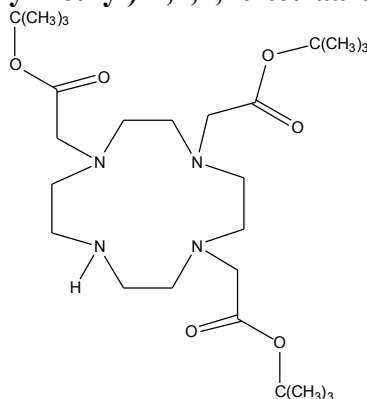


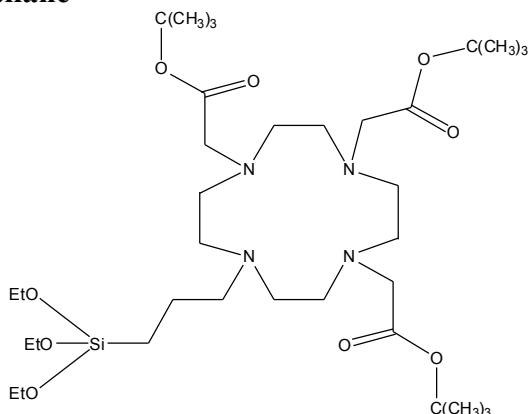
1,4,7-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane



0.750 g (4.21 mmol) of 1,4,7,10-Tetraazacyclododecane (cyclen) and 1.17 g of NaHCO₃ (13.90 mmol) were stirred on 25 mL of dried CH₃CN at 0°C. 2.03 mL (13.90 mmol) of *tert*-butyl bromoacetate was added dropwise. The reaction was left to react for 30 hours. Protected cyclen was separated by column chromatography (SiO₂ CH₂Cl₂:MeOH). Yield:46 %

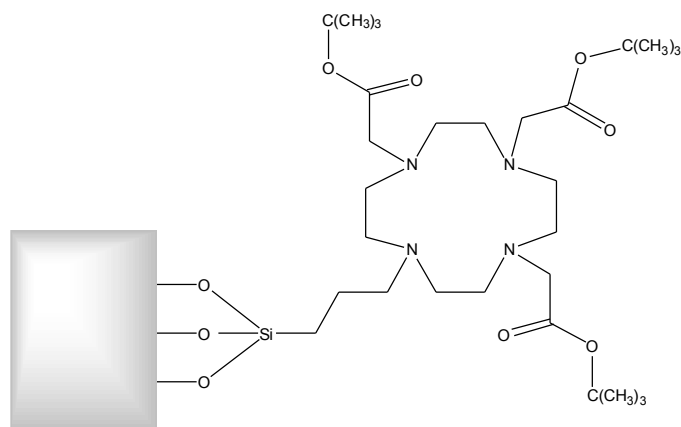
NMR: δ_{H} :1.44(27H, s, *tert*-Bu), 2.87(4H, s, CH₂), 2.90(8H, s, CH₂), 3.08(4H, s, CH₂-amine), 3.27(2H, s, CH₂-CO₂), 3.36(4H, s, CH₂-CO₂), 9.96(1H, s, NH). δ_{C} 28.5, 47.8, 51.7, 58.5, 82.0,170.0, 170.8; *m/z* (CI) 515(MH⁺).

N-{3-[4,7,10-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecan-1-yl]propyl}trimethoxysilane



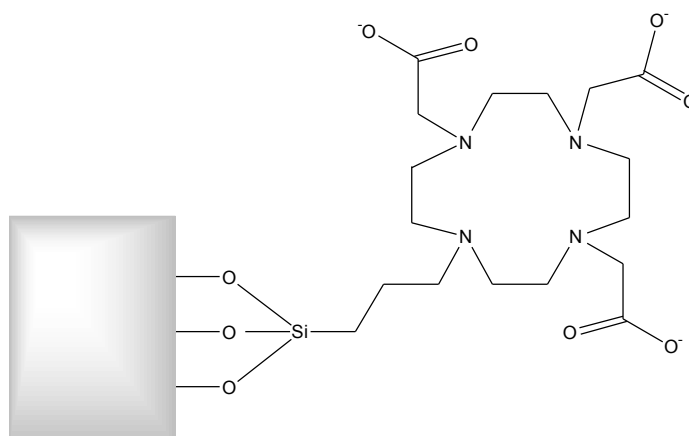
0.100 g (0.94553 mmol) of protected cyclen and 0.26 g (1.94553 mmol) of K₂CO₃ were stirred in dry CH₃CN under reflux. 39.27 μ L (0.94553 mmol) of (3-iodopropyl)trimethoxysilane were added and the mixture refluxed for 48 hours. After 48 h se solution was cooled at room temperature and the solvent vacuum removed. The oil obtained is used for the next step without further purification.

