Electronic Supplementary Information (ESI)

Sugar/Gadolinium-Loaded Gold Nanoparticles for Labelling and Imaging Cells by Magnetic Resonance Imaging

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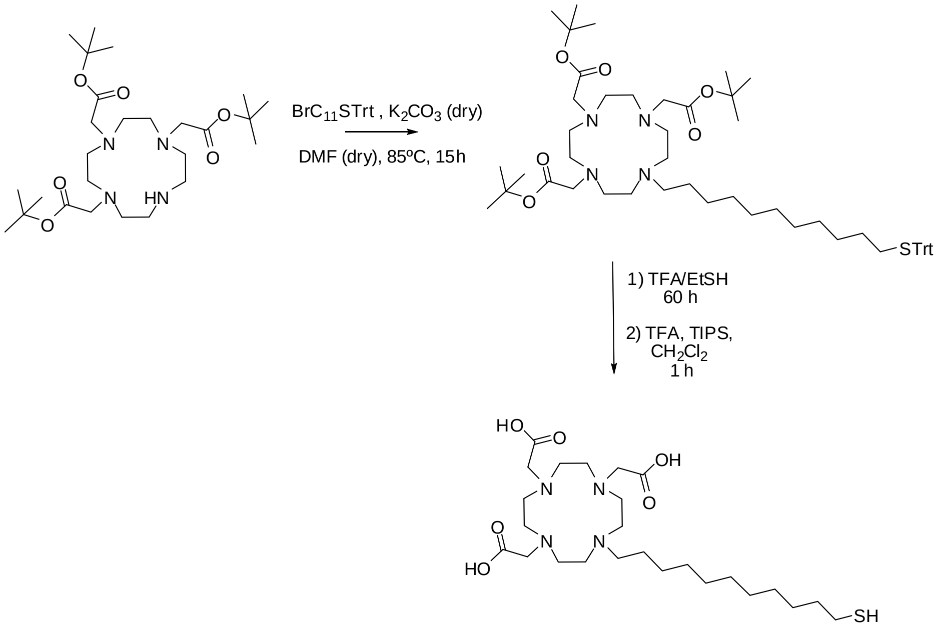
General. All chemicals were purchased as reagent grade from Sigma-Aldrich and were used without further purification. UV-Vis spectra were carried out with a Beckman Coulter DU 800 spectrometer. Infrared spectra (IR) were recorded from 4000 to 500 cm^{-1} with a JASCO FT/IR 410 model spectrometer: solids were pressed into a KBr plate and oils were subjected to attenuated total reflection (ATR). ^{1}H NMR and ^{13}C NMR spectra were recorded Bruker AVANCE (500 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to the residual signal of the solvent used. Coupling constants (*J*) are reported in Hz. Splitting patterns are described by using the following abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were carried out with an Esquire 6000 ESIIon Trap from Bruker Daltonics. High resolution mass spectra (HR-MS) were obtained using the matrix-assisted laser desorption/ionization (MALDI) technique with a 4700 Proteomics Analyzer (Applied Biosystems) with MALDI-time-of-flight (TOF) configuration. For transmission electron microscopy (TEM) examinations, a single drop (1 μL) of the aqueous solution (ca. 0.1 mg/mL in milliQ water) of the gold glyconanoparticles (GNPs) was placed onto a copper grid coated with a carbon film (Electron Microscopy Sciences). The grid was left to dry in air for several hours at room temperature. TEM analysis was carried out in a Philips JEOL JEM-2100F working both at 200 kV. The average diameter and number of gold atoms of the GNPs was deduced according to a previous work. [1S] House distilled water was further purified using a Milli-Q reagent grade water system (Millipore).

Synthesis of neoglycoconjugates. The neoglycoconjugates of β-glucose (2-mercaptoethyl β-D-glucopyranoside, GlcC_2S [2S]; 3-mercaptopropyl β-D-glucopyranoside, GlcC_3S [3S]; 5-mercaptopentyl β-D-glucopyranoside, GlcC_5S [4S]; 7-mercaptoheptyl β-D-glucopyranoside, GlcC_7S; 9-mercaptononyl β-D-glucopyranoside, GlcC_9S), β-galactose (5-mercaptopentyl β-D-galactopyranoside, GalC_5S), α-mannose (5-mercaptopentyl α-D-mannopyranoside, ManC_5S) [4S], β-maltose (5-mercaptopentyl α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside, *maltose*C_5S), β-cellobiose (5-mercaptopentyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside, *cellobiose*C_5S) and β-lactose (5-mercaptopentyl β-D-galactopyranosyl(1→4)-β-D-glucopyranoside, LacC_5S) [5S] having thiol-ending aliphatic linker were synthesized following established procedures based on the chemistry of carbohydrate protecting groups/glycosidation/deprotection of the glycoconjugates. The monosaccharides conjugated to a protected thiol-ending linker (GlcC_3SAc, GlcC_5SAc [4S], ManC_5SAc [4S], GalC_5SAc) were obtained after radical addition of thioacetic acid to the double bond of the corresponding peracetylated *n*-alkenyl glycosides, in turn obtained by Fisher glycosylation using alken-1-ols as glycosyl acceptors. A similar strategy was used to obtain *cellobiose*C_5SAc, but in this case a classic Köenigs-Knorr reaction was performed on peracetylated cellobiosyl bromide using penten-1-ol as acceptor before the radicalic addition of thioacetic acid. Longer thiol-ending aliphatic linkers were inserted into peracetylated glucose in order to obtain GlcC_7SAc and GlcC_9SAc after Fisher glycosylation using the

[1S] Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. Alkanethiolate Gold Cluster Molecules with Core Diameters from 1.5 to 5.2 nm: Core and Monolayer Properties as a Function of Core Size. *Langmuir* **1998**, *14*, 17-30.
[2S] Ojeda, R.; de Paz, J. L.; Barrientos, A. G.; Martín-Lomas, M.; Penadés, S. Preparation of multifunctional glyconanoparticles as a platform for potential carbohydrate-based anticancer vaccines. *Carbohydr. Res.* **2007**, 342, 448–459.
[3S] Houseman, B. T.; Gawalt, E. S.; Mrksich, M. Maleimide-Functionalized Self-Assembled Monolayers for the Preparation of Peptide and Carbohydrate Biochips. *Langmuir,* **2003**, 19, 1522-1531.
[4S] Martínez-Ávila, O.; Hijazi, K.; Marradi, M.; Clavel, C.; Campion, C.; Kelly, C.; Penadés, S. Gold Manno-Glyconanoparticles: Multivalent Systems to Block HIV-1 gp120 Binding to the Lectin DC-SIGN. *Chem. Eur. J.* **2009**, 15, 9874-9888.
[5S] Barrientos, A. G.; de la Fuente, J. M.; Rojas, T. C.; Fernández , A.; Penadés, S. Gold Glyconanoparticles: Synthetic Polyvalent Ligands Mimicking Glycocalyx-Like Surfaces as Tools for Glycobiological Studies. *Chem. Eur. J.*, **2003**, 9, 1909-1921.

corresponding bromo-alcohols as acceptors and further displacement of the bromine by nucleophilic substitution. This latter approach was also used to obtain *maltose*C_5SAc. On the other hand, anomeric trichloroacetimidates were used as glycosyl donors to obtain lactose- and glucose-conjugates with five and two carbon-atoms linkers respectively by using pent-4-en-1-ol and 2-bromoethanol as acceptors (LacC_5SAc, GlcC_2SAc). [5S] Methanolysis [6S] was used as final step to deprotect the *S*-acetyl and *O*-acetyl protecting groups (*O*-benzoyl in the case of LacC_5S). The glycosylation reactions were highly diastereoselective (> 95%) and the major anomer (β for glucose, galactose, maltose and lactose, and α for mannose conjugates).

Synthesis of 1, 4, 7-tris(carboxymehyl)-10-(11-mercaptoundecyl)-1, 4, 7, 10-tetraazacyclododecane ($SC_{11}DO3A$).



1, 4, 7-tris(tertbutylacetate)-10-(11-thiotriphenylundecyl)-1, 4, 7, 10-tetraazacyclododecane: K_2CO_3 anhydrous (400.0 mg, 2.9 mmol, 3.0 eq.) was added to a solution of DO3A^{t}Bu (500.0 mg, 1.0 mmol, 1.0 eq.) in DMF dry (12.5 mL). Then, the linker *S*-11-bromoundecyl ethanethioate (791.0 mg, 1.5 mmol, 1.5 eq.) was added and the mixture was stirred under argon atmosphere at 85 ^{o}C for 15 hours. After concentrating, the resulting product was purified by column chromatography (d = 3 cm; h = 11 cm) using CH_2Cl_2/MeOH 9/1 as an eluent to give the corresponding TrtSC_{11} DO3A^{t}Bu (963 mg).
R_f =0.47 (CH_2Cl_2/MeOH 9/1).^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50-7.20 (m, 15H, Ph), 3.70-2.20 (m, 24H, -NCH_2-), 2.12 (t, 2H, J=7.2 Hz, -CH_2SPh), 1.60-1.30 (m, 27H, *tert*-butyl),

[6S] Zemplén, G. Decomposition of reducing disaccharides, VII Determination of the constitution of maltose. *Ber. Dtsch. Chem. Ges.* **1927**, 60, 1555-1564.

1.30-1.10 (m, 17H, -CH_2-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (*C*OO^{t}Bu), 144.8, 129.4, 127.6 and 126.3 (4 *C*-Ph), 81.6 (-*C*CH_3) 66.2 (-*C*Ph_3), 56.7 (-*C*H_2N-), 52.5 (-N*C*$H_2CH_2CH_2$-), 52.5-50.1 (-N*C*H_2*C*H_2N-), 47.6 (-N*C*H_2CH_2N-), 31.8 (-*C*H2S-), 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.6, 27.4, 27.3, 26.3 (-CH_2CH_2). MS (ESI) *m/z*: 943 $[M+H]^+$; Calcd. MS *m/z* 942.6 [M]

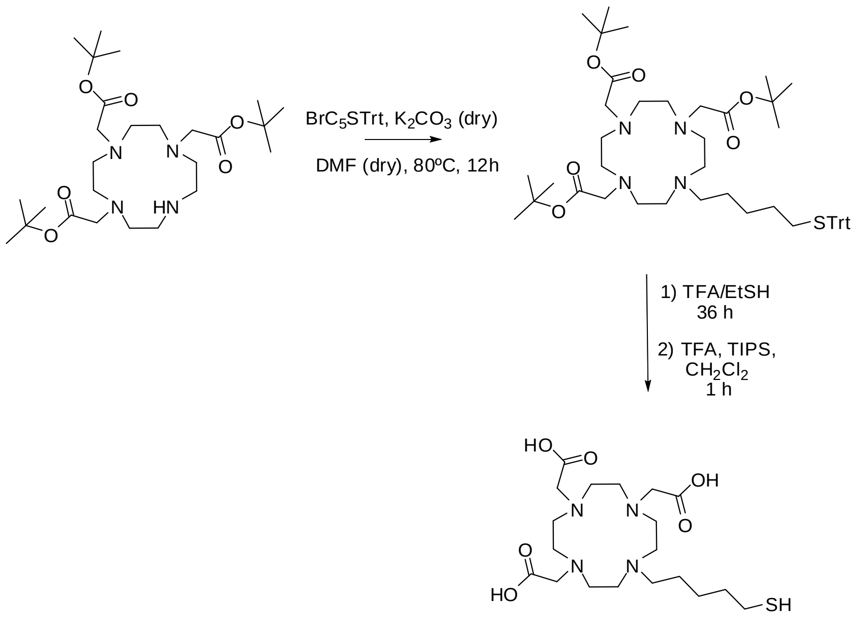
1, 4, 7-tris(carboxymethyl)-10-(11-mercaptoundecyl)-1, 4, 7, 10-tetraazacyclododecane: Trifluoroacetic acid (TFA) (15.7 mL, 204 mmol, 200 eq.) was added to a solution of $TrtSC_{11}DO3A^tBu$ (963.0 mg, 1.0 mmol, 1.0 eq.) in ethanethiol (EtSH) (51 mL) and it was stirred for 60 hours. The reaction mixture was concentrated and, then, CH_2Cl_2 (28 mL), trifluoroacetic acid (TFA) (3 mL) and triisopropylsilyl (TIPS) (3 mL) were added. The mixture was stirred for 1 hour and concentrated. The concentrated product was dissolved in CH_2Cl_2/MeOH 1/1 (3 mL) and it was poured into Et_2O (500 mL) to afford a white solid (overnight). This product was dissolved in CH_2Cl_2/MeOH 1/1 (40 mL), concentrated and freeze-dried to afford $SC_{11}DO3A$ (608 mg, 0.9 mmol, 89%).

^{1}H NMR (D_2O, 500 MHz) δ 3.75-3.03 (m, 22H, -CH_2-ciclen), 2.64 (s, 2H, -CH_2-S-S- CH_2), 2.46 (t, 2H, J= 7.4 Hz), 1.62-1.48 (m, 2H, CH_2-CH_2-N-), 1.23-1.21 (m, 18H, -CH_2-); ^{13}C NMR (75 MHz, DMSO, 80 ºC) δ 173.8 (*C*OOH), 57.1 (-*C*H_2-COOH) 54.3, 53.4, 51.8, 51.1 (-N*C*H_2*C*H_2N-) 32.7 (-*C*H_2S-), 31.4, 30.7, 30.4, 30.3, 29.6, 29.0 (- CH_2CH_2-). IR (KBr) 3417, 2925, 2853, 1637, 1406, 1203 cm^{-1}; MS (ESI) m/z: 531 $[M-H]^-$. Calcd. MS *m/z* 532.3 [M]

Incubation of $SC_{11}DO3A$ derivatives with Gd (III) ($SC_{11}DO3A$-Gd). $SC_{11}DO3A$ (1 eq.) in 1.5 mL of HEPES buffer (pH=7.4) was incubated with 0.9 equivalents of an aqueous 0.1 M solution of $GdCl_3$ (0.5 mL) at 25 ºC. The freshly prepared HEPES solution was used for the ligand place exchange reaction (LPE) with the 100% sugar nanoparticles.

1, 4, 7-tris(carboxymehyl)-10-(11-mercaptoundecyl)-1, 4, 7, 10-tetraazacyclododecane-Gd ($SC_{11}DO3A$-Gd). The $SC_{11}DO3A$-Gd complex can form micelles at 3 mM concentration. The relaxativity value r_1 of the $SC_{11}DO3A$-Gd ligand below the critical micellar concentration (c.m.c) is r_1=6.6 $mM^{-1}s^{-1}$ and 16.3 $mM^{-1}s^{-1}$ above the c.m.c.; ^{17}O NMR: $q = 2.0 \pm 0.2$; IR (KBr): 3452, 2926, 2853, 1592,1397 cm^{-1}.

