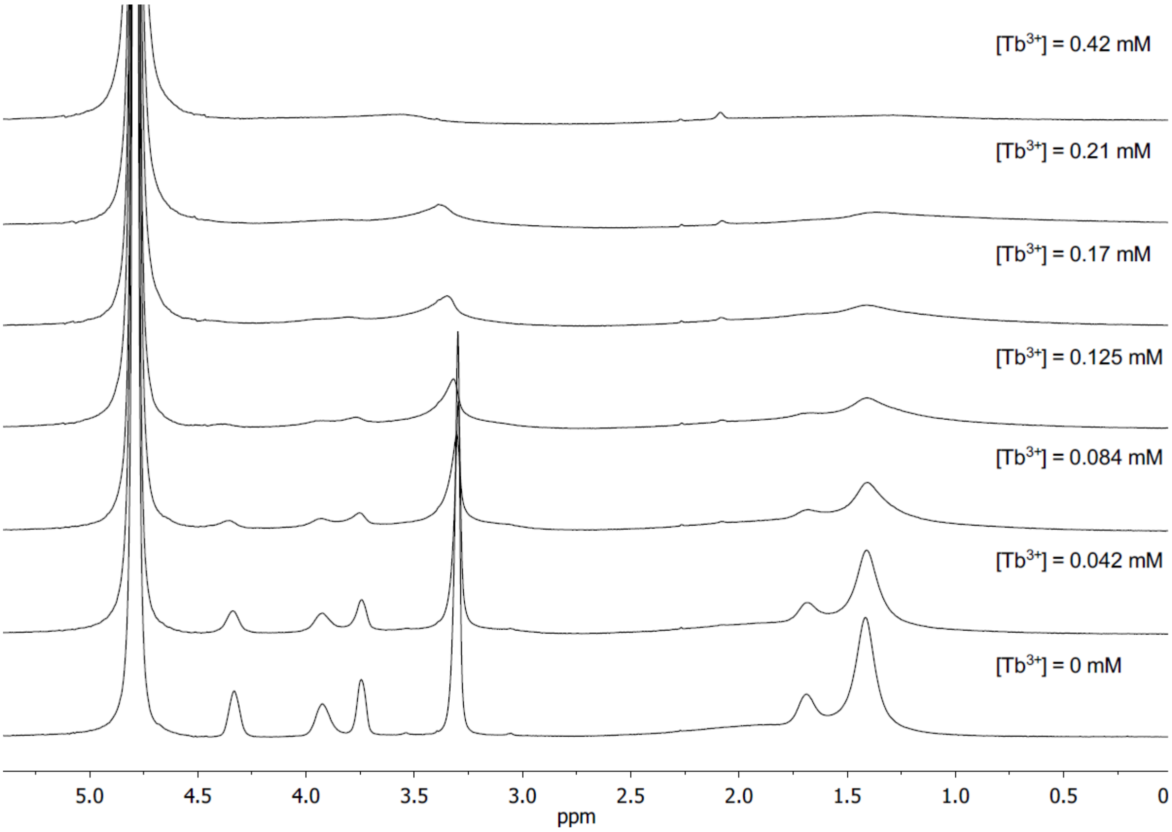

Figure S5. ^{1}H-NMR spectra of a D_2O solution of thiol **1**-coated gold nanoparticles recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**1**] = 5 mM, the intense signal at 4.6 ppm is residual water).

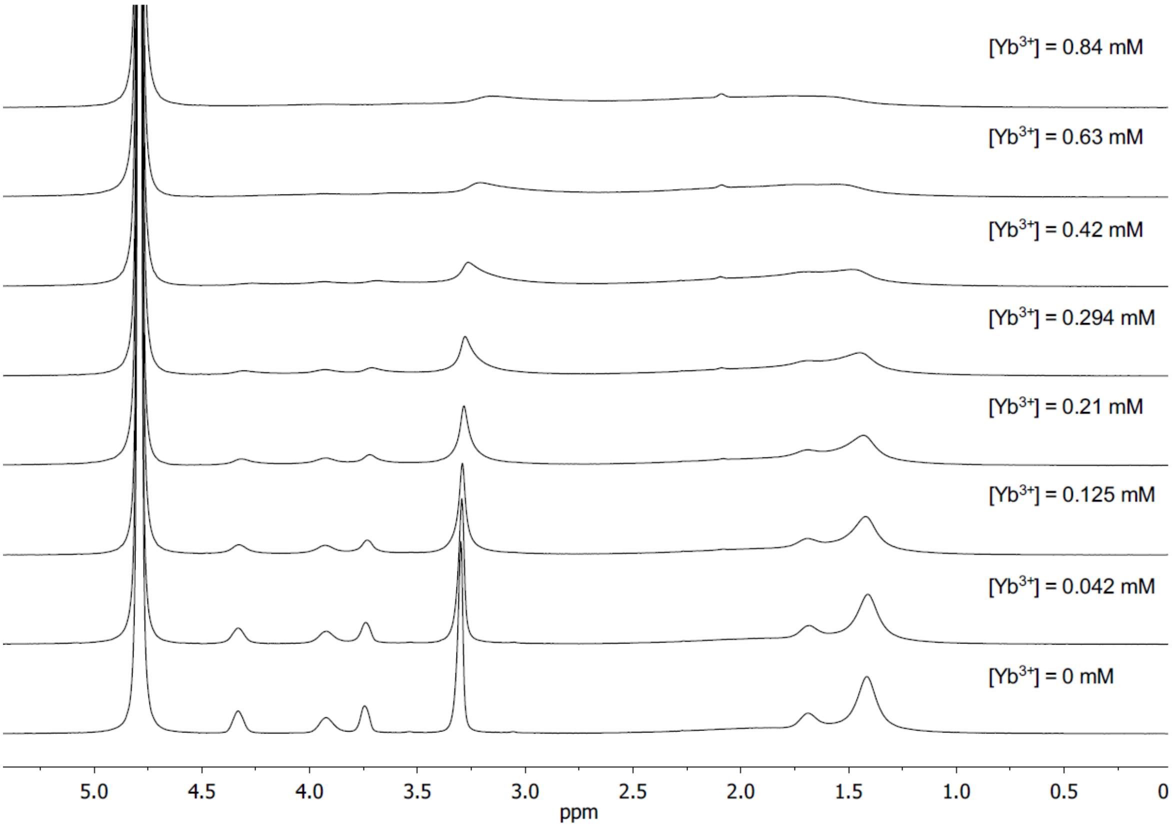

Figure 6. ^{1}H-NMR spectra of a D_2O solution of thiol **1**-coated gold nanoparticles recorded upon addition of increasing amounts of an acetonitrile solution of $Yb(CF_3SO_3)_3$. ([**1**] = 5 mM, the intense signal at 4.6 ppm is residual water).