Grafted cyclen-silane



The oil obtained from the previous step was dissolved in toluene. To this solution was added 0.291 mmol of boehmite and the mixture refluxed for 24 hours. The solid is separated by centrifugation at 4000 rpm for 10 minutes and washed 4 times with EtOH. No unreacted (3-iodopropyl)trimethoxysilane or the hydrolyzed form was found in the nanoparticles as measured later on by EDX.

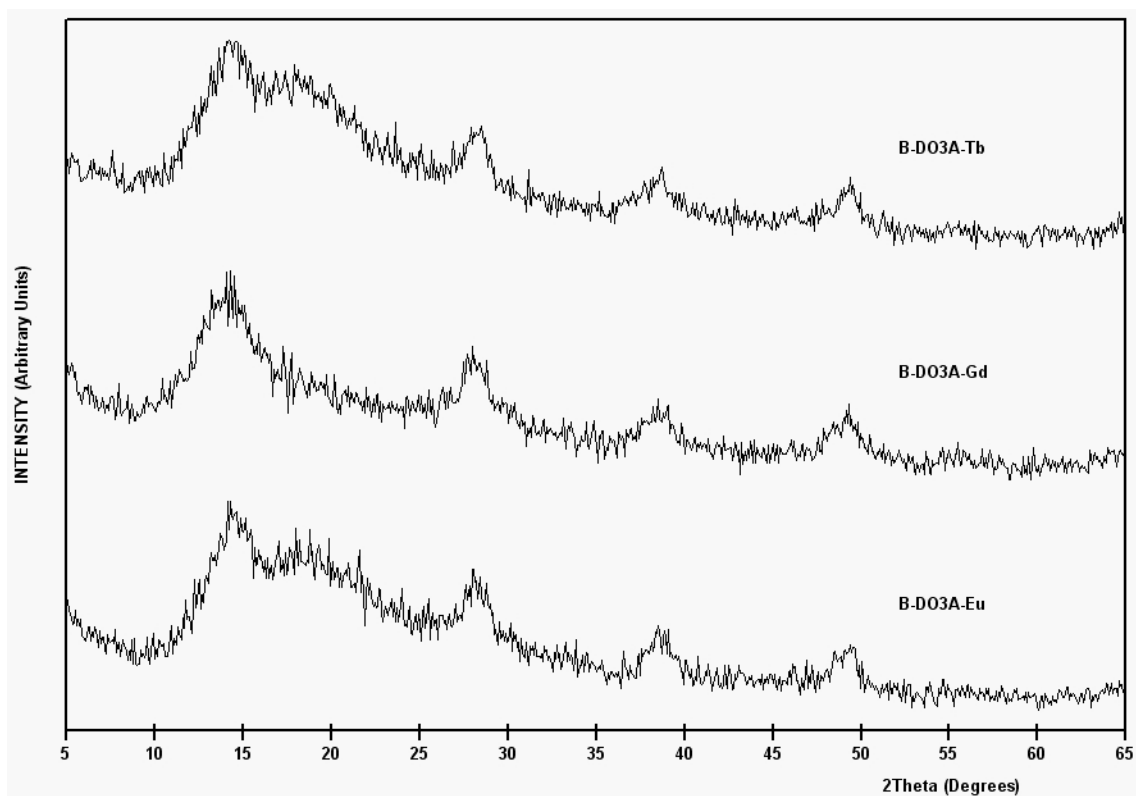
Desprotected cyclen



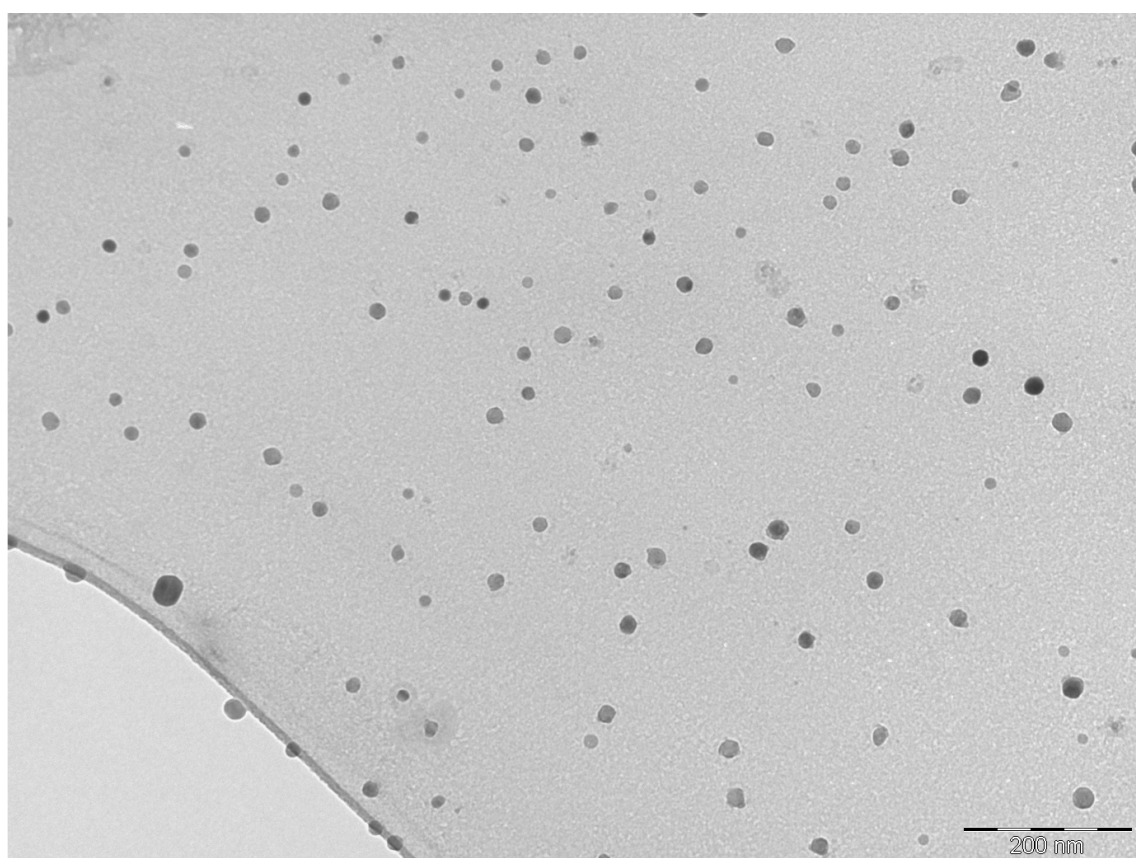
The solid obtained is stirred for 3-4 hours in a mixture of CH_2Cl_2 :TFA (3:1). The acid is removed by vacuum evaporation. The traces of acid are removed by washing and centrifuging the solid with CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{EtOH}$ and EtOH.

Lanthanide complexes