Synthesis of 1, 4, 7-tris(carboxymethyl)-10-(5-mercaptopentyl)-1, 4, 7, 10-tetraazacyclododecane (SC$_5$DO3A)



1, 4, 7-tris(tertbutylacetate)-10-(5-thiotriphenylpentyl)-1, 4, 7, 10-tetraazacyclododecane (MMS115): K_2CO_3 (95 mg, 0.69 mmol, 3 eq.) was added to a solution of DO3A^{t}Bu (118 mg, 0.23 mmol, 1.0 eq.) in DMF (3 mL). Then, the linker *S*-5-bromopentyl ethanethioate (146 mg, 0.34 mmol, 1.4 eq.) dissolved in DMF (1.5 mL) was added drop by drop and the mixture was stirred with refrigeration at 80 ^oC for 12 hours. The reaction mixture was diluted with CH_2Cl_2, filtered and concentrated. The resulting product was purified by column chromatography using a gradient of CH_2Cl_2/MeOH (from 0% to 5%) to give TrtSC$_5$DO3A^{t}Bu (179 mg, 0.21 mmol, 91 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.19 (m, 15H, Ph), 3.50-2.20 (ma, 24H, -NCH_2-), 2.13 (t, 2H, *J*=7.1 Hz, -CH_2SPh), 1.45 (s, 18H), 1.43 (s, 9H), 1.41-1.34 (m, 2H, -CH_2-CH$_2$STr), 1.33-1.24 (m, 4H, -CH_2-CH$_2$SPh and -CH_2-CH$_2$CH$_2$N-). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.5 (*C*OO*t*Bu), 172.7 (2C, *C*OO*t*Bu), 144.9 (3C, C1-Ph), 129.5 (6C, C3-Ph), 127.8 (6C, C2-Ph), 126.5 (3C, C4-Ph), 82.6 and 82.3 (3C, COO*C*(CH$_3$)$_3$), 66.4 (–*C*Ph$_3$), 56.4, 55.8 and 54.1 (4C, -N*C*H$_2$COO*t*Bu and –N*C*H$_2$CH$_2$CH$_2$-), 50.3 (broad signal (8C, t), -N*C*H$_2$*C*H$_2$N-) 31.9 (-*C*H$_2$STr), 31.6 (*C*H$_2$STr), 28.5 (-*C*H$_2$CH$_2$STr), 27.9, 27.8. IR (KBr): 3084, 3058, 2957, 2931, 2852, 1723, 1456, 1393, 1368 cm^{-1}. MS (ESI) *m/z*: 859.6 [M+H]$^+$; Calcd. MS *m/z* 859.2 [M]

1, 4, 7-tris(carboxymethyl)-10-(5-mercaptopentyl)-1, 4, 7, 10-tetraazacyclododecane (MME014): Trifluoroacetic acid (TFA) (3.2 mL, 42 mmol, 200 eq.) was added to a solution of TrtSC$_5$DO3A^{t}Bu (179 mg, 0.21 mmol, 1 eq.) in ethanothiol (EtSH) (10 mL) and it was stirred for 36 hours. Triisopropylsilane (TIPS) (430 uL, 21 mmol, 100 eq.) was added and the mixture was stirred for 1 hour. The crude was concentrated, the obtained product was dissolved in CH_2Cl_2/MeOH 1/1 and it was added into cold Et_2O (overnight). The obtained product was freeze-dried to afford SC_5DO3A (85 mg, 0.189 mmol, 90%).

^{1}H NMR (D_2O, 500 MHz) δ 4.05-4.03 (bs, 2H, -NC*H*$_2$COOH), 3.67-3.43 (m, 12H, -NC*H*$_2$-), 3.30 (t, 2H, *J*= 7.1 Hz, -NC*H*$_2$CH$_2$CH$_2$-), 3.21-3.02 (m, 8H, -NC*H*$_2$-), 2.78 (t, 2H, *J*= 7.0 Hz, -C*H*$_2$S), 1.81-1.74 (m, 4H, -C*H*$_2$-CH$_2$S and -CH$_2$C*H*$_2$CH$_2$N-), 1.51-1.49 (m, 2H, -C*H*$_2$-CH$_2$CH$_2$N-). ^{13}C NMR (D_2O, 500 MHz) δ 174.3 (*C*OOH), 55.9 (-N*C*H$_2$COOH), 54.3 (–N*C*H$_2$CH$_2$CH$_2$-), 53.1, 51.7, 49.9, 48.9, 48.4 and 48.1 (-N*C*H$_2$*C*H$_2$N- and –N*C*H$_2$COOH), 37.4 (-*C*H$_2$S-), 27.7 (-*C*H$_2$CH$_2$S-), 24.6 (-*C*H$_2$CH$_2$CH$_2$N-), 22.4 (-CH$_2$*C*H$_2$CH$_2$N-). IR (KBr): 3550-3250, 2928, 2853, 1683, 1409, 1203, 1133 cm^{-1}. MS (ESI) *m/z* 449.2 [M+H]$^+$. Calcd. MS *m/z* 448.2 [M]. HR-FAB-MS *m/z* 471.223 [M+Na]$^+$ ($C_{19}H_{36}N_4NaO_6S^+$ requires 471.225).

Incubation of SC_5DO3A derivatives with Gd (III) (SC_5DO3A-Gd). SC_5DO3A (1 eq.) in 1.5 mL of HEPES buffer (pH=7.4) was incubated with 0.9 equivalents of an aqueous 0.1 M solution of $GdCl_3$ (0.5 mL) at 25 ºC. The freshly prepared HEPES solution was used for the ligand place exchange reaction (LPE) with the 100% sugar nanoparticles.

1, 4, 7-tris(carboxymethyl)-10-(5-mercaptopentyl)-1, 4, 7, 10-tetraazacyclododecane-Gd (SC_5DO3A-Gd). r_1=6.4 mM^{-1}s^{-1}; ^{17}O NMR: $q = 2.1 \pm 0.2$; IR (KBr): 3550-3250, 2928, 2853, 1588, 1397 cm^{-1}.

Preparation of 100% sugar-coated glyconanoparticles.

General procedure. Gold glyconanoparticles 100%-coated with the glycoconjugates of β-glucose ($GlcC_2S$, $GlcC_3S$, $GlcC_5S$, $GlcC_7S$, $GlcC_9S$), β-galactose ($GalC_5S$), α-mannose ($ManC_5S$), β-lactose ($LacC_5S$), β-maltose (*maltose*C_5S), and β-cellobiose (*cellobiose*C_5S) were prepared by *in situ* procedure through reduction of a gold salt ($HAuCl_4$) with $NaBH_4$ in the presence of the glycoconjugates following a reported procedure. [5S]

Briefly, a 0.025 M solution of $HAuCl_4$ (1 eq.) in MilliQ water was added to a 0.012 M solution of glycoconjugate (3 eq.) in MeOH. A freshly prepared 1 M solution (27 eq.) of $NaBH_4$ was then added in four portions as the reaction is exothermic and the mixture was stirred for 2 hours in an orbital shaker at 25 ºC and 180 rpm. The supernatant was taken off from the batches and the residue was washed five times with MeOH. The residue was dissolved in MilliQ water and purified by dialysis (MWCO=10000) using 5–10 cm segments of SnakeSkin pleated dialysis tubing (Pierce, 10000 MWCO), which were placed in a 3 L beaker of water, recharging with fresh distilled water every 3–4 h over the course of 72 h. The solution in the membrane was then freeze-dried to afford the GNP.

$GlcC_2S$-Au glyconanoparticles (DAP284): $GlcC_2SH$ (40 mg, 0.168 mmol, 3 eq.), MeOH (16.4 mL), $HAuCl_4$ (9.5 mg, 0.028 mmol, 1 eq.), $NaBH_4$ (28.5 mg, 0.756 mmol, 27 eq.). After freeze-drying, 7.1 mg of a black solid was obtained.

TEM: 1.7 ± 0.2 nm. IR (KBr): 3430 (broad band), 2917, 2848, 1078 cm^{-1}. UV: No surface plasmon band. ^1H NMR (D_2O, 500 MHz): δ 4.53 (bs, 1H, H1), 4.29-3.49 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{201}(C_8H_{16}O_6S)_{121}$ C 16.93 %, H 2.84 %, S 5.65 %; Found: C 16.94 %, H 2.93 %, S 5.74 %.

$GlcC_3S$-Au glyconanoparticles (AI099): $GlcC_3SH$ (50 mg, 0.197 mmol, 3 eq.), MeOH (16.4 mL), $HAuCl_4$ (22.26 mg, 0.066 mmol, 1 eq.), $NaBH_4$ (66.92 mg, 1.77 mmol, 27 eq.). After freeze-drying, 9.2 mg of a black solid was obtained.

TEM: 2.1± 0.3 nm. IR (KBr): 3401 (broad band), 2914, 2857, 1071 cm^{-1}. UV: λ= 526 nm, surface plasmon band. ^1H NMR (D_2O, 500 MHz): δ 4.46 (bdd, 1H, H1), 4.10-3.23 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 2.16 (bs, -CH_2). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{314}(C_9H_{17}O_6S)_{55}$ C 7.85%, H 1.24%, S 2.33%; Found: C 7.76 %, H 1.51 %, S 3.90 %.

$GlcC_5S$-Au glyconanoparticles (AI084): $GlcC_5S$ (120 mg, 0.425 mmol, 3 eq.), MeOH (35.4 mL), $HAuCl_4$ (48.25 mg, 0.142 mmol, 1 eq.), $NaBH_4$ (145.0 mg, 3.83 mmol, 27 eq.). After freeze-drying, 23 mg of a black solid was obtained.

TEM: double distribution 1.2 ± 0.9 nm (77%) and 4.9 ± 0.6 nm (23%). IR (KBr): 3417 (broad band), 2917, 2847, 1071 cm^{-1}. UV: λ= 525 nm, surface plasmon band. ^1H NMR (D_2O, 500 MHz) δ 4.44 (bs, 1H, H1), 4.00-3.24 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 2.00-1.50 (bm, 6H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{140}(C_{11}H_{21}O_6S)_{87}$ C 22.08 %, H 3.54 %, S 5.36 %; Found: C 22.07 %, H 3.95 %, S 4.51 %.

$GlcC_7S$-Au glyconanoparticles (AI100): $GlcC_7SH$ (40 mg, 0.129 mmol, 3 eq.), MeOH (10.7 mL), $HAuCl_4$ (14.61 mg, 0.043 mmol, 1 eq.), $NaBH_4$ (43.89 mg, 1.16 mmol, 27 eq.). After freeze-drying, 9.5 mg of a black solid was obtained.

TEM: 1.9 ± 0.3 nm. IR (KBr): 3433 (broad band), 2920, 2850, 1071 cm^{-1}. UV: λ= 520 nm, surface plasmon band. ^1H NMR (D_2O, 500 MHz) δ 4.44 (d, 1H, H1), 3.95-3.20 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 1.78-1.23 (bm, 10H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{225}(C_{13}H_{25}O_6S)_{126}$ C 23.62%, H 3.81%, S 4.85%; Found: C 23.59%, H 3.94%, S 4.95%.

$GlcC_9S$-Au glyconanoparticles (AI102): $GlcC_9SH$ (30 mg, 0.089 mmol, 3 eq.), MeOH (7.4 mL), $HAuCl_4$ (10 mg, 0.029 mmol, 1 eq.), $NaBH_4$ (30.17 mg, 0.80 mmol, 27eq.). After freeze-drying, 8.5 mg of a black solid was obtained.

TEM: 2.1 ± 0.3 nm. IR (KBr): 3430 (broad band), 2920, 2847, 1071 cm^{-1}. UV: λ= 519 nm, surface plasmon band. ^1H NMR (D_2O, 500 MHz): δ 4.42 (d, 1H, H1), 3.95-3.31 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 1.83-1.23 (bm, 12H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{314}(C_{15}H_{29}O_6S)_{150}$ C 24.03%, H 3.90%, S 4.28%; Found: C 24.07 %, H 3.95%, S 4.51%.

$GalC_5S$-Au glyconanoparticles (AI113): $GalC_5S$ (40.6 mg, 0.144 mmol, 3 eq.), MeOH (12 mL), $HAuCl_4$ (16.3 mg, 0.048 mmol, 1 eq.), $NaBH_4$ (49.2 mg, 1.3 mmol, 27 eq.) After freeze-drying, 10.4 mg of a brown solid was obtained.

TEM: 1.8 ± 0.1 nm. IR (KBr): 3420 (broad band), 2920, 2850, 1074 cm^{-1}. UV: No surface plasmon band. ^1H NMR (D_2O, 500 MHz) δ 4.40 (bd, 1H, H1), 3.95-3.54 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 2.04-1.48 (bm, 6H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{201}(C_{11}H_{21}O_6S)_{97}$ C 19.16%, H 3.07%, S 4.65%; Found: C 19.13 %, H 3.19 %, S 5.54 %.

$ManC_5S$-Au glyconanoparticles (AI111): $ManC_5S$ (40 mg, 0.142 mmol, 3 eq.), MeOH (11.8 mL), $HAuCl_4$ (16 mg, 0.047 mmol, 1 eq.), $NaBH_4$ (48.3 mg, 1.3 mmol, 27 eq.). After freeze-drying, 7.8 mg of a brown solid was obtained.

TEM: 2.1 ± 0.3 nm. IR (KBr): 3420 (broad band), 2923, 2847, 1093cm^{-1}. UV: λ= 520 nm, surface plasmon band. ^1H NMR (D_2O, 500 MHz) δ 3.89-3.49 (bm, 8H, OCH_2, H2, H3, H4, H5, H6a, H6b), 1.89-1.02 (bm, 6H, -CH_2-). CH_2S not detected presumably due to gold quenching. Anomeric proton not detected due to water suppression pulse in NMR. Elemental analysis calculated for $Au_{314}(C_{11}H_{21}O_6S)_{148}$ C 18.89%, H 3.03%, S 4.59%; Found: C 18.82 %, H 3.17 %, S 5.20 %.

$LacC_5S$-Au glyconanoparticles (AI114): $LacC_5S$ (39.6 mg, 0.089 mmol, 3 eq.), MeOH (7.4 mL), $HAuCl_4$ (10.2 mg, 0.030 mmol, 1 eq.), $NaBH_4$ (30.3 mg, 0.801 mmol, 27 eq.). After freeze-drying, 9.9 mg of a clear solid was obtained.

TEM: 2.0 ± 0.3 nm. IR (KBr): 3404 (broad band), 2920, 2853, 1071 cm^{-1}. UV: No surface plasmon band. ^1H NMR (D_2O, 500 MHz) δ 4.54 (bs, 2H, H1, H1’), 4.15-3.37 (bm, 14H, OCH_2, H2’, H3’, H4’, H5’, H6’a, H6’b, H2, H3, H4, H5, H6a, H6b), 2.29-1.45 (bm, 6H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for: $Au_{314}(C_{17}H_{31}O_{11}S)_{138}$ C 22.90%, H 3.50%, S 3.60%; Found: C 22.84 %, H 3.85 %, S 5.06 %.

***cellobiose*C_5S-Au glyconanoparticles (AI112):** *cellobiose*C_5S (40 mg, 0.090 mmol, 3 eq.), MeOH (7.5 mL), $HAuCl_4$ (10.2 mg, 0.03 mmol, 1 eq.), $NaBH_4$ (30.6 mg, 0.81 mmol, 27 eq.) After freeze-drying, 8.0 mg of a black solid was obtained.

TEM: 2.0 ± 0.1 nm. IR (KBr): 3420 (broad band), 2917, 2850, 1074 cm^{-1}. UV: λ= 520 nm, surface plasmon band. ^{1}H NMR (D_2O, 500 MHz) Broad signals. Elemental analysis calculated for $Au_{314}(C_{17}H_{31}O_{11}S)_{73}$ C 15.82%, H 2.42%, S 2.48%; Found: C 15.83 %, H 2.70 %, S 3.79 %.