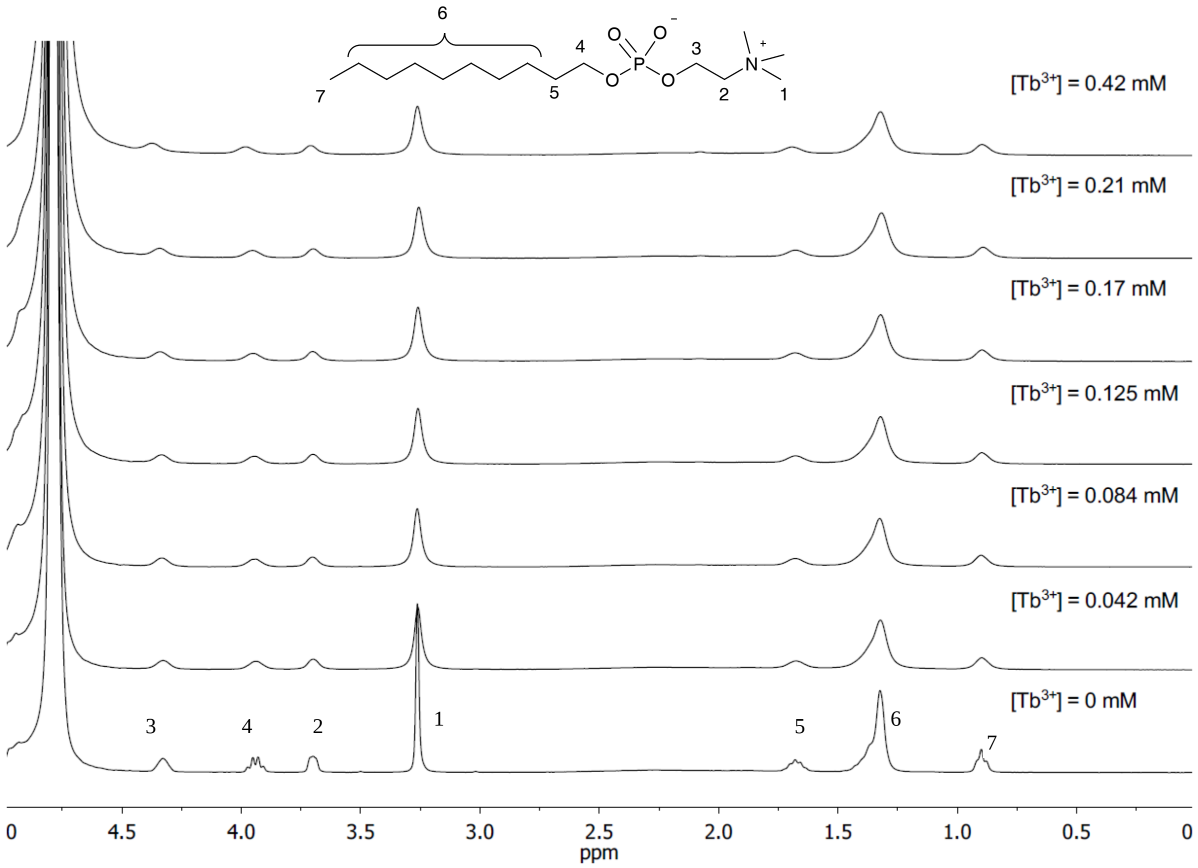

Figure S7. ^{1}H-NMR spectra of a D_2O solution of **2** recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**2**] = 5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

