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^{1}H NMR Relaxivity of Aqueous Suspensions of Titanium Dioxide Nanoparticles Coated with a Gadolinium(III) Chelate of a DOTA-monoamide with a Phenylphosphonate Pendant Arm

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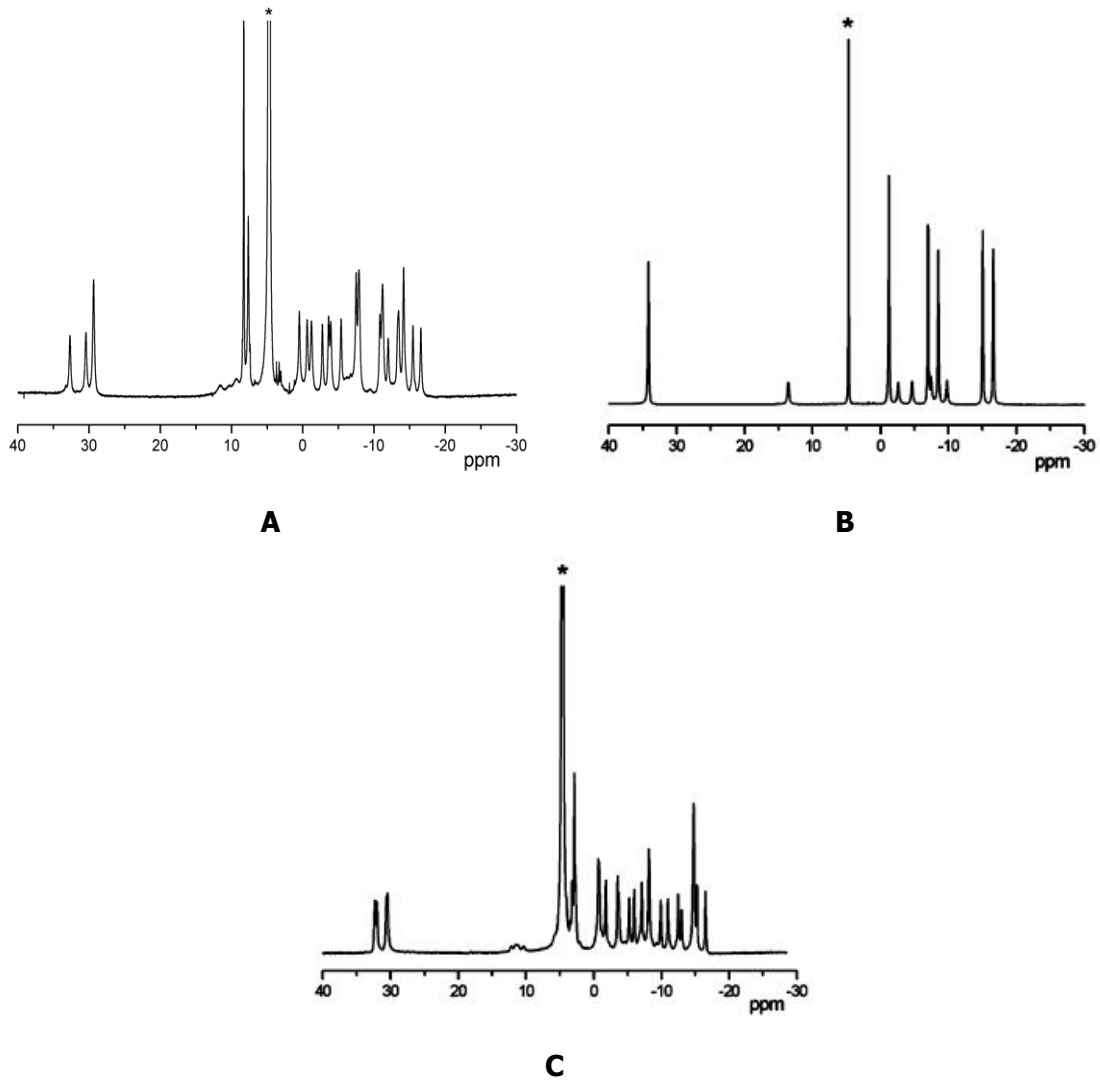

Figure S1. ^{1}H NMR spectrums of EuDOTAPP (A), EuDOTA (B) and EuBPAMD (C). Signal of water is marked with asterisk

Table S1. Relaxometric parameters of Gd-DOTAPP

Parameter	DOTAPP
k_{ex}^{298} [10^6 s^{-1}]	1.00±0.08
$\Delta H^{\#}$ [kJ mol^{-1}]	35±3
τ_R^{298} [ps]	135±4
E_R [kJ mol^{-1}]	18±1
τ_v^{298} [ps]	21±1
E_v [kJ mol^{-1}]	1.00 (fixed)
$A/\hbar$ [10^6 rad s^{-1}]	-4.1±0.7
C_{os}	0.09±0.09
Δ^2 [10^{20} s^{-2}]	0.33±0.03
δg_L^2 [10^{-2}]	4±1
$\chi(1+\eta^2/3)^{1/2}$ [MHz]	7.58 (fixed)
D_{GH}^{298} [10^{-10} m^2 s^{-1}]	22.2 (fixed)
E_{GdH} [kJ mol^{-1}]	18.2 (fixed)