***maltose*C_5S-Au glyconanoparticles (AI115):** *maltose*C_5S (30 mg, 0.067 mmol, 3 eq.), MeOH (5.6 mL), $HAuCl_4$ (7.5 mg, 0.022 mmol, 1 eq.), $NaBH_4$ (22.8 mg, 0.603 mmol, 27 eq.). After freeze-drying, 6.7 mg of a brown solid was obtained.

TEM: 2.1 ± 0.3 nm. IR (KBr): 3423 (broad band), 2917, 2847, 1071 cm^{-1}. UV: λ= 520 nm, surface plasmon band. ^{1}H NMR (D_2O, 500 MHz) δ 5.45 (bs, 1H, H1'), 4.53 (bs, 1H, 1H), 4.16-3.64 (bm, 14H, OCH_2, H2', H3', H4', H5', H6'a, H6'b, H2, H3, H4, H5, H6a, H6b), 1.90-1.46 (bm, 6H, -CH_2-). CH_2S not detected presumably due to gold quenching. Elemental analysis calculated for $Au_{314}(C_{17}H_{31}O_{11}S)_{159}$ C 24.53%, H 3.75%, S 3.85%; Found: C 24.52 %, H 3.95 %, S 3.45 %.

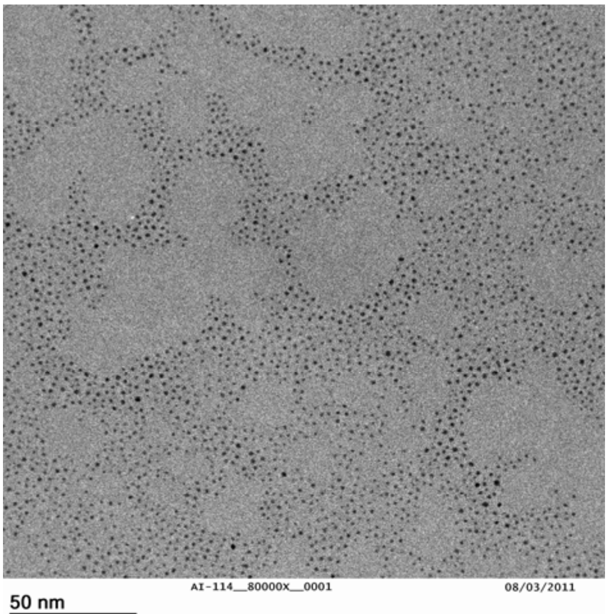


Figure S1. TEM image of LacC_5SGNP. To obtain the size distribution at least 300 particles were count and no less than 3 different TEM photographs per GNP were used.

Preparation of Gd-glyconanoparticles (Gd-GNPs) incorporating DO3A derivates by LPE reaction.

General procedure. Gold GNPs (1 eq. of the sugar) were dissolved in MilliQ water and previously prepared SC_xDO3A-Gd (1.1 eq.) solution was added. The mixture was shaked for 44 hours at 25 ºC and 180 r.p.m. The solution was filtered with "*Amicon*" filters (MWCO=10000 $gmol^{-1}$). The Gd-GNPs were diluted in MilliQ water and freeze-dried.

$GlcC_2S$-Au-$SC_{11}DO3A$-Gd glyconanoparticles (AI107): $GlcC_2S$-Au (5.35 mg, 0.077 µmol, 9.52 µmol of glucose, 1 eq. of glucose) was dissolved in 5 mL of MilliQ water and previously prepared $SC_{11}DO3A$-Gd^{3+} solution (5.1 mg, 9.57 µmol, 1.1 eq., 95.7 µL of Gd^{3+} solution) was added. 6.84 mg of the corresponding Gd-GNP AI107 were obtained.

TEM: 1.8 ± 0.2 nm. UV: No surface plasmon band. IR (KBr): 3411 (broad band), 2923, 2851, 1594, 1400, 1078 cm^{-1}. ^1H NMR (D_2O, 500 MHz): δ broad signal due to Gd ion. ICP: Gd 3.38%. Calculated average formula: $Au_{201}(C_8H_{15}O_6S)_{105}(C_{25}H_{47}N_4O_6S)_{16}Gd_{16}$ (Au 52.27 %, Gd 3.32% and S 5.12 %). At 1.4 T, r_1= 7.1 $(smM)^{-1}$ and r_2= 11.1 $(smM)^{-1}$; at 11.7 T, r_1= 1.8 $(smM)^{-1}$.

$GlcC_3S$-Au-$SC_{11}DO3A$-Gd glyconanoparticles (AI106): The $GlcC_3S$-Au glyconanoparticle (4.60 mg, 0.241 µmol, 3.37 µmol of glucose, 1 eq. of glucose) was dissolved in 5 mL of MilliQ water and previously prepared $SC_{11}DO3A$-Gd^{3+} solution (2.0 mg, 3.75 µmol, 1.1 eq., 37.5 µL of Gd^{3+} solution) was added. 4.09 mg of the corresponding Gd-GNP AI106 were obtained.

TEM: 1.9± 0.3 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3420 (broad band), 2920, 2847, 1597, 1078 cm^{-1}. ^1H NMR (D_2O, 500 MHz): δ broad signal due to Gd ion. ICP: Gd 3.34%. Calculated average formula: $Au_{314}(C_9H_{17}O_6S)_{20}(C_{25}H_{47}N_4O_6S)_{33}Gd_{33}$ (Au 74.35%, Gd3.21% and S 2.12%). At 1.4 T, r_1= 6.3 $(smM)^{-1}$ and r_2= 10.5 $(smM)^{-1}$; at 11.7 T, r_1= 2.1 $(smM)^{-1}$.

$GlcC_5S$-Au-$SC_{11}DO3A$-Gd glyconanoparticles (AI101): The $GlcC_5S$-Au glyconanoparticle (8.15 mg, 0.310 µmol, 11.78 µmol of glucose, 1 eq. of glucose) was dissolved in 6 mL of MilliQ water and previously prepared $SC_{11}DO3A$-Gd^{3+} solution (6.5 mg, 12.2 µmol, 1.1 eq., 122 µL of Gd^{3+} solution) was added. 8.43 mg of the corresponding Gd-GNP AI101 were obtained.

TEM: double distribution 1.5 ± 0.3 nm (75%) and 4.3 ± 0.6 nm (25%). UV: λ= 521 nm, surface plasmon band. IR (KBr): 3443 (broad band), 2920, 2848, 1616, 1088 cm^{-1}. ^1H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 4.68 %. Calculated average formula:

$Au_{140}(C_{11}H_{21}O_6S)_{70}(C_{25}H_{47}N_4O_6S)_{17}Gd_{17}$ (Au 46.75 %, Gd 4.53% and S 4.73 %). At 1.4 T, r_1= 7.4 $(smM)^{-1}$ and r_2= 11.8 $(smM)^{-1}$; at 11.7 T, r_1= 2.5 $(smM)^{-1}$.

GlcC$_5$S-Au-SC$_5$DO3A-Gd glyconanoparticles (AI119): The GlcC$_5$S-Au glyconanoparticle (3.87 mg, 0.185 μmol, 3.51 μmol of glucose, 1 eq. of glucose) was dissolved in 4mL of MilliQ water and previously prepared SC$_5$DO3A-Gd^{3+} solution (3.0 mg, 3.79 μmol, 1.1 eq., 38.0 μL of Gd^{3+} solution) was added. 3.3 mg of the corresponding Gd-GNP AI119 were obtained.

TEM: double distribution 2.0 ± 0.3 nm (75%) and 4.8 ± 0.5 nm (25%). UV: λ= 514 nm, surface plasmon band. IR (KBr): 3440 (broad band), 2917, 2848, 1616, 1081 cm^{-1}

^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.14 %. Calculated average formula: $Au_{140}(C_{11}H_{21}O_6S)_{76}(C_{19}H_{35}N_4O_6S)_{11}Gd_{11}$ (Au 49.58%, Gd 3.11% and S 5.02%). At 1.4 T, r_1= 16.9 $(smM)^{-1}$ and r_2= 27.4 $(smM)^{-1}$; at 11.7 T, r_1= 4.0 $(smM)^{-1}$.

GlcC$_7$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI104): The GlcC$_7$S-Au glyconanoparticle (5.66 mg, 0.049 μmol, 8.5 μmol of glucose, 1 eq. of glucose) was dissolved in 5 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (4.9 mg, 9.2 μmol, 1.1 eq., 92.0 μL of Gd^{3+} solution) was added. 7.40 mg of the corresponding Gd-GNP AI104 were obtained.

TEM: 1.8 ± 0.3 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3421 (broad band), 2920, 2848, 1600, 1078 cm^{-1}. ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 4.14 %. Calculated average formula: $Au_{225}(C_{13}H_{25}O_6S)_{100}(C_{25}H_{47}N_4O_6S)_{26}Gd_{26}$ (Au 47.57%, Gd 4.39% and S 4.34%). At 1.4 T, r_1= 7.1 $(smM)^{-1}$ and r_2= 11.8 $(smM)^{-1}$; at 11.7 T, r_1= 2.0 $(smM)^{-1}$.

GlcC$_9$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI105): The GlcC$_9$S-Au glyconanoparticle (5.68 mg, 0.050 μmol, 7.6 μmol of glucose, 1 eq. of glucose) was dissolved in 5 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (4.3 mg, 8.1 μmol, 1.1 eq., 81.0 μL of Gd^{3+} solution) was added. 7.49 mg of the corresponding Gd-GNP AI105 were obtained.

TEM: 1.8 ± 0.2 nm. UV: λ= 519 nm, surface plasmon band. IR (KBr): 3433 (broad band), 2917, 2848, 1625, 1078 cm^{-1} ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.21%. Calculated average formula: $Au_{314}(C_{15}H_{29}O_6S)_{125}(C_{25}H_{47}N_4O_6S)_{25}Gd_{25}$ (Au 51.01%, Gd 3.24% and S 3.97%). At 1.4 T, r_1= 7.5 $(smM)^{-1}$ and r_2= 13.0 $(smM)^{-1}$; at 11.7 T, r_1= 2.7 $(smM)^{-1}$.

GalC$_5$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI118): The GalC$_5$S-Au glyconanoparticle (4.86 mg, 0.046 μmol, 7.05 μmol of galactose, 1 eq. of galactose) was dissolved in 4.2 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (4.1 mg, 7.7 μmol, 1.1 eq., 77.0 μL of Gd^{3+} solution) was added. 4.15 mg of the corresponding Gd-GNP AI118 were obtained.

TEM: 1.7 ± 0.1 nm. UV: No surface plasmon band. IR (KBr): 3436 (broad band), 2924, 2851, 1594, 1401, 1084 cm^{-1} ^1H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 4.18 %. Calculated average formula: $Au_{201}(C_{11}H_{21}O_6S)_{77}(C_{25}H_{47}N_4O_6S)_{20}Gd_{20}$ (Au 52.76%, Gd 4.19% and S 4.15%). At 1.4 T, r_1= 8.0 $(smM)^{-1}$ and r_2= 12.9 $(smM)^{-1}$; at 11.7 T, r_1= 2.1 $(smM)^{-1}$.

GalC$_5$S-Au-SC$_5$DO3A-Gd glyconanoparticles (AI121): The GalC$_5$S-Au glyconanoparticle (3.26 mg, 0.031 μmol, 4.3 μmol of galactose, 1 eq. of galactose) was dissolved in 3 mL of MilliQ water and previously prepared SC$_5$DO3A-Gd^{3+} solution (3.5 mg, 0.44 μmol, 1.1 eq., 44.3 μL of Gd^{3+} solution) was added. 3.14 mg of the corresponding Gd-GNP AI121 were obtained.

TEM: 1.7 ± 0.2 nm. UV: No surface plasmon band. IR (KBr): 3430 (broad band), 2917, 2851, 1625, 1410, 1081 cm^{-1} ^1H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.62 %. Calculated average formula: $Au_{201}(C_{11}H_{21}O_6S)_{80}(C_{19}H_{35}N_4O_6S)_{17}Gd_{17}$ (Au 54.70%, Gd 3.69% and S 4.30%). At 1.4 T, r_1= 18.0 $(smM)^{-1}$ and r_2= 30.4 $(smM)^{-1}$; at 11.7 T, r_1= 4.1 $(smM)^{-1}$.

ManC$_5$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI116): The ManC$_5$S-Au glyconanoparticle (4.72 mg, 0.046 μmol, 6.74 μmol of mannose, 1 eq. of mannose) was dissolved in 4.2 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (4 mg, 7.5 μmol, 1.1 eq., 75.1 μL of Gd^{3+} solution) was added. 5.44 mg of the corresponding Gd-GNP AI116 were obtained.

TEM: 2.4 ± 0.4 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3417 (braod band), 2920, 2848, 1594, 1401, 1087 cm^{-1}. ^1H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.0 %. Calculated average formula: $Au_{314}(C_{11}H_{21}O_6S)_{127}(C_{25}H_{47}N_4O_6S)_{21}Gd_{21}$ (Au 55.20%, Gd 2.95% and S 4.24%). At 1.4 T, r_1= 9.7 $(smM)^{-1}$ and r_2= 16.3 $(smM)^{-1}$; at 11.7 T, r_1= 2.3 $(smM)^{-1}$.

ManC$_5$S-Au-SC$_5$DO3A-Gd glyconanoparticles (AI120): The ManC$_5$S-Au glyconanoparticle (2.07 mg, 0.0199 μmol, 2.96 μmol of mannose, 1 eq. of mannose) was dissolved in 3.0 mL of MilliQ water and previously prepared SC$_5$DO3A-Gd^{3+} solution (2.5 mg, 3.2 μmol, 1.1 eq., 31.6 μL of Gd^{3+} solution) was added. 3.60 mg of the corresponding Gd-GNP AI120 were obtained.

TEM: 1.8 ± 0.2 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3421 (broad band), 2927, 2851, 1594, 1401, 1087 cm^{-1} ^1H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion.

ICP: Gd 4.06 %. Calculated average formula: $Au_{314}(C_{11}H_{21}O_6S)_{119}(C_{19}H_{35}N_4O_6S)_{29}Gd_{29}$ (Au 54.80%, Gd 4.04% and S 4.20%). At 1.4 T, r_1= 15.5 $(smM)^{-1}$ and r_2= 25.6 $(smM)^{-1}$; at 11.7 T, r_1= 3.8 $(smM)^{-1}$.

LacC$_5$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI123): The LacC$_5$S-Au glyconanoparticle (4.41 mg, 0.032 µmol, 4.94 µmol of lactose, 1 eq. of lactose) was dissolved in 4.0 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (2.8 mg, 5.3 µmol, 1.1 eq., 52.6 µL of Gd^{3+} solution) was added. 4.97 mg of the corresponding Gd-GNP AI123 were obtained.

TEM: 1.7 ± 0.3 nm. UV: No surface plasmon band. IR (KBr): 3424 (broad band), 2924, 2851, 1606, 1397, 1081 cm^{-1} ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 2.69 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_{11}S)_{116}(C_{25}H_{47}N_4O_6S)_{22}Gd_{22}$ (Au 48.15%, Gd 2.69% and S 3.44%). At 1.4 T, r_1= 12.9 $(smM)^{-1}$ and r_2= 15.7 $(smM)^{-1}$; at 11.7 T, r_1= 4.4 $(smM)^{-1}$.

LacC$_5$S-Au-SC$_5$DO3A-Gd glyconanoparticles (AI126): The LacC$_5$S-Au glyconanoparticle (2.8 mg, 0.023 µmol, 3.14 µmol of lactose, 1 eq. of lactose) was dissolved in 3.0 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (3 mg, 3.8 µmol, 1.1 eq., 38.0 µL of Gd^{3+} solution) was added. 2.2 mg of the corresponding Gd-GNP AI126 were obtained.