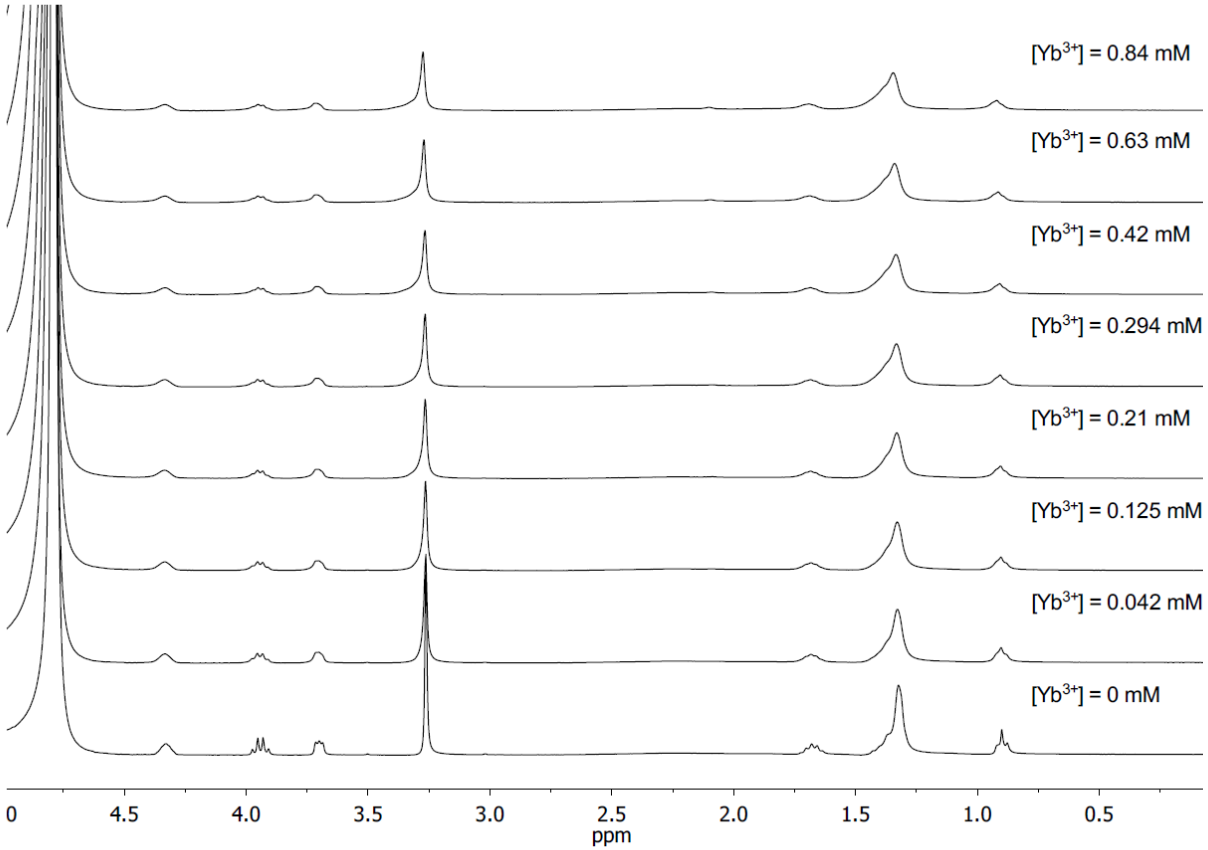

Figure S8. ^{1}H-NMR spectra of a D_2O solution of **2** recorded upon addition of increasing amounts of an acetonitrile solution of $Yb(CF_3SO_3)_3$. ([**2**] = 5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

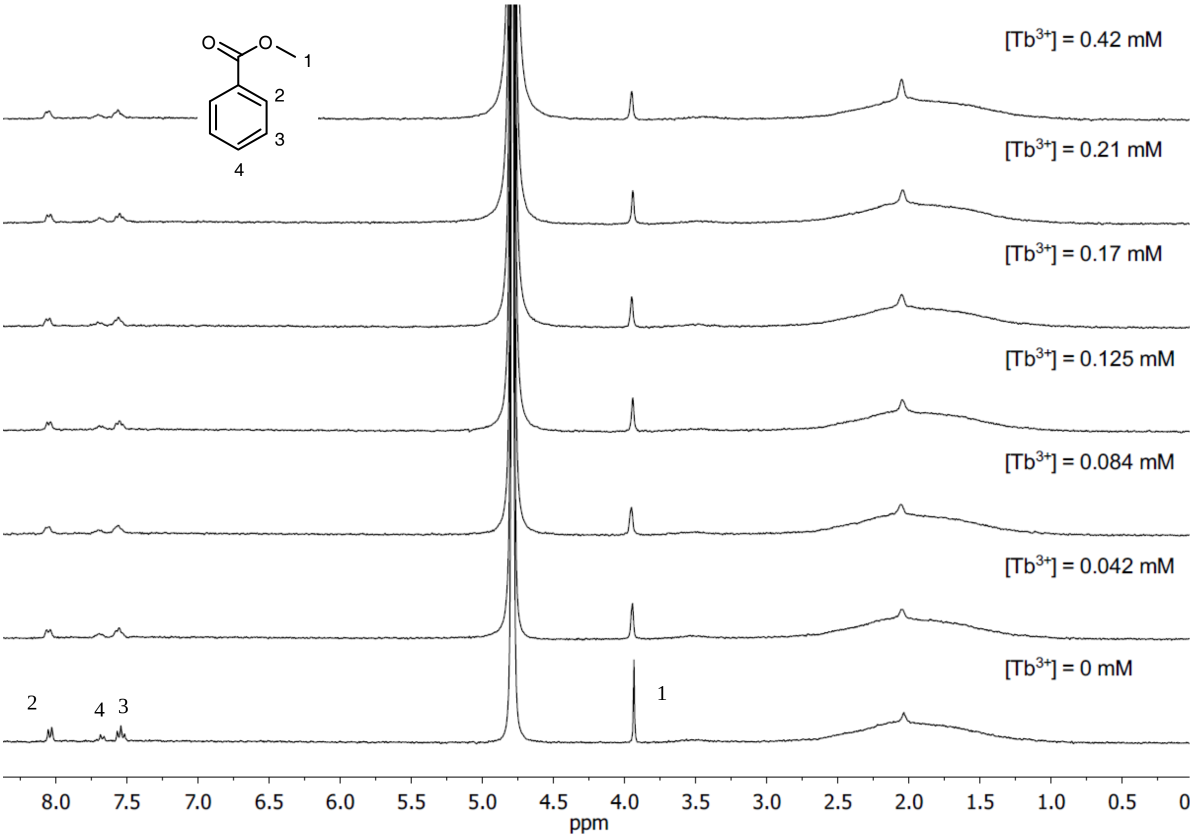

Figure S9. ^{1}H-NMR spectra of a D_2O solution of **3** recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**3**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