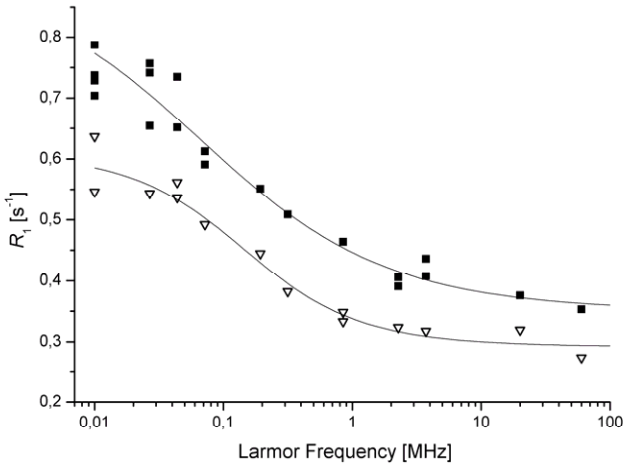

Figure S2. NMRD Profiles of TiO_2 suspension at 25 °C (squares) and 37 °C (triangles). The concentration of TiO_2 is the same as in the GdDOTAPP – TiO_2 sample (5 g/L). The data were fitted using a Cole-Cole model.

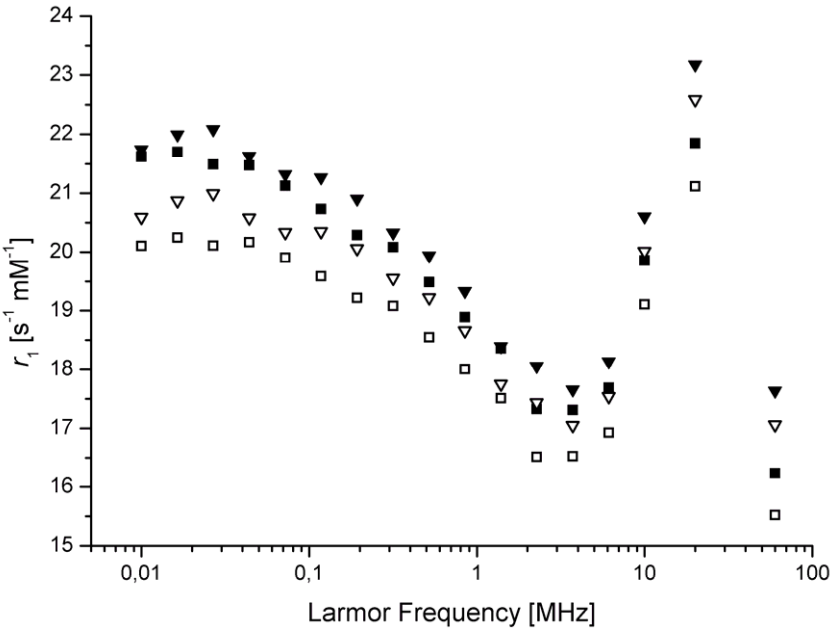

Figure S3. NMRD profile of GdDOTAPP suspension, Gd concentration 0.52 mM, pH 3.5; measured at 25 (squares) and 37 (triangels) °C before (full shapes) and after (empty shapes) substraction of diamagnetic contribution

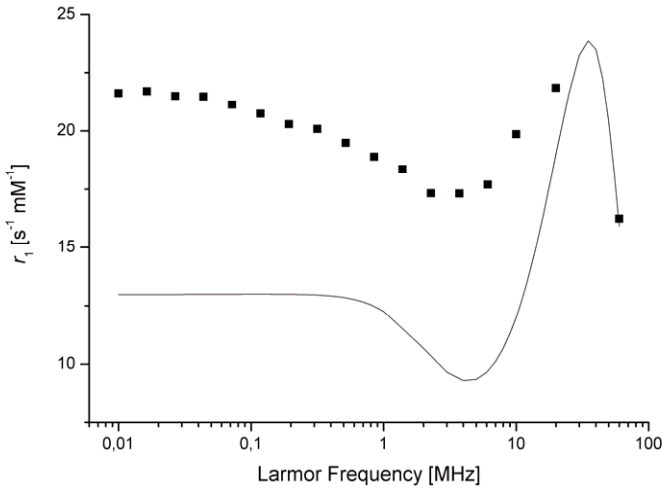

Figure S4. Simulation of Gd(III)-DOTAPP + TiO_2 NMRD profile at 25 °C, using τ_{RH} value of 3 ms and with the other parameters the same as those of free Gd(III)-DOTAPP. Squares represent experimental data after substraction of diamagnetic contribution

Synthesis of diethyl 4-acetamidophenylphosphonate[1]

4-bromoacetanilide (5.14 g, 24 mmol) and tetrakis(triphenylphosphine)palladium (1.50 g, 1.2 mmol) were put together into a 25 ml flask. Diethylphosphite (12 ml, 93 mmol) and triethylamine (3.66 ml, 26 mmol) were added under the argon atmosphere. The mixture was stirred under the argon atmosphere for 36 hours at 90 °C. The reaction mixture was extracted between 100 ml of water and 100 ml of chloroform. The chloroform extract was evaporated with a rotavap and the crude product was purified by column chromatography (silica, CH_2Cl_2:MeOH 20:1, R_f = 0.6). The product was obtained in a form of yellow powder in yield 3.78 g (58 %). The yellow color is due to the presence of of Pd complexes.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.29(t, 6H, -CH_2-C***H***$_3$, $^3J_{HH}$ = 7.2 Hz), 2.17(s, 3H, -CO-C***H***$_3$), 4.06(m, 4H, -C***H***$_2$-), 7.68(m, 4H, C***H***$_2$ Ar.) ^{31}P {^{1}H} NMR ($CDCl_3$, 400 MHz) δ 19.5(s) MS: calcd. 271.8, obsd. 271.9

1 T. Hirao, T. Masunaga, Y. Ohshiro, T. Agawa, *Synthesis* 1981, ***1***, 56–57.