TEM: 1.6 ± 0.2 nm. UV: No surface plasmon band. IR (KBr): 3417 (broad band), 2924, 2848, 1606, 1397, 1078 cm^{-1}. ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.69 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_{11}S)_{108}(C_{19}H_{35}N_4O_6S)_{30}Gd_{30}$ (Au 48.36%, Gd 3.69% and S 3.46%). At 1.4 T, r_1= 17.0 $(smM)^{-1}$ and r_2= 29.2 $(smM)^{-1}$; at 11.7 T, r_1= 3.8 $(smM)^{-1}$.

***cellobiose*C$_5$S-Au-SC$_{11}$DO3A-Gd glyconanoparticles (AI117):** The *cellobiose*C$_5$S-Au glyconanoparticle (5.53 mg, 0.131 µmol, 4.32 µmol of cellobiose, 1 eq. of cellobiose) was dissolved in 4.5 mL of MilliQ water and previously prepared SC$_{11}$DO3A-Gd^{3+} solution (2.3 mg, 7.5 µmol, 1.1 eq., 43.17 µL of Gd^{3+} solution) was added. 5.84 mg of the corresponding Gd-GNP AI117 were obtained.

TEM: 1.8 ± 0.2 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3421 (broad band), 2924, 2848, 1622, 1074 cm^{-1} ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 2.12 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_6S)_{61}(C_{25}H_{47}N_4O_6S)_{12}Gd_{12}$ (Au 66.97%, Gd 2.04% and S 2.53%). At 1.4 T, r_1= 11.2 $(smM)^{-1}$ and r_2= 20.9 $(smM)^{-1}$; at 11.7 T, r_1= 2.8 $(smM)^{-1}$.

***cellobiose*C_5S-Au-SC_5DO3A-Gd glyconanoparticles (AI125):** The *cellobiose*C_5S-Au glyconanoparticle (1.03 mg, 0.024 µmol, 0.781 µmol of cellobiose, 1 eq. of cellobiose) was dissolved in 2 mL of MilliQ water and previously prepared SC_5DO3A-Gd^{3+} solution (1 mg, 1.27 µmol, 1.1 eq., 12.65 µL of Gd^{3+} solution) was added. 3.60 mg of the corresponding Gd-GNP AI125 were obtained.

TEM: 2.0 ± 0.1 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3436 (braod band), 2917, 2848, 1622, 1078 cm^{-1}. ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 2.10 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_6S)_{61}(C_{19}H_{35}N_4O_6S)_{12}Gd_{12}$ (Au 67.76%, Gd 2.07% and S 2.56%). At 1.4 T, r_1= 16.6 $(smM)^{-1}$ and r_2= 30.4 $(smM)^{-1}$; at 11.7 T, r_1= 0.2 $(smM)^{-1}$.

***maltose*C_5S-Au-SC_{11}DO3A-Gd glyconanoparticles (AI124):** The *maltose*C_5S-Au glyconanoparticle (3.22 mg, 0.024 µmol, 3.86 µmol of maltose, 1 eq. of maltose) was dissolved in 4.0 mL of MilliQ water and previously prepared SC_{11}DO3A-Gd^{3+} solution (2.2 mg, 4.1 µmol, 1.1 eq., 41.3 µL of Gd^{3+} solution) was added. 3.94 mg of the corresponding Gd-GNP AI124 were obtained.

TEM: 1.8 ± 0.2 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3430 (broad band), 2920, 2848, 1638, 1078 cm^{-1}. ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.05 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_{11}S)_{131}(C_{25}H_{47}N_4O_6S)_{28}Gd_{28}$ (Au 44.42%, Gd 3.16% and S 3.66%). At 1.4 T, r_1= 12.8 $(smM)^{-1}$ and r_2= 21.2 $(smM)^{-1}$; at 11.7 T, r_1= 3.5 $(smM)^{-1}$.

***maltose*C_5S-Au-SC_5DO3A-Gd glyconanoparticles (AI127):** The *maltose*C_5S-Au glyconanoparticle (1.0 mg, 0.0128 µmol, 2.04 µmol of maltose, 1 eq. of maltose) was dissolved in 3.0 mL of MilliQ water and previously prepared SC_5DO3A-Gd^{3+} solution (2.0 mg, 2.5 µmol, 1.1 eq., 25.3 µL of Gd^{3+} solution) was added. 1.77 mg of the corresponding Gd-GNP AI127 were obtained.

TEM: 1.8 ± 0.2 nm. UV: λ= 520 nm, surface plasmon band. IR (KBr): 3430 (broad band), 2917, 2848, 1638, 1074 cm^{-1}. ^{1}H NMR (D_2O, 500 MHz) δ broad signal due to Gd ion. ICP: Gd 3.59 %. Calculated average formula: $Au_{314}(C_{17}H_{31}O_{11}S)_{127}(C_{19}H_{35}N_4O_6S)_{32}Gd_{32}$ (Au 44.97%, Gd 3.66% and S 3.71%). At 1.4 T, r_1= 14.7 $(smM)^{-1}$ and r_2= 25.5 $(smM)^{-1}$; at 11.7 T, r_1= 0.8 $(smM)^{-1}$.

Transmission Electron Microscopy (TEM). TEM micrographs allowed the determination of the gold nanoclusters size (average diameter with the approximation of spherical shape). To obtain the size distribution at least 300 particles were count and no less than 3 different TEM photographs per GNP were used (Figure S2).

TEM and Size Histogram

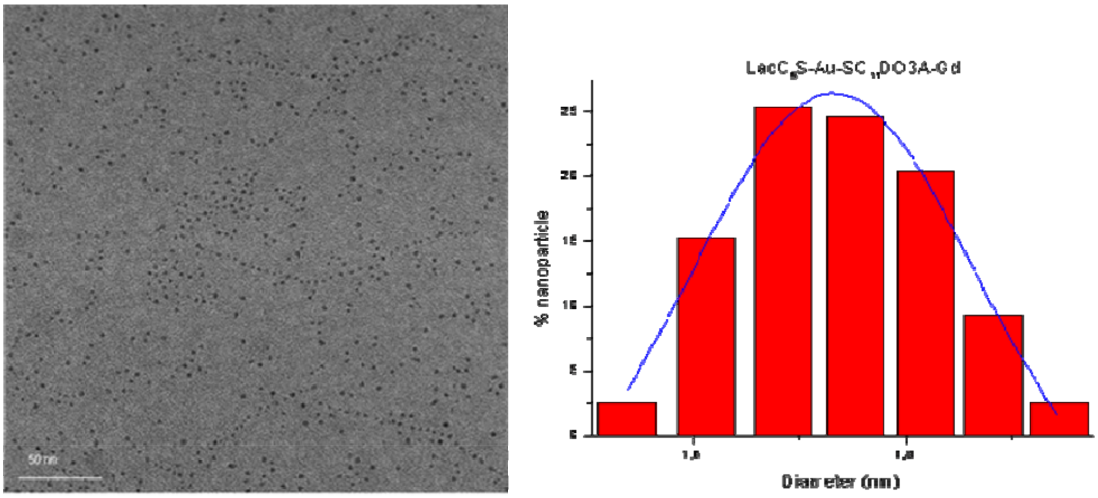


Figure S2. TEM and size histogram of $LacC_5S$-Au-SC_{11}DO3A-Gd GNPs. To obtain the size distribution at least 300 particles were count and no less than 3 different TEM photographs per GNP were used.

Table S1 shows the diameter of the different Gd-GNPs. No significant change in size was noticed after LPE reactions on 100% sugar-coated GNPs. Based on the data of TEM (average gold diameters), ICP-AES and elemental analysis, an average molecular formula for the Gd-based paramagnetic GNPs (Gd-GNPs) was assigned (Table S1).

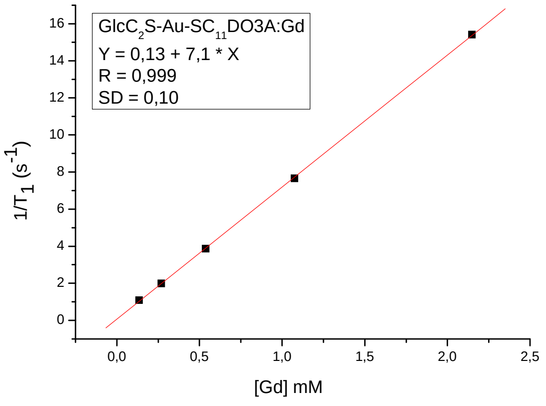
Table S1: Chemical properties of the prepared Gd-based paramagnetic glyconanoparticles (Gd-GNPs).[a]

GNPs	% Gd	TEM (nm)	MW (KDa)	Calculated Average Molecular Formula
$GlcC_2S$-Au-SC_{11}DO3A-Gd	3.4±0.2	1.8±0.2	76	$Au_{201}(C_8H_{15}O_6S)_{105}(C_{25}H_{47}N_4O_6S)_{16}Gd_{16}$
$GlcC_3S$-Au-SC_{11}DO3A-Gd	3.3±0.2	1.9±0.3	83	$Au_{314}(C_9H_{17}O_6S)_{20}(C_{25}H_{47}N_4O_6S)_{33}Gd_{33}$
$GlcC_5S$-Au-SC_{11}DO3A-Gd (Glc-GNP)	4.7±0.1	1.5±0.3 4.3±0.6	59	$Au_{140}(C_{11}H_{21}O_6S)_{70}(C_{25}H_{47}N_4O_6S)_{17}Gd_{17}$
$GlcC_7S$-Au-SC_{11}DO3A-Gd	4.1±0.2	1.8±0.3	93	$Au_{225}(C_{13}H_{25}O_6S)_{100}(C_{25}H_{47}N_4O_6S)_{26}Gd_{26}$
$GlcC_9S$-Au-SC_{11}DO3A-Gd	3.2±0.2	1.8±0.2	121	$Au_{314}(C_{15}H_{29}O_6S)_{125}(C_{25}H_{47}N_4O_6S)_{25}Gd_{25}$
$GlcC_5S$-Au-SC_5DO3A-Gd	3.1±0.2	2.0±0.3 4.8±0.5	56	$Au_{140}(C_{11}H_{21}O_6S)_{76}(C_{19}H_{36}N_4O_6S)_{11}Gd_{11}$
$GalC_5S$-Au-SC_{11}DO3A-Gd (Gal-GNP)	4.2±0.2	1.7±0.1	75	$Au_{201}(C_{11}H_{21}O_6S)_{77}(C_{25}H_{47}N_4O_6S)_{20}Gd_{20}$
$GalC_5S$-Au-SC_5DO3A-Gd	3.6±0.2	1.7±0.2	72	$Au_{201}(C_{11}H_{21}O_6S)_{80}(C_{19}H_{35}N_4O_6S)_{17}Gd_{17}$
$ManC_5S$-Au-SC_{11}DO3A-Gd (Man-GNP)	3.0±0.2	2.4±0.4	112	$Au_{314}(C_{11}H_{21}O_6S)_{127}(C_{25}H_{47}N_4O_6S)_{21}Gd_{21}$
$ManC_5S$-Au-SC_5DO3A-Gd	4.1±0.2	1.8±0.2	113	$Au_{314}(C_{11}H_{21}O_6S)_{119}(C_{19}H_{35}N_4O_6S)_{29}Gd_{29}$
$LacC_5S$-Au-SC_{11}DO3A-Gd (Lac-GNP)	2.7±0.2	1.7±0.3	128	$Au_{314}(C_{17}H_{31}O_{11}S)_{116}(C_{25}H_{47}N_4O_6S)_{22}Gd_{22}$
$LacC_5S$-Au-SC_5DO3A-Gd	3.7±0.2	1.6±0.2	128	$Au_{314}(C_{17}H_{31}O_{11}S)_{108}(C_{19}H_{35}N_4O_6S)_{30}Gd_{30}$
cellobioseC_5S-Au-SC_{11}DO3A-Gd (*cellobiose*-GNP)	2.1±0.2	1.8±0.2	92	$Au_{314}(C_{17}H_{32}O_6S)_{61}(C_{25}H_{47}N_4O_6S)_{12}Gd_{12}$
cellobioseC_5S-Au-SC_5DO3A-Gd	2.1±0.2	2.0±0.1	91	$Au_{314}(C_{17}H_{31}O_6S)_{61}(C_{19}H_{35}N_4O_{60}S)_{12}Gd_{12}$
maltoseC_5S-Au-SC_{11}DO3A-Gd	3.1±0.2	1.8±0.2	139	$Au_{314}(C_{17}H_{31}O_{11}S)_{131}(C_{25}H_{47}N_4O_6S)_{28}Gd_{28}$
maltoseC_5S-Au-SC_5DO3A-Gd	3.6±0.2	1.8±0.2	137	$Au_{314}(C_{17}H_{31}O_{11}S)_{127}(C_{19}H_{35}N_4O_6S)_{32}Gd_{32}$

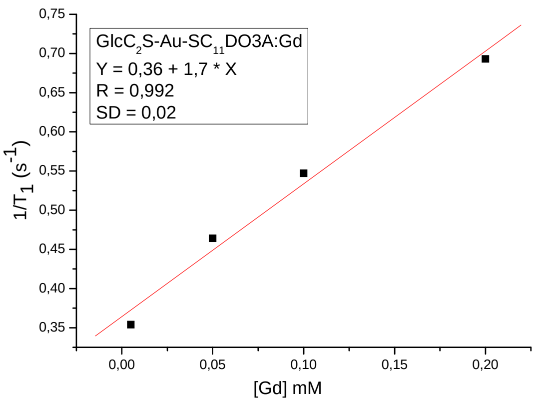
[a] Gd content calculated from ICP-AES analysis**,** size of gold cores from TEM, and molecular formula of the GNPs by combining elemental analysis and TEM.

***T_1* measurements.** The ability of a paramagnetic contrast agent to reduce the longitudinal relaxation time T_1 is described by the relaxivity (r_1), which is the slope of the curve obtained by plotting the concentration of the contrast agent in terms of Gd(III) millimolarity *vs* the corresponding $1/T_1$ (T_1 in seconds). The ratio between the transverse and longitudinal relaxivities (r_2/r_1) in the paramagnetic GNPs is in the range 1.5-1.8, i.e. these nanoparticles have a large paramagnetic property (high r_1) with tiny magnetic anisotropy (low r_2) in agreement with the typical relaxation properties of T_1-agents.