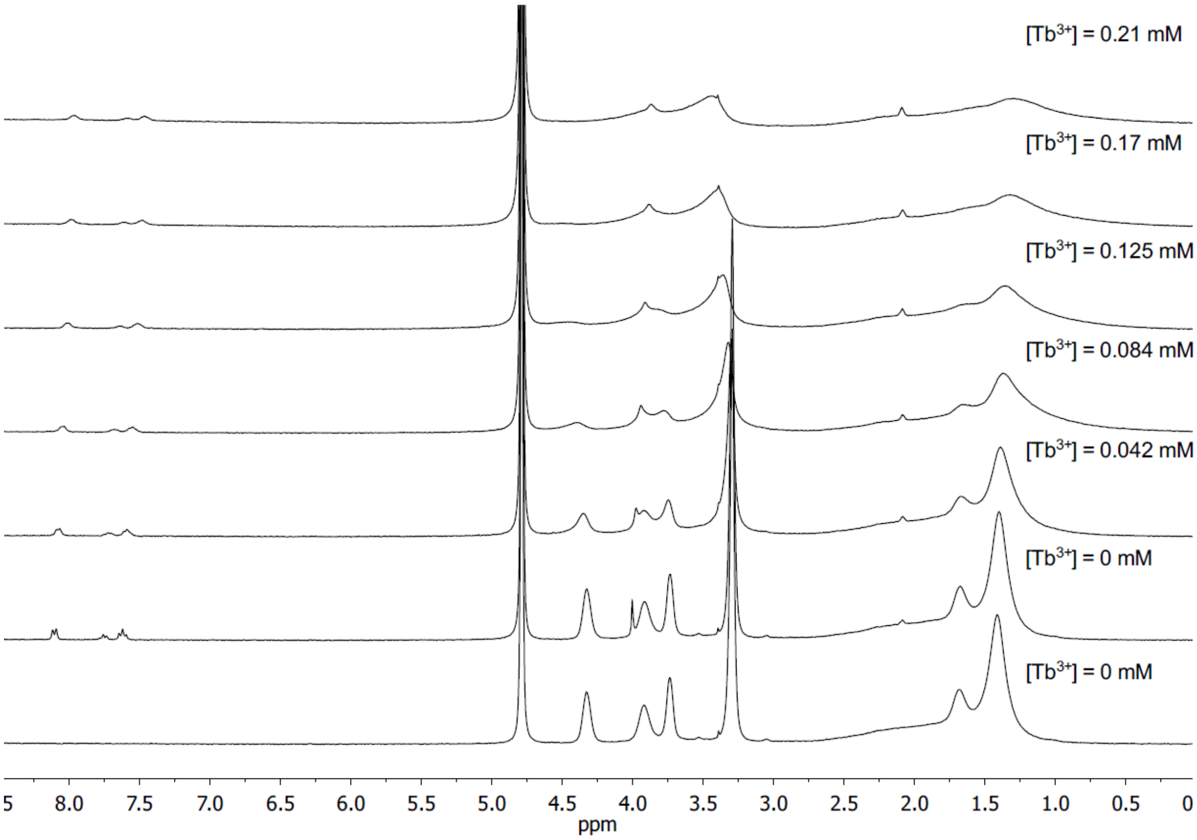

Figure S10. ^{1}H-NMR spectra of **1**-coated gold nanoparticles in D_2O ([**1**] = 5 mM) recorded upon addition of increasing amounts of a CD_3CN solution of $Tb(CF_3SO_3)_3$ in the presence of **3** ([**3**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

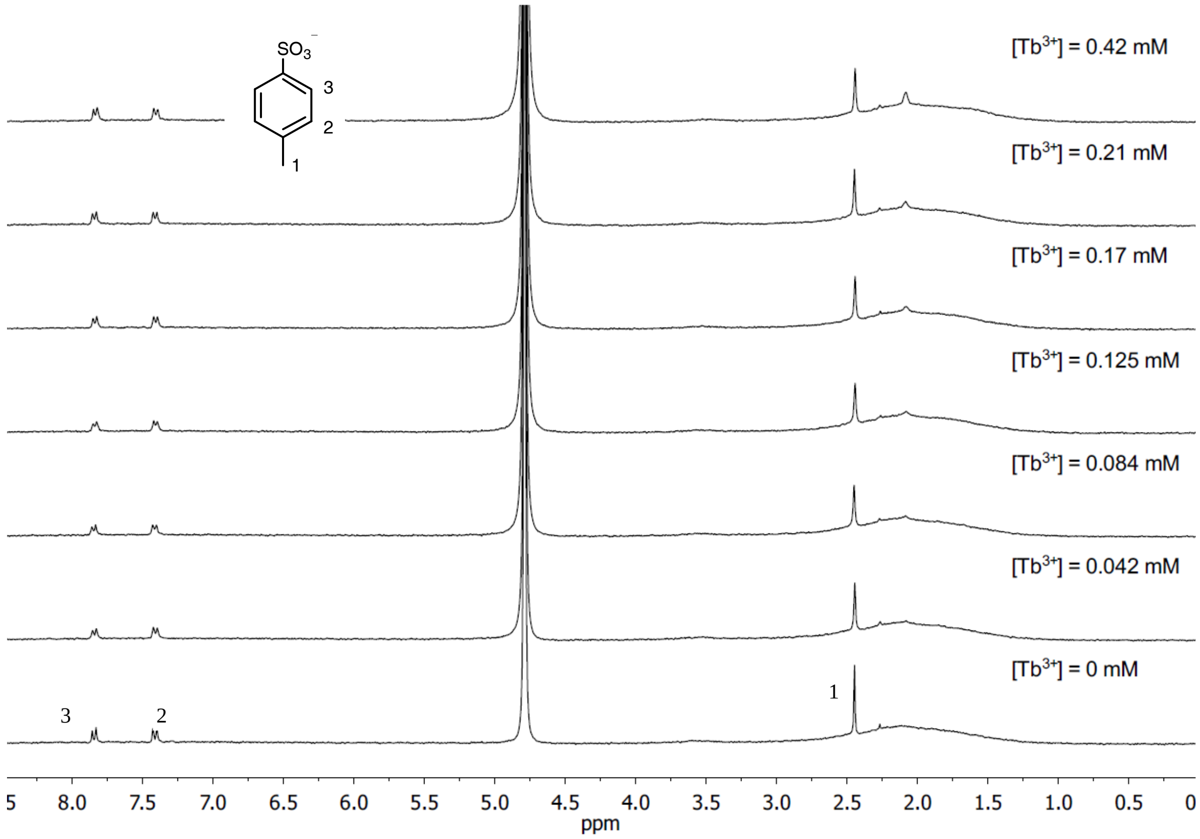

Figure S11. ^{1}H-NMR spectra of a D_2O solution of **4** recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**4**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