The solid obtained is dispersed in 25 mL of CH_3CN and an equimolar quantity of lanthanide chloride is added.



DRX reflection pattern for Tb-boehmite, Gd-boehmite and Eu-boehmite.



TEM micrograph of Gd-boehmite nanoparticles.

Lifetime measurements

	$\tau(\text{H}_2\text{O})/\text{ms}$	$\tau(\text{D}_2\text{O})/\text{ms}$	q
Eu-Boeh pH 2	0.42	1.01	1.34
	0.47	1.49	1.45 ^a
Eu-Boeh pH 2 + NaCl	0.38	1.36	1.97
Eu-Boeh pH 5.5	0.35	1.25	2.17
	0.35	1.26	2.18 ^b
Eu-Boeh pH 5.5 + NaCl	0.37	1.12	1.87
Tb-Boeh pH 2	0.85	1.24	1.55
Tb-Boeh pH 2 + NaCl	0.77	1.14	1.81
Tb-Boeh pH 5.5	0.82	1.24	1.76
Tb-Boeh pH 5.5 + NaCl	0.86	1.30	1.67

^ameasured 3 hours after being prepared

^bmeasured 2 weeks after being prepared

Relaxivity calculations

	r_{1p} (mM ⁻¹ s ⁻¹) in situ	r_{1p} (mM ⁻¹ s ⁻¹) 1 month later
Gd-Boeh pH 2	11.71 (2)	14.95 (8)
Gd-Boeh pH 2 + NaCl 0.9%	3.55 (2)	10.46 (8)
Gd-Boeh pH 4