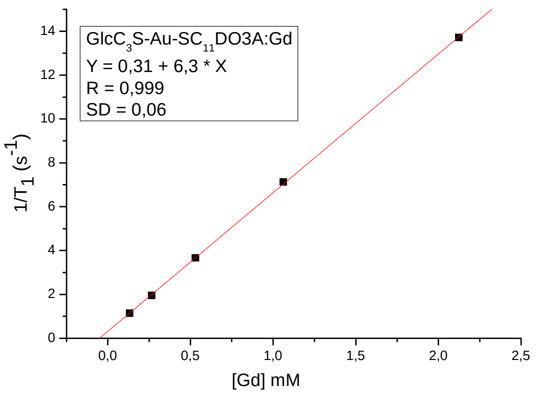
AI107 (Gd 3.4%) 1.41T



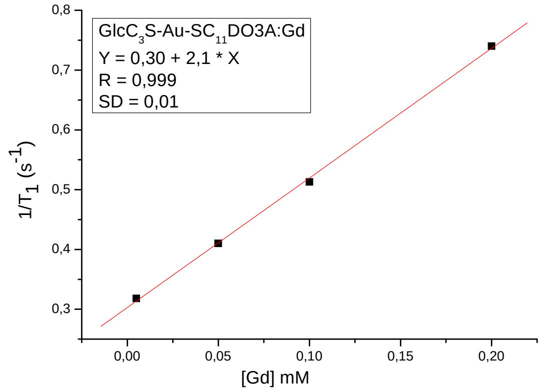
AI107 (Gd 3.4%) 11.7 T



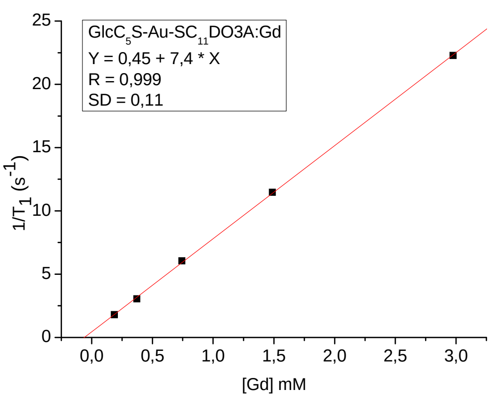
AI106 (Gd 3.3%) 1.41T



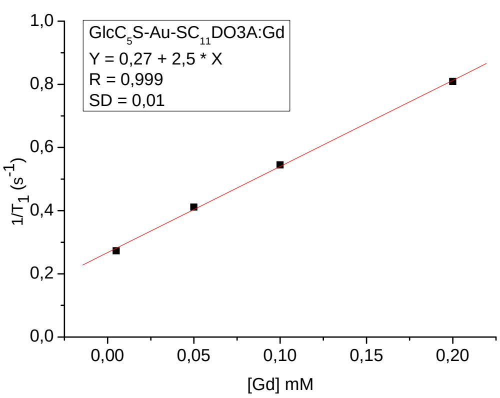
AI106 (Gd 3.3%) 11.7T



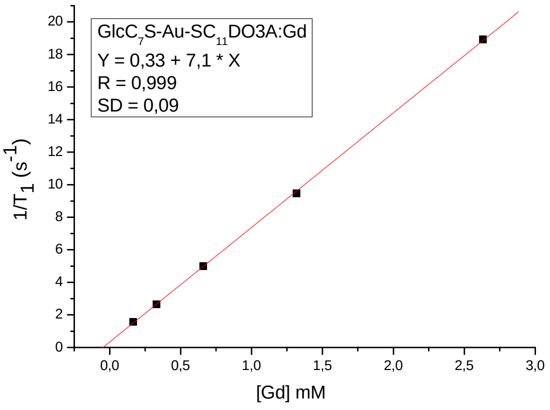
AI101 (Gd 4.68%) 1.41 T



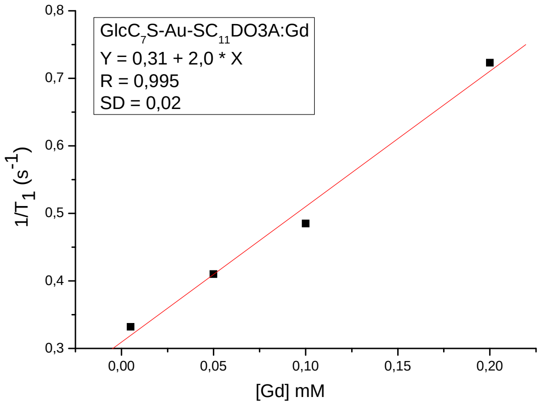
AI101 (Gd 4.68%) 11.7 T



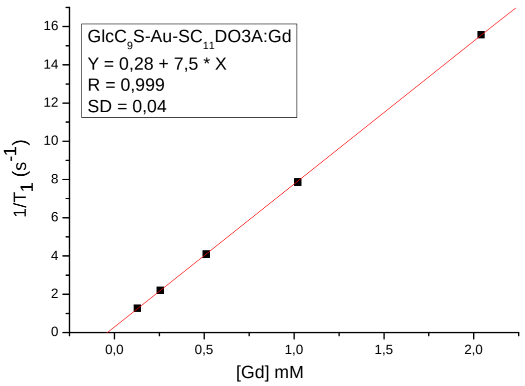
AI104 (Gd 4.1%) 1.41T



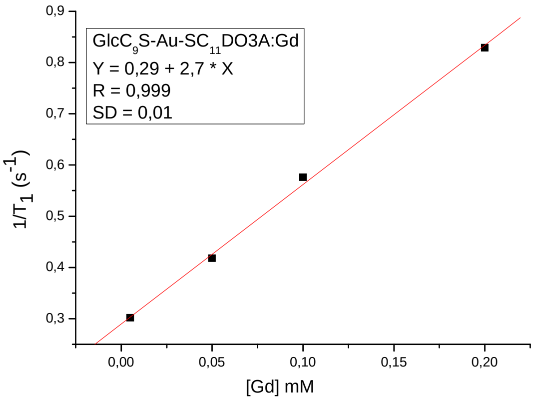
AI104 (Gd 4.1%) 11T



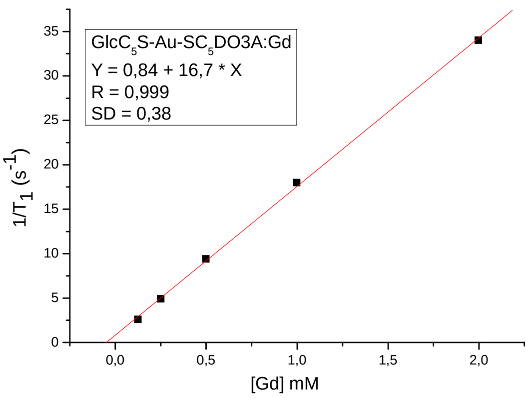
AI105 (Gd 3.2%) 1.41T



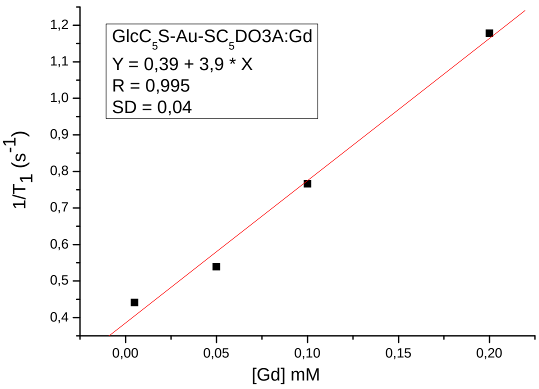
AI105 (Gd 3.2%) 11.7T



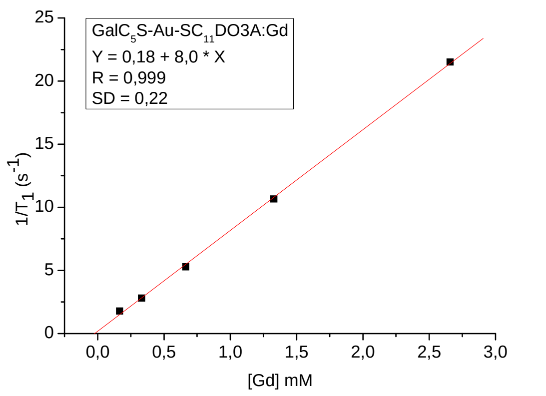
AI119 (Gd 3.1%) 1.41T



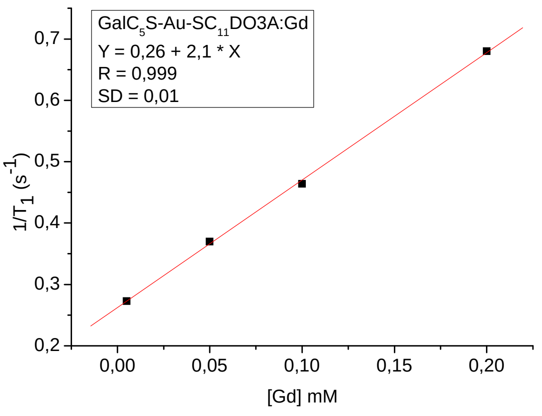
AI119 (Gd 3.1%) 11.7T



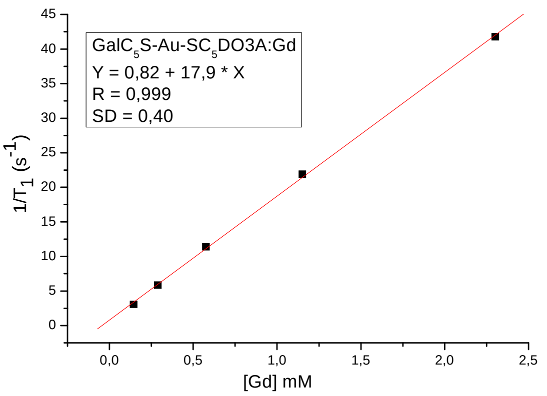
AI118 (Gd 4.18%) 1.41T



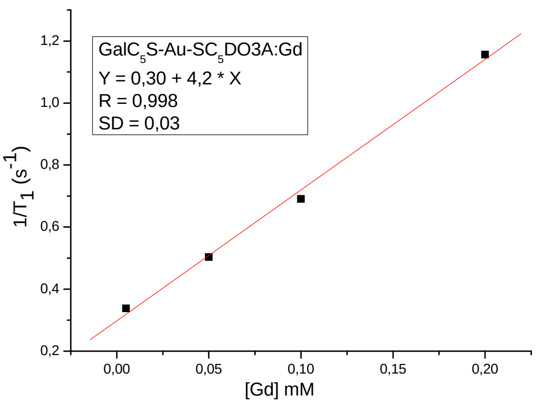
AI118 (Gd 4.18%) 11.7T



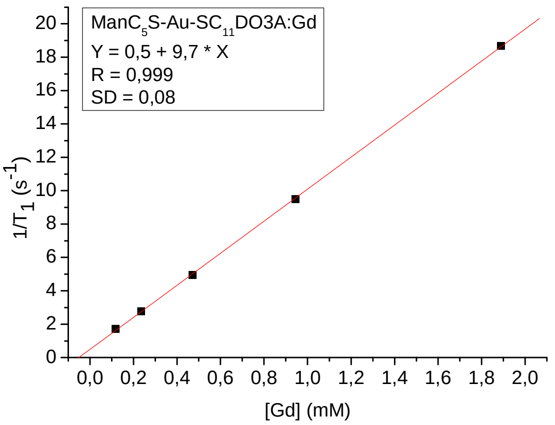
AI121 (Gd 3.6%) 1.41T



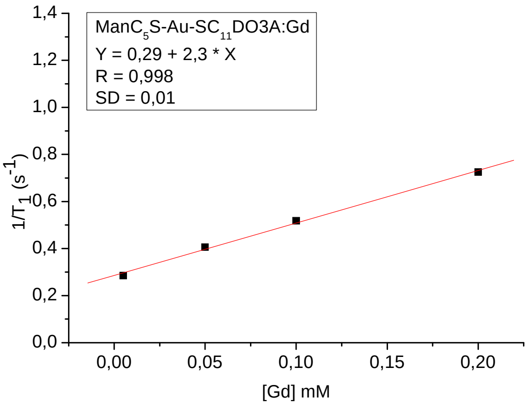
AI121 (Gd 3.6%) 11.7T

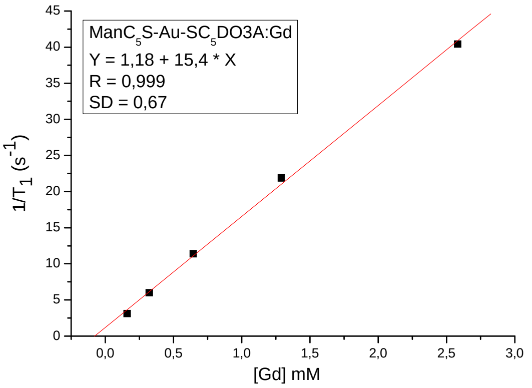
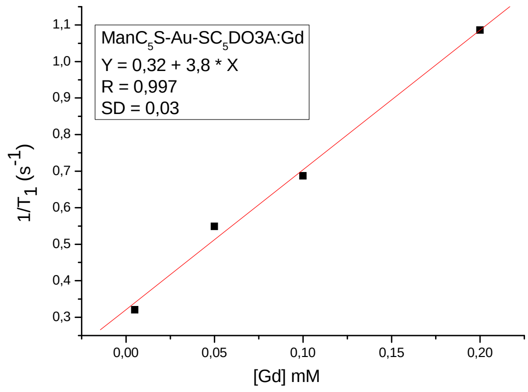


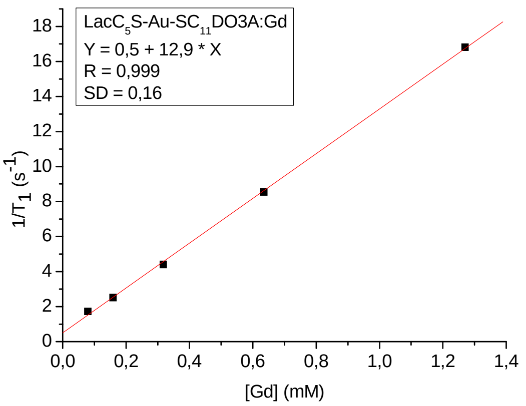
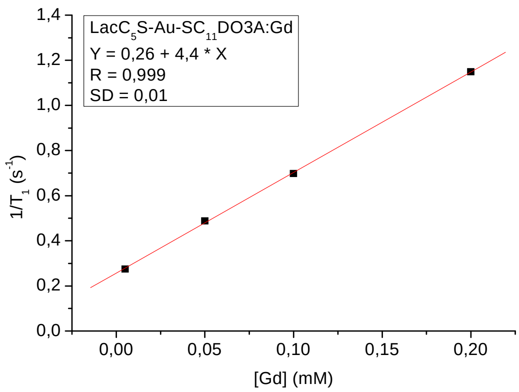
AI116 (Gd 2.97%) 1.41 T

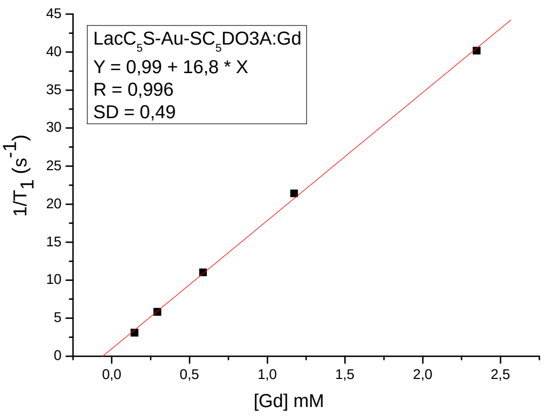
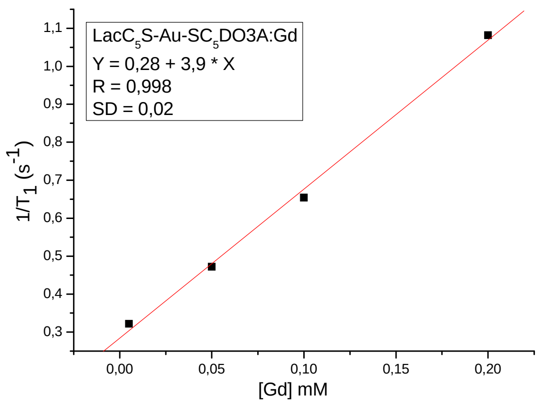