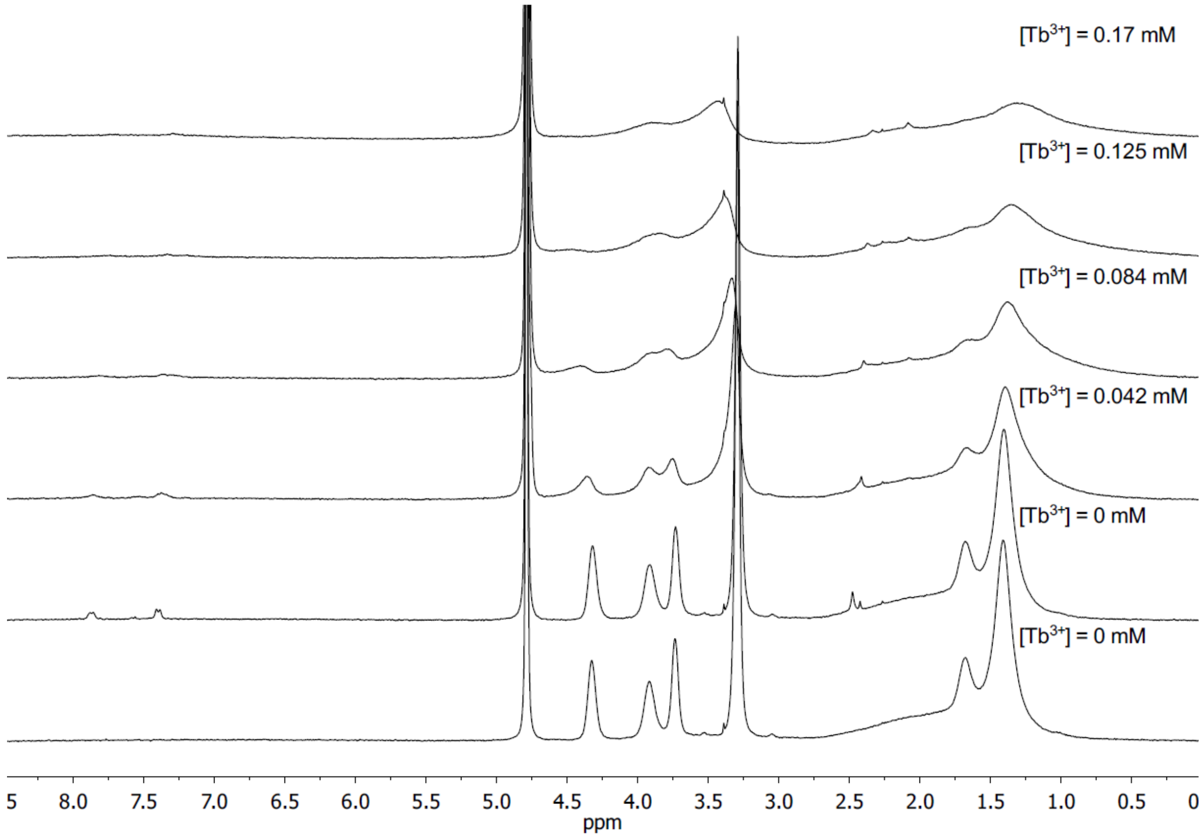

Figure S12. ^{1}H-NMR spectra of **1**-coated gold nanoparticles in D_2O ([**1**] = 5 mM) recorded upon addition of increasing amounts of a CD_3CN solution of $Tb(CF_3SO_3)_3$ in the presence of **4** ([**4**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