AI116 (Gd 2.97%) 11.7 T

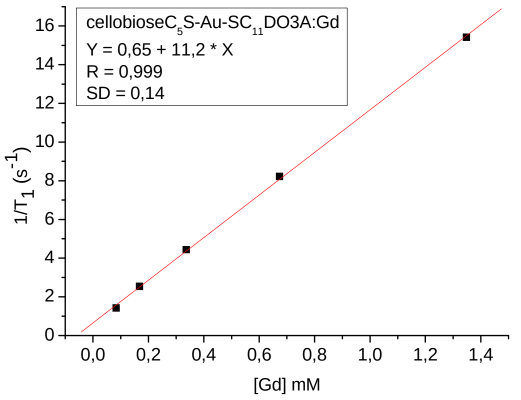


AI120 (Gd 4.1%) 1.41T	AI120 (Gd 4.1%) 11.7T
	

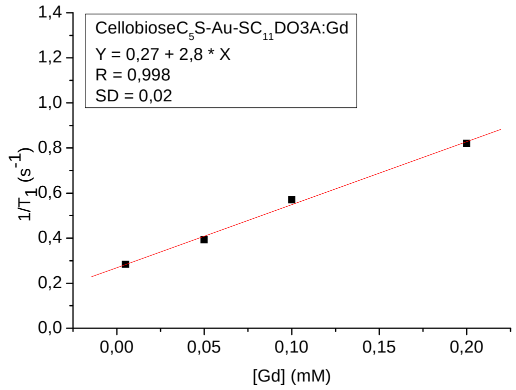
AI123 (Gd 2.69%) 1.41 T	AI123 (Gd 2.69%) 11.7 T
	

AI126 (Gd 3.7%) 1.41T	AI126 (Gd 3.7%) 11.7T
	

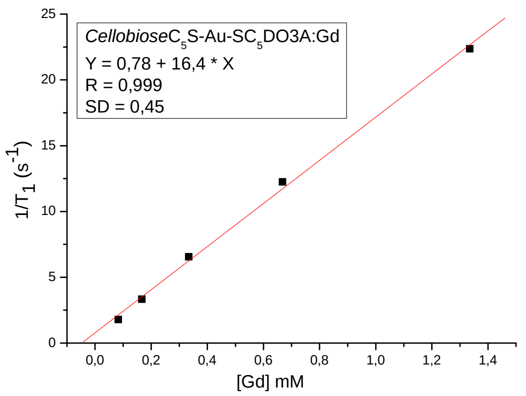
AI117 (Gd 2.12%) 1.41 T



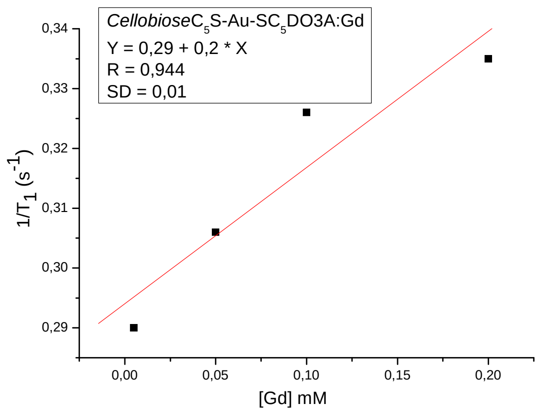
AI117 (Gd 2.12%) 11.7 T



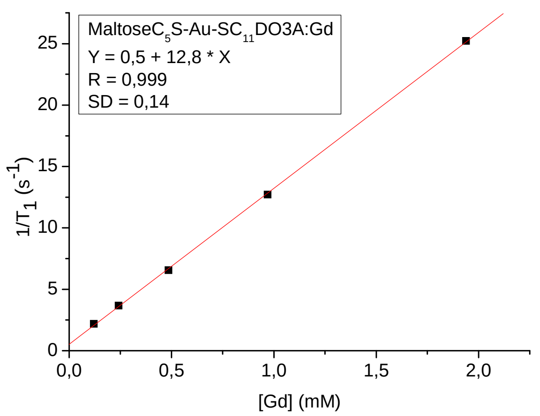
AI125 (Gd 2.1%) 1.41T



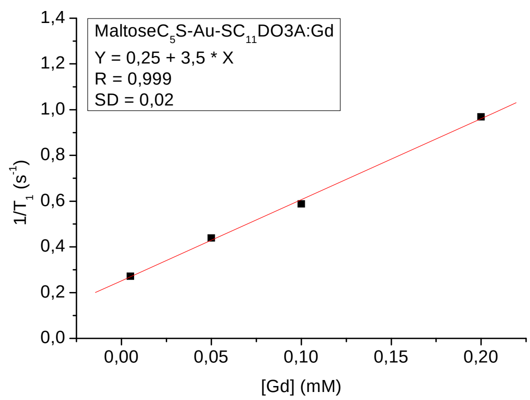
AI125 (Gd 2.1%) 11.7T



AI124 (Gd 3.05%) 1.41 T



AI124 (Gd 3.05%) 11.7 T



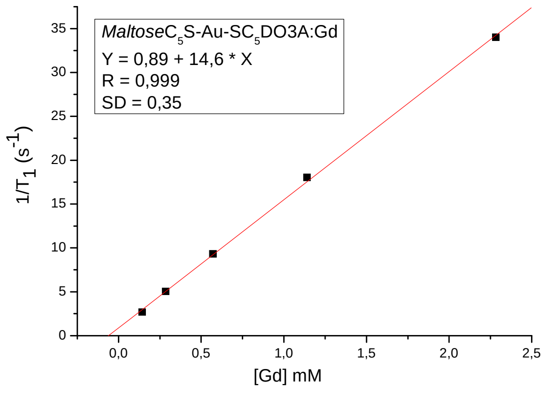
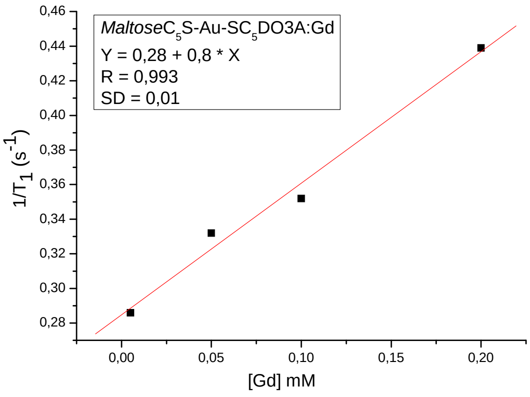
AI127 (Gd 3.6%) 1.41T	AI127 (Gd 3.6%) 11.7T
	

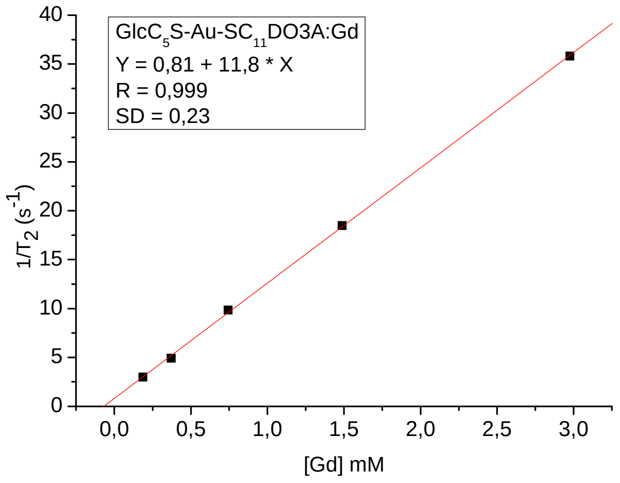
Figure S3. Calculation of the relaxivity values r_1 of the Gd-GNPs at 1.41 T and 11.7 T

r_2 (AI101) 11.8 $s^{-1}mM^{-1}$

GlcC$_5$S-Au-SC$_{11}$DO3A-Gd

(Gd 4.7%)

1.41 T

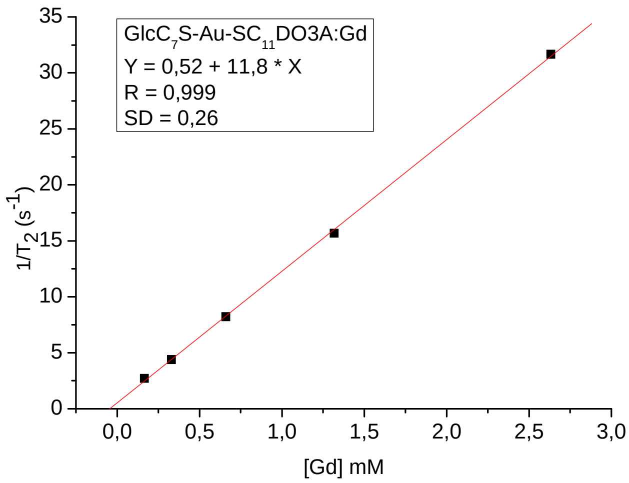


r_2 (AI104) 11.8 $s^{-1}mM^{-1}$

GlcC$_7$S-Au-SC$_{11}$DO3A-Gd

(Gd 4.1%)

1.41 T

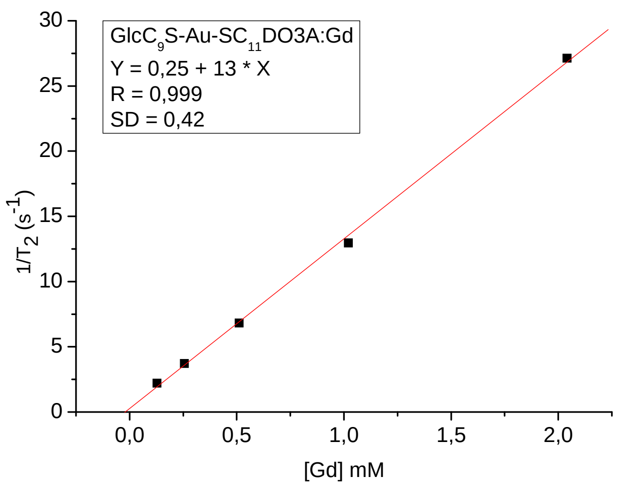


r_2 (AI105) 13.0 $s^{-1}mM^{-1}$

GlcC$_9$S-Au-SC$_{11}$DO3A-Gd

(Gd 3.2%)

1.41 T

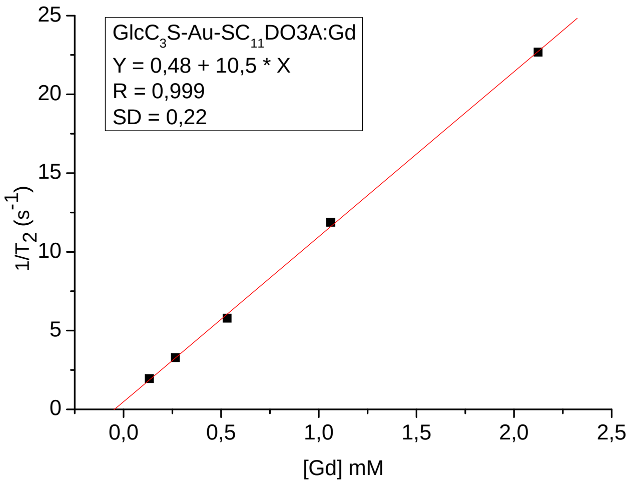


r_2 (AI106) 10.5 $s^{-1}mM^{-1}$

GlcC$_3$S-Au-SC$_{11}$DO3A-Gd

(Gd 3.3%)

1.41 T

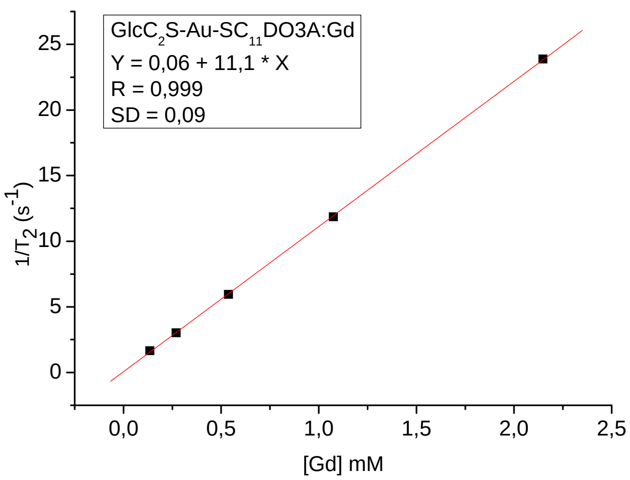


r_2 (AI107) 11.1 $s^{-1}mM^{-1}$

GlcC$_2$S-Au-SC$_{11}$DO3A-Gd

(Gd 3.4%)

1.41 T

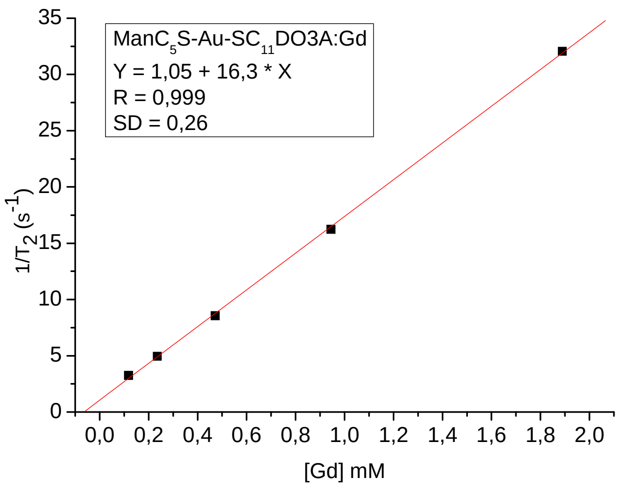


r_2 (AI116) 16.3 $s^{-1}mM^{-1}$

ManC$_5$S-Au-SC$_{11}$DO3A-Gd

(Gd 3.0%)

1.41 T



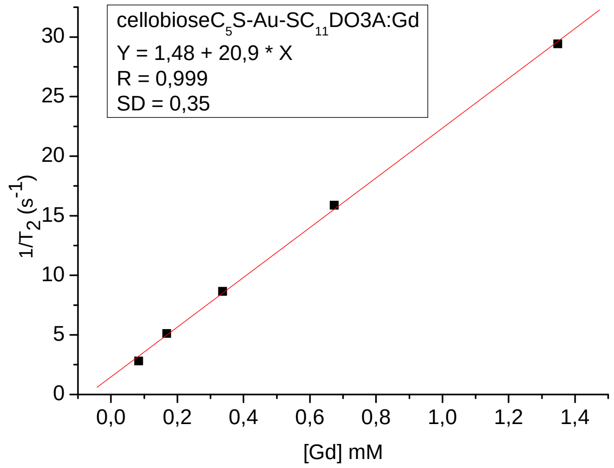
r_2 (AI117) 20.9 $s^{-1}mM^{-1}$

cellobioseC_5S-Au-

SC_{11}DO3A-Gd

(Gd 2.1%)

1.41 T

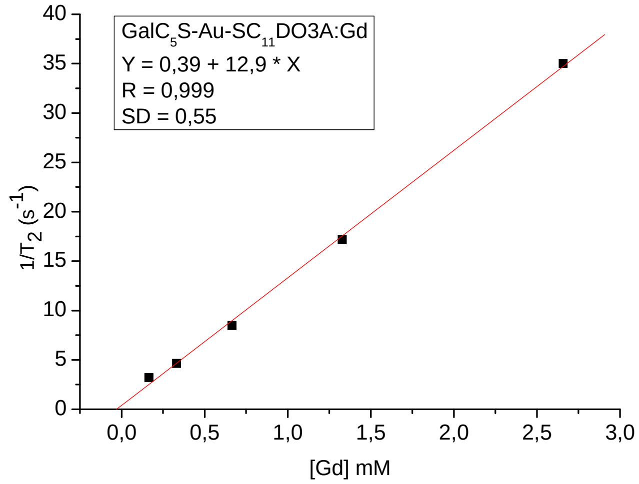


r_2 (AI118) 12.9 $s^{-1}mM^{-1}$

GalC_5S-Au-SC_{11}DO3A-Gd

(Gd 4.2%)

1.41 T

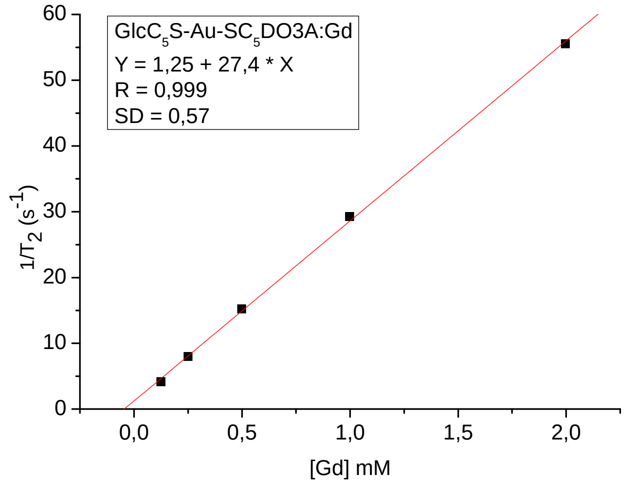


r_2 (AI119) 27.4 $s^{-1}mM^{-1}$

GlcC_5S-Au-SC_5DO3A-Gd

(Gd 3.1%)

1.41 T

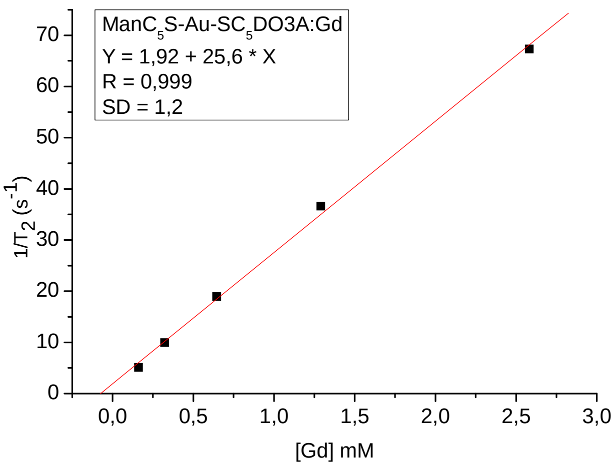


r_2 (AI120) 25.6 $s^{-1}mM^{-1}$

ManC$_5$S-Au-SC$_5$DO3A-Gd

(Gd 4.1%)

1.41 T

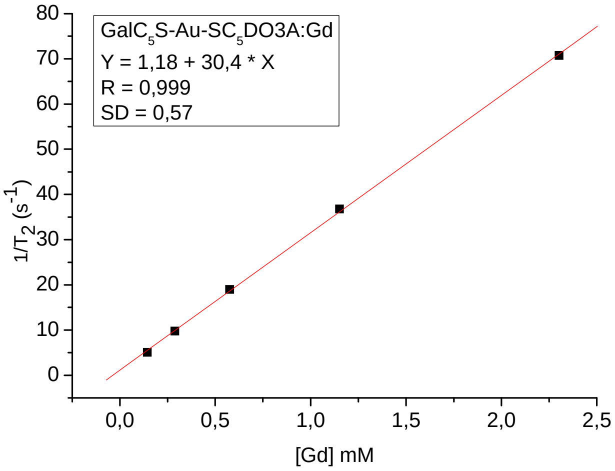


r_2 (AI121) 30.4 $s^{-1}mM^{-1}$

GalC$_5$S-Au-SC$_5$DO3A-Gd

(Gd 3.6%)

1.41 T

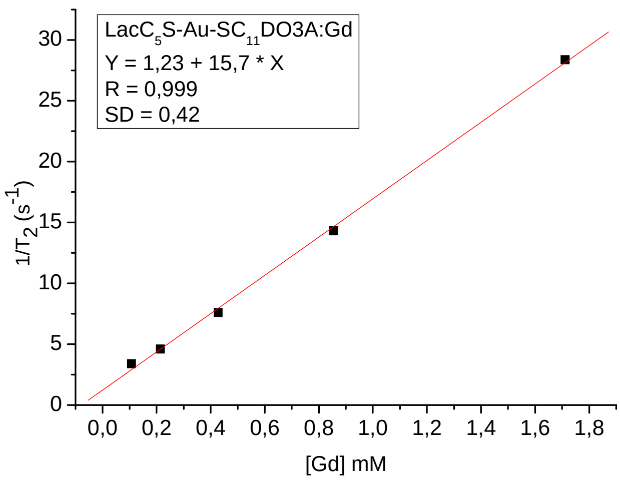


r_2 (AI123) 15.7 $s^{-1}mM^{-1}$

LacC$_5$S-Au-SC$_{11}$DO3A-Gd

(Gd 2.7%)

1.41 T

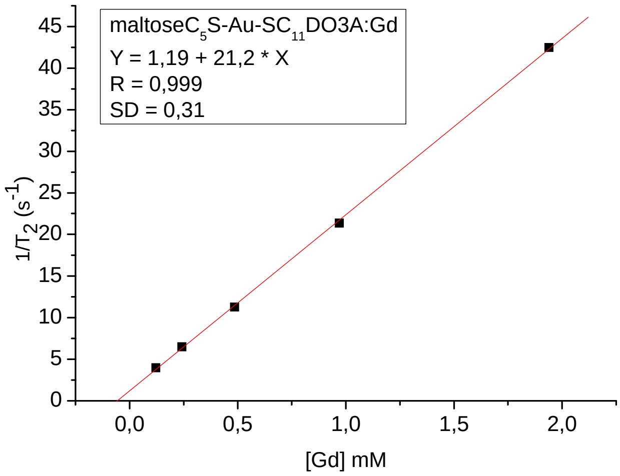


r_2 (AI124) 21.2 $s^{-1}mM^{-1}$

maltoseC_5S-Au-SC_{11}DO3A-Gd

(Gd 3.1%)

1.41 T

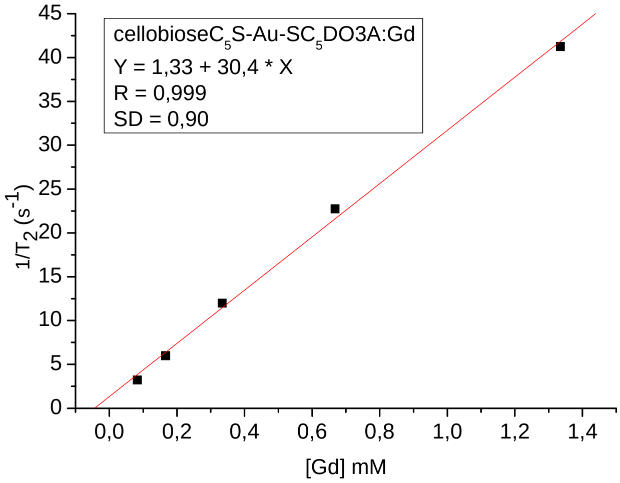


r_2 (AI125) 30.4 $s^{-1}mM^{-1}$

cellobioseC_5S-Au-SC_5DO3A-Gd

(Gd 2.1%)

1.41 T

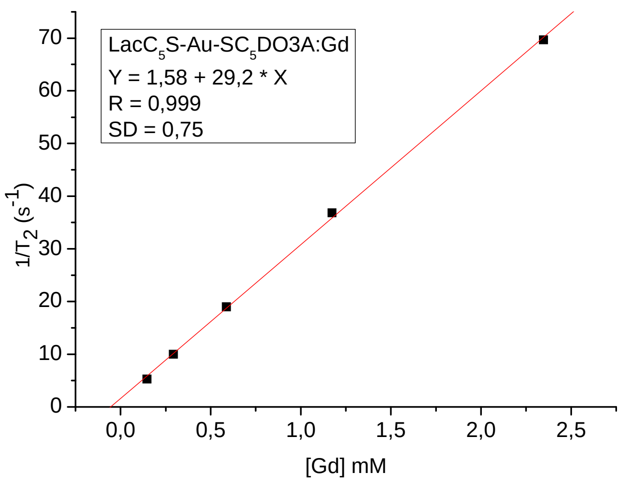


r_2 (AI126) 29.2 $s^{-1}mM^{-1}$

LacC_5S-Au-SC_5DO3A-Gd

(Gd 3.7%)

1.41 T



r_2 (AI127) 25.5 $s^{-1}mM^{-1}$

maltoseC_5S-Au-

SC_5DO3A-Gd

(Gd 3.6%)

1.41 T

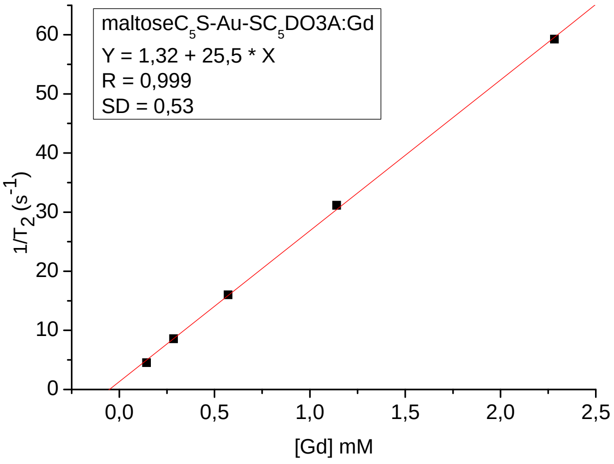


Figure S3bis. Calculation of the relaxivity values r_2 of the Gd-GNPs at 1.41 T

MRI phantoms. T_1 measurements, at different concentrations of Gd(III) (0, 5, 50, 100 and 200 μM), were performed in a Bruker Biospec at 11.7 T using a 72 mm volumetric quadrature coil at room temperature. Saturation recovery pulse sequence with static TE (11 ms) and variable TR (300, 650, 730, 1100, 1500, 2100, 2800, 3800, 5500, 12500 ms) values. Imaging parameters were as follows: Field of view (FOV) = 34 x 34 mm2, matrix size (MTX) = 320 x 320, slice thickness 0.5 mm, and four averages. T_1 analysis was carried out using the image sequence analysis tool in Paravision 5 software (Bruker BioSpin, Ettlingen, Germany) with monoexponential curve-fitting of image intensities of selected regions of interest (ROIs). T1 weighted images we acquired usiGradient Echo Sequence with 400 ms repetition time and 4.7 ms echo time.

T_1-weighted images were acquired using a Gradient Echo Sequence with 400 ms repetition time and 4.7 ms echo time. Imaging parameters were as follows: Field of view (FOV) = 34 x 34 mm2, matrix size (MTX) = 320 x 320, slice thickness 0.5 mm, and four averages.

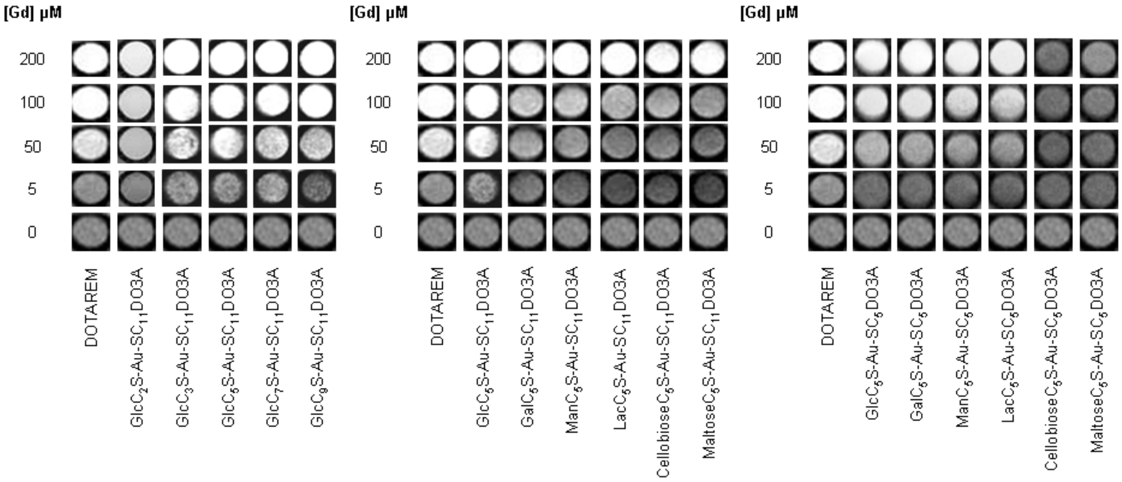


Figure S4. T_1-weighted MR images (phantoms) of GlcC$_n$S-Au-SC$_{11}$DO3A-Gd, glycoC$_5$S-Au-SC$_{11}$DO3A-Gd, glycoC$_5$S-Au-SC$_5$DO3A-Gd GNPs and Dotarem® at different concentrations, acquired at 11.7 T and 25 ºC in water.

^{17}O NMR experiments. The presence of water molecules in the inner-sphere of a paramagnetic lanthanide complex is reflected in the ^{17}O NMR data of water. The number of the water molecules directly coordinated to the Gd(III) ion (q) is calculated as described.[7S] Number q was determined for an aqueous (D_2O) solution of GlcC$_5$S-Au-SC$_{11}$DO3A-Gd ManC$_5$S-Au-SC$_{11}$DO3A-Gd and GalC$_5$S-Au-SC$_{11}$DO3A-Gd containing 6 mM, 5.6 mM and 6.2 mM of Gd(III) respectively. As expected for a heptadentate chelating agent (DO3A), the Gd-GNP showed q~2 (Table S2).

Table S2: Paramagnetic ion concentration, temperature and ^{17}O NMR water chemical shifts (ppm) in experiments for the calculation of the number of the water molecules directly coordinated to the Gd(III) ion (q).

Compound	[Gd] or [Dy] (mM)	T (ºC)	$\delta_{observed}$ (ppm)	δ_{D2O} (ppm)	q
SC$_{11}$DO3A-Dy	6.4	70	-1.88	-1.40	~2.0
SC$_5$DO3A-Dy	6.1	70	-1.90	-1.45	~2.1
GlcC$_5$S-Au-SC$_{11}$DO3A-Gd	6	60	-1.51	-1.06	~1.8
GalC$_5$S-Au-SC$_{11}$DO3A-Gd	6.2	60	-1.91	-1.46	~1.8
ManC$_5$S-Au-SC$_{11}$DO3A-Gd	5.6	60	-1.89	-1.46	~1.9

[7S] Djanashvili, K; Peters, J.A. How to determine the number of inner-sphere water molecules in Lanthanide(III) complexes by ^{17}O NMR spectroscopy. A technical note *Contrast Media Mol. Imaging*, **2007**, *2*, 67-71.