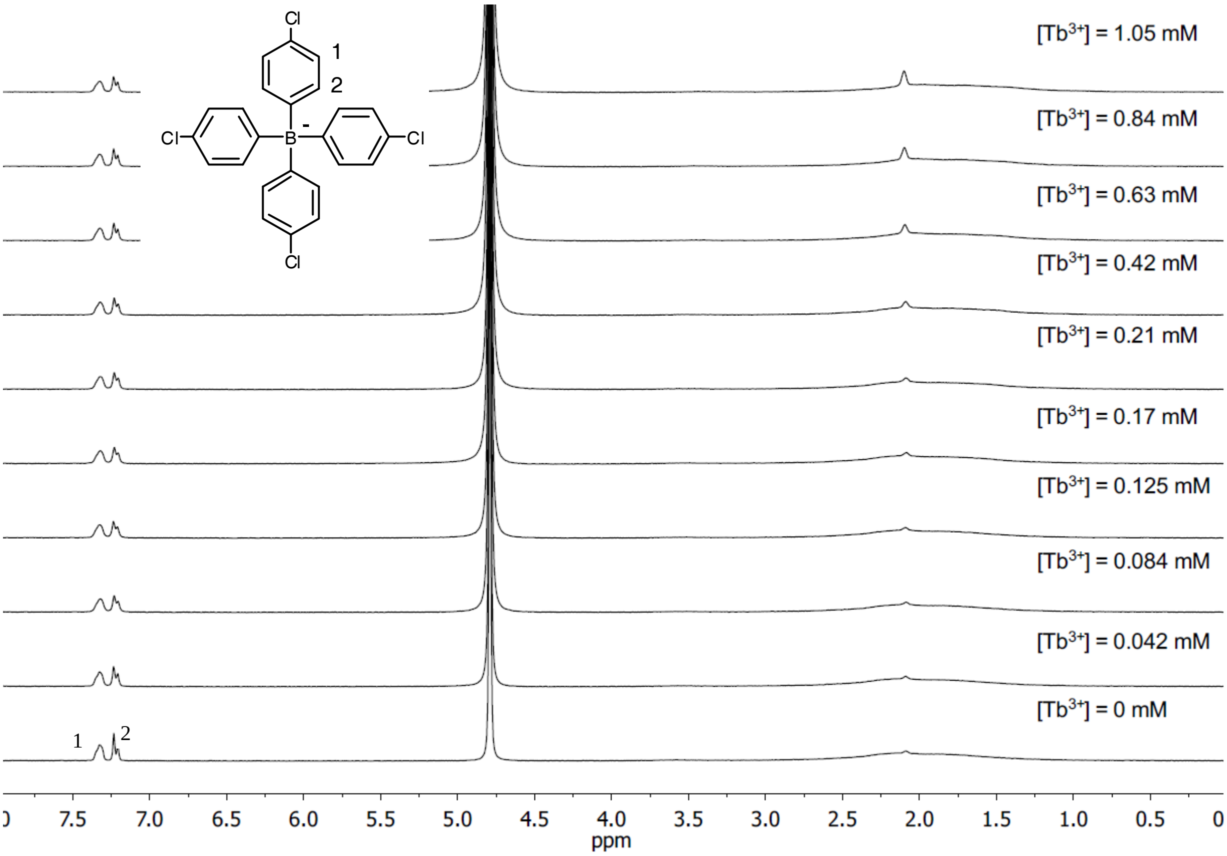

Figure S13. ^{1}H-NMR spectra of a D_2O solution of **5** recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**5**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, increasing signal at 2.05 ppm is CH_3CN).

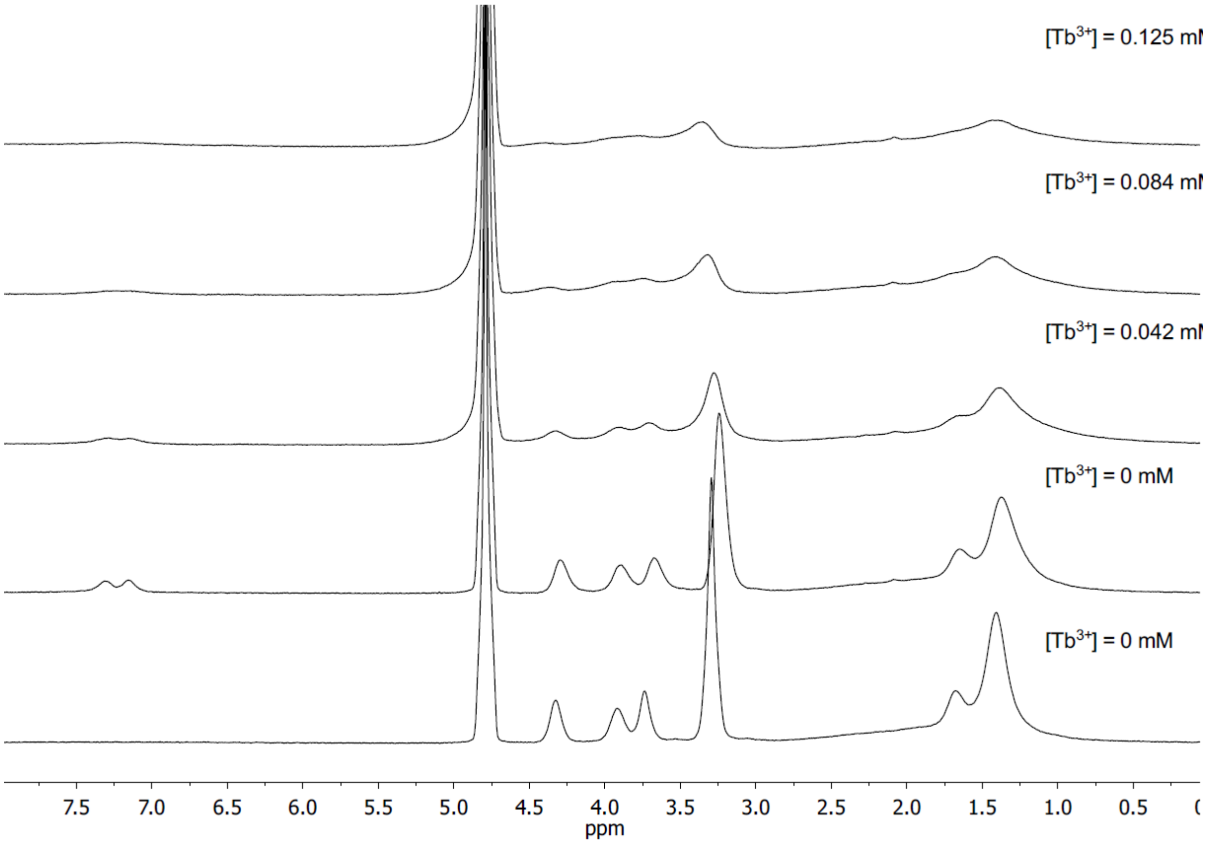

Figure S14. ^{1}H-NMR spectra of **1**-coated gold nanoparticles in D_2O ([**1**] = 5 mM) recorded upon addition of increasing amounts of a CD_3CN solution of $Tb(CF_3SO_3)_3$ in the presence of **5** ([**5**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

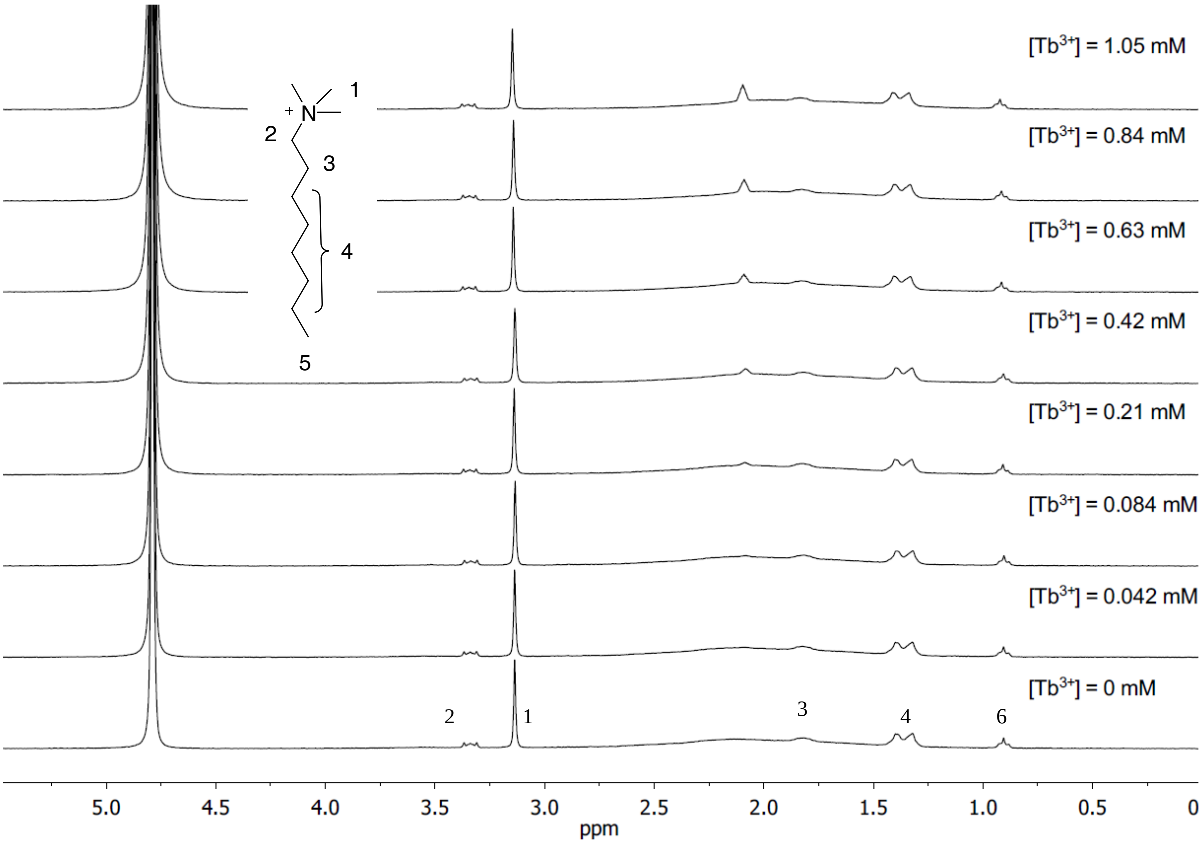

Figure S15. ^{1}H-NMR spectra of a D_2O solution of **6** recorded upon addition of increasing amounts of an acetonitrile solution of $Tb(CF_3SO_3)_3$. ([**6**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, increasing signal at 2.05 ppm is CH_3CN).

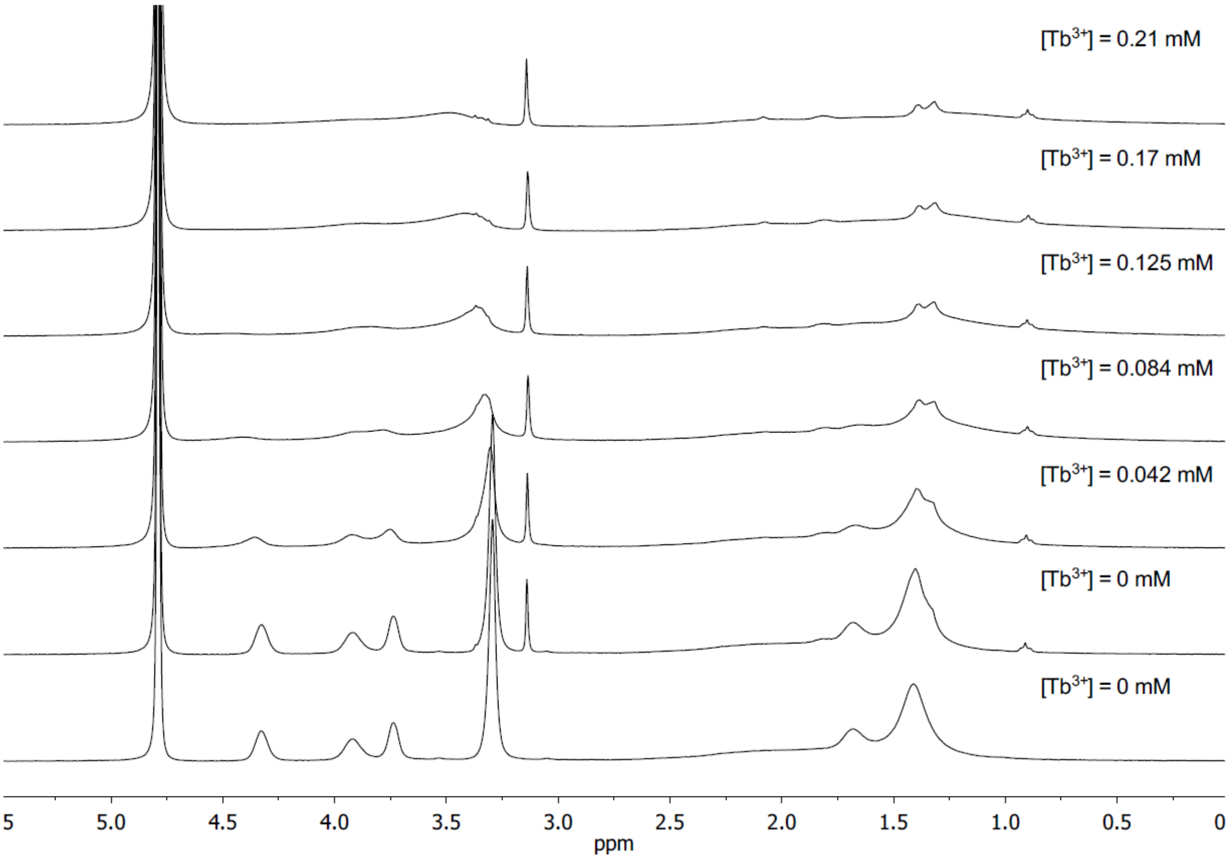

Figure S16. ^{1}H-NMR spectra of **1**-coated gold nanoparticles in D_2O ([**1**] = 5 mM) recorded upon addition of increasing amounts of a CD_3CN solution of $Tb(CF_3SO_3)_3$ in the presence of **6** ([**6**] = 0.5 mM, the intense signal at 4.6 ppm is residual water, the increasing signal at 2.05 ppm is CH_3CN).