Dynamic light scattering of the nanoparticles. We have measured the hydrodynamic diameter for two GNPs: *cellobiose*C_5S-Au and *cellobiose*C_5S-Au-SC_{11}DO3A-Gd *(cellobiose-GNP)* at a concentration of 100 µg/mL. These size measurements were performed in water using a MALVERN Zetasizer Nano ZS with a 4mW He-Ne laser operating at a wavelength of 633nm. Our nanoparticles have a gold core of approximately 2 nm (TEM) and the molecules of the coating (organic shell) is approximately of the same size, so that Gd-GNPs *per se* are expected to have 6 nm diameter assuming a spherical size. The volume size distributions obtained show that ~96.5% of *cellobiose*C_5S-Au consists of small GNPs having a hydrodynamic diameter of 11,8 ± 2,5 nm (Figure below) and that ~96% of *cellobiose*C_5S-Au-SC_{11}DO3A-Gd consists of small Gd-GNPs having a hydrodynamic diameter 11,8 ± 2,7 nm (Figure below).

Size Distribution Report by Volume

v2.1

Malvern

Sample Details

Sample Name:	gnp cello 1
SOP Name:	mansettings.nano
General Notes:	Average result created from record number(s): 14 15 16

File Name:	cellobioseC5S_Au.dts	Dispersant Name:	Water
Record Number:	51	Dispersant RI:	1.330
Material RI:	0.93	Viscosity (cP):	0.8872
Material Absorbtion:	0.001	Measurement Date and Time:	Thursday, November 08, 20...

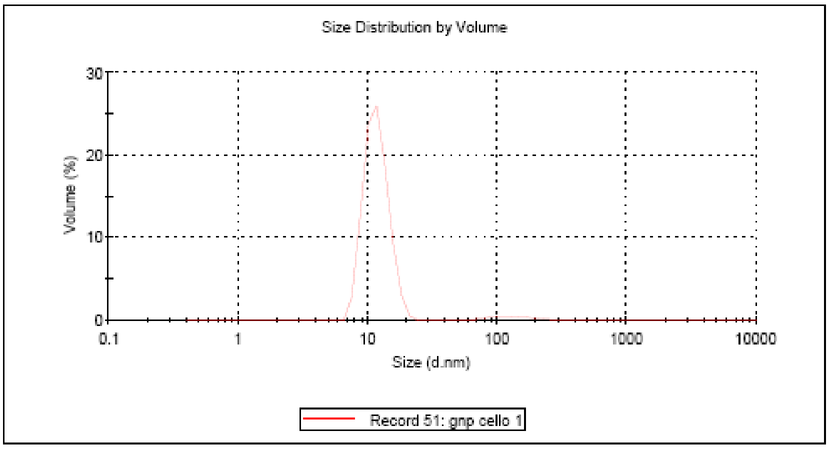
System

Temperature (°C):	25.0	Duration Used (s):	60
Count Rate (kcps):	243.8	Measurement Position (mm):	3.00
Cell Description:	Disposable micro cuvette (40µl)	Attenuator:	9

Results

			Size (d.nm):	% Volume	Width (d.nm):
Z-Average (d.nm):	108.0	Peak 1:	137.2	3.5	52.61
PdI:	0.301	Peak 2:	11.81	96.5	2.519
Intercept:	0.797	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report



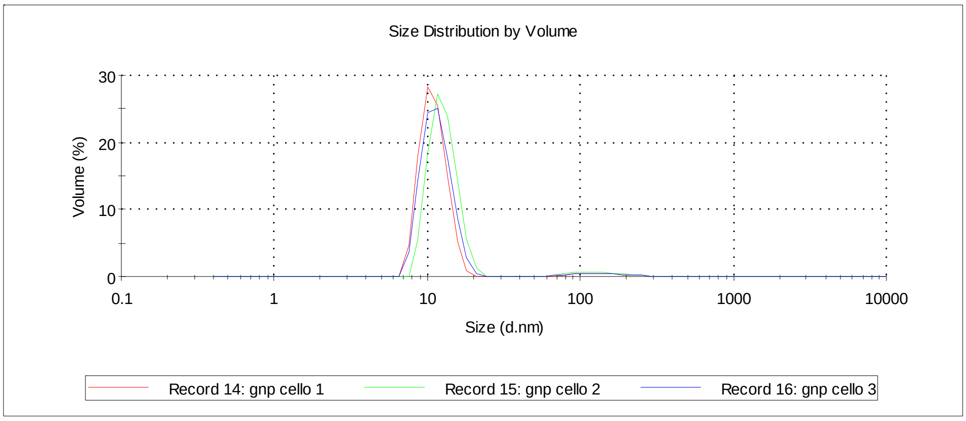


Figure A. DLS measurement of *cellobiose*C_5S-Au. Top: Average size distribution of (bottom) three rounds of assays (n. 14, 15 and 16)

Size Distribution Report by Volume

v2.1

Malvern

Sample Details

Sample Name: Cello/Gd7filt/spin 1

SOP Name: mansettings.nano

General Notes: Average result created from record number(s): 37 44 47

File Name:	cellobioseC5S_Au.dts	Dispersant Name:	Water
Record Number:	48	Dispersant RI:	1.330
Material RI:	0.93	Viscosity (cP):	0.8872
Material Absorbtion:	0.001	Measurement Date and Time:	Thursday, November 08, 20...

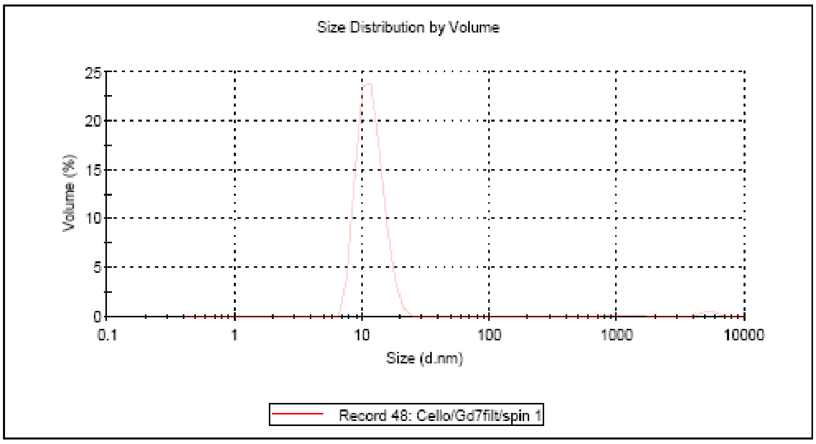
System

Temperature (°C):	25.0	Duration Used (s):	120
Count Rate (kcps):	618.3	Measurement Position (mm):	5.00
Cell Description:	Disposable micro cuvette (40µl)	Attenuator:	11

Results

			Size (d.nm):	% Volume	Width (d.nm):
Z-Average (d.nm):	110.8	Peak 1:	135.7	0.8	73.22
PdI:	0.786	Peak 2:	1222	1.6	523.5
Intercept:	0.194	Peak 3:	11.77	98.1	2.719

Result quality : Refer to quality report



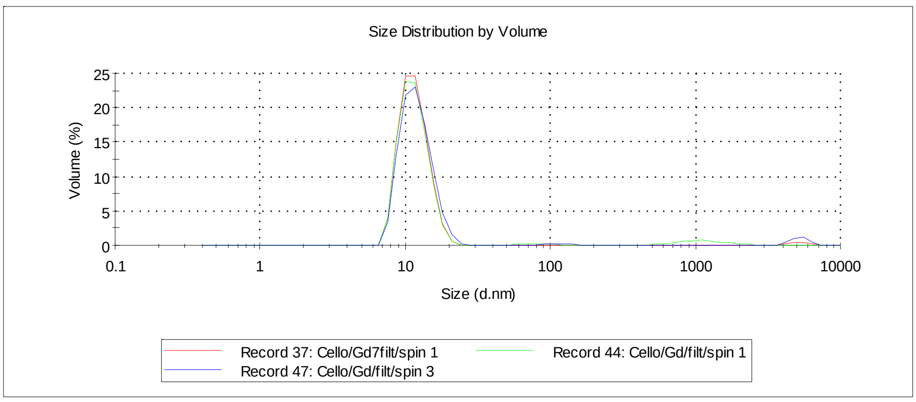


Figure B. DLS measurement of *cellobiose*C_5S-Au-SC_{11}DO3A-Gd *(cellobiose-GNP).* Top: Average size distribution of (bottom) three rounds of assays (n. 37, 44 and 47)

Cells and culture conditions. Raji and Raji+ cells were a kind gift from José Alcami (Instituto de Salud Carlos III, Madrid) and GL261 cells were donated by Carles Arus (Universitat Autónoma de Barcelona) with permission of the National Cancer Institute (NCI, Frederick, MD, USA). All media and reagents were obtained from commercial suppliers (Sigma-Aldrich or Lonza). The Raji line of lymphoblast-like cells, established from a Burkitt's lymphoma, and Raji-DC-SIGN transfectants (transfectants generation) were grown in Roswell Park Memorial Institute (RPMI)-1640 medium supplemented with 10% fetal bovine serum (FBS), 2 mM L-glutamine and streptomycin/penicillin (100 UmL^{-1} penicillin and 100 μgmL^{-1} streptomycin). Cells were subcultured following American Type Culture Collection (ATCC) recommendations at 37 ºC in an atmosphere of 5% CO_2 and 95 % air. The murine glioma cells, GL261 line, were grown as monolayer on culture flasks in RPMI-1640 medium supplemented with 10% fetal bovine serum **(**FBS) and 4 mM L-glutamine at 37 ºC in an atmosphere of 5 % CO_2 and 95% air. The HepG2 line, established from hepatocellular carcinoma, was cultured in Minimum Essential Medium Eagle (M-5650), supplemented with 10% FBS and 2 mM L-glutamine at 37 ºC in an atmosphere of 5% CO_2 and 95% air.

Cytotoxicity assay. The viability of GL261 and HepG2 cells was determined by using the MTT method. Briefly, 10^4 cells/well were seeded into 96-well plates in 100 µL complete medium and incubated at 37 ºC in 5% CO_2 atmosphere. After 24 hours, the medium was replaced with a fresh one containing nanoparticles at different concentrations (0-100 μgmL^{-1}). After 20 hours incubation period, 20 µL of MTT (5 mg mL^{-1} in phosphate buffer pH 7.4) was added to each well. After 4 hours of incubation at 37 ºC and 5% CO_2 for exponentially growing cells and 15 min for steady-state confluent cells, the medium was removed, formazan crystals were dissolved with 200 µL of DMSO, and the solution was vigorously mixed to dissolve the reacted dye. The absorbance of each well was read on a multiplate reader (GENios Pro instrument from TECAN) at 550 nm.

The toxicity of the GNPs towards Raji cells was studied at 0-100 μgmL^{-1} concentration range using a MTS standard protocol. $1 \cdot 10^4$ cells/well were seeded into 96-well plates in 80 µL complete medium and then, GNPs solution (20 µL) at desired concentration was added and incubated at 37 ºC, 5% CO_2 atmosphere. After 20 h, 20 µL of MTS solution (5 mg mL^{-1}) were added to each well and cells were still incubated for 4 h at 37 ºC, 5% CO_2 atmosphere. Finally, the absorbance of the samples was measured at 490 nm on the multiplate reader. The standard deviations (±SD) were obtained on a triplicate analysis (n = 3).

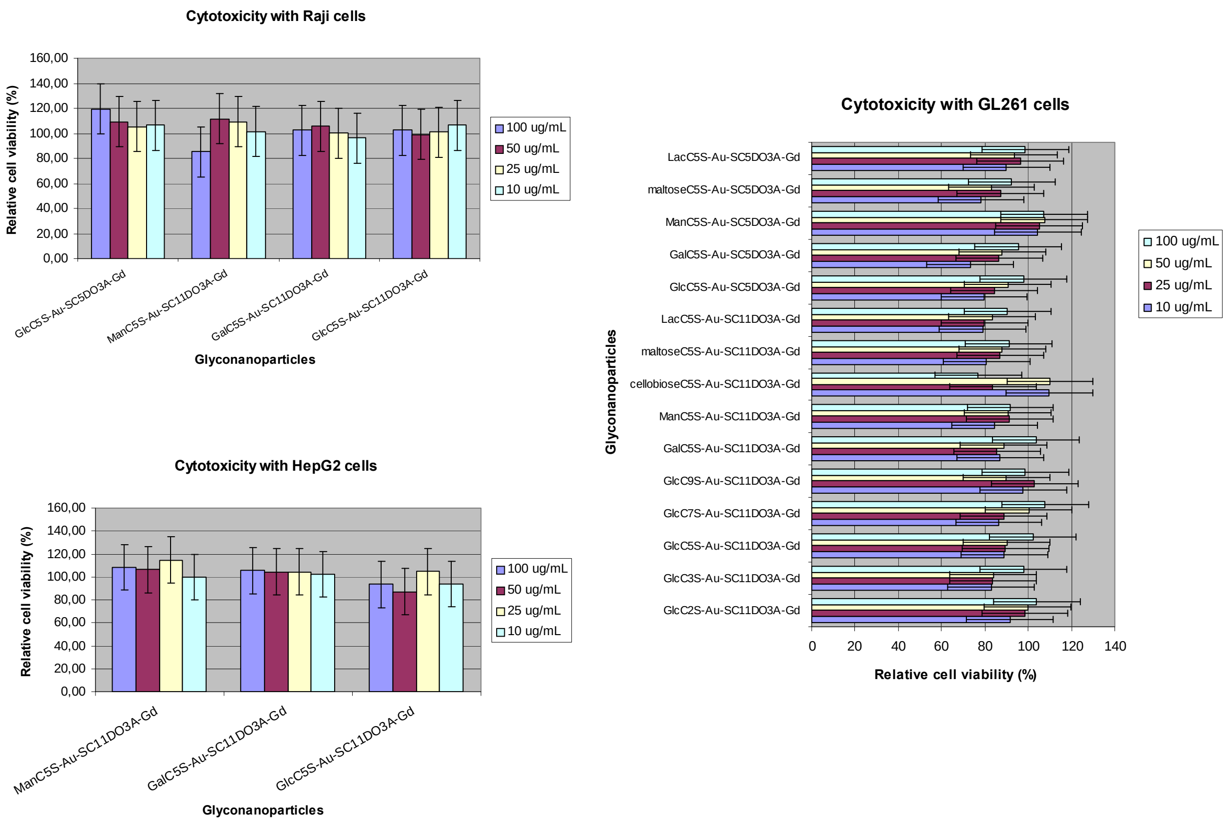


Figure S5. Determination of viability of Raji, HepG2 and GL261 cells after incubation for 24 h at concentrations up to 100 μgmL^{-1} of Gd-GNPs.

Table S3. Representative T_1 values (ms) and percentage change of T_1 (%ΔT_1) of fixed, live and lysed cells after incubation with selected Gd-GNPs at 50 μM concentration of gadolinium.*

	Fixed		Live		Lysed	
	T1	**%ΔT1**	**T1**	**%ΔT1**	**T1**	**%ΔT1**
Raji/media	2484±62		2497±11		2415±37	
Raji/Man-GNP	1038±17	58%	2298±29	8%	2172±45	10%
Raji+/media	2513±61		2464±29		2426±98	
Raji+/Man-GNP	1003±16	60%	1750±22	29%	1545±75	36%
HepG2/media	2661±69		2946±97		2793±28	
HepG2/Gal-GNP	1885±73	29%	2360±58	20%	2153±64	23%
GL261/media	2876±112		3080±57		N.D	
GL261/ Glc-GNP	2193±178	24%	2394±79	27%	N.D	

* Representative values of different experiments