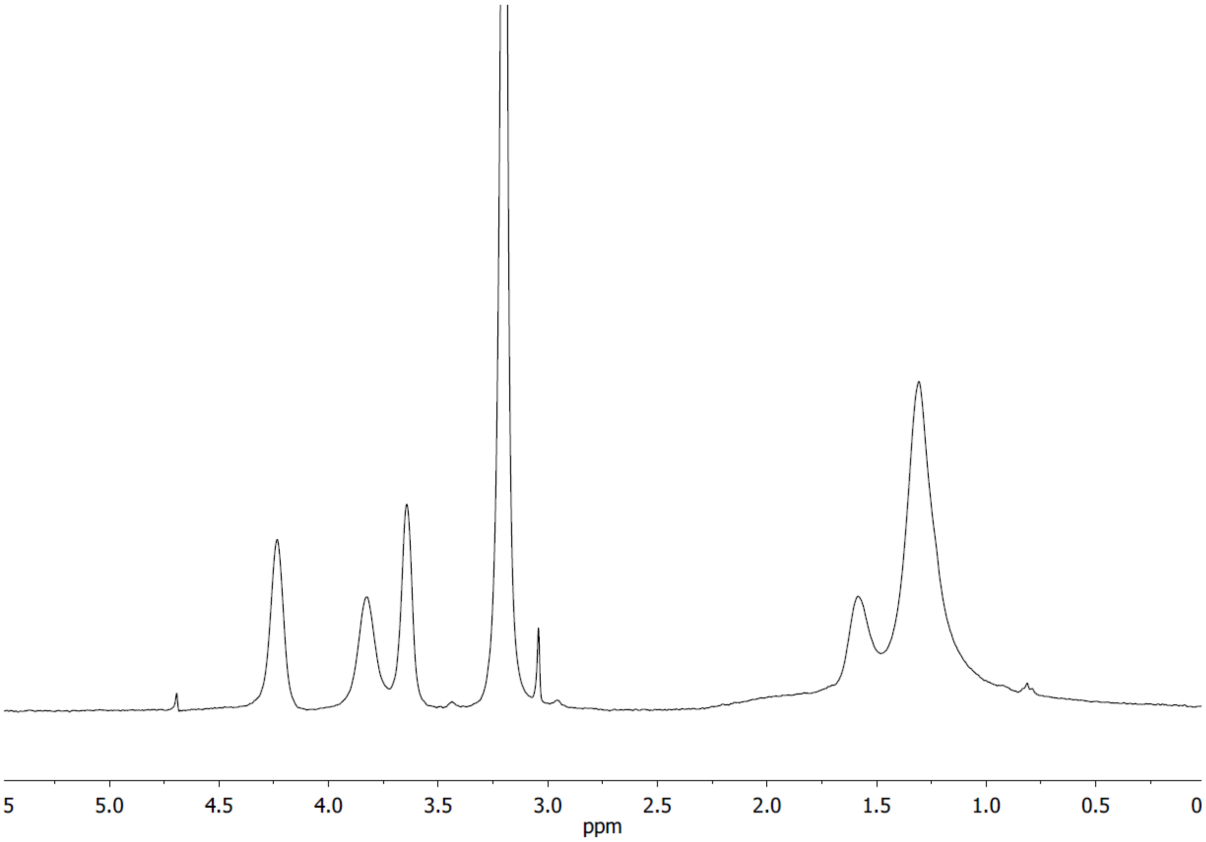

Figure S17. Diffusion filtered ^{1}H-NMR (300 MHz) spectra of a solution of **1**-coated gold nanoparticles and **6** in D_2O. [**1**] = 5 mM, [**6**] = 0.5 mM, mixing time 0.3 sec, T = 28 °C. Note the complete cancellation of the water peak at 4.6 ppm.

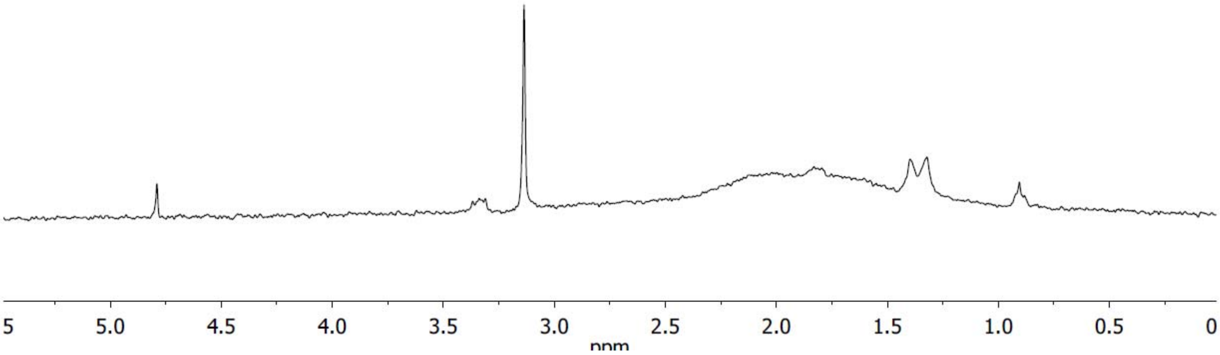

Figure S18. Diffusion filtered ^{1}H-NMR (300 MHz) spectra of a solution of **6** in D_2O. [**6**] = 0.5 mM, mixing time 0.3 sec, T = 28 °C. Note the complete cancellation of the water peak at 4.6 ppm.

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4) I. M. Rio-Echevarria , R. Tavano, V. Causin, E. Papini, F. Mancin, A. Moretto, *J. Am. Chem. Soc.* **2011**, *133*, 8-11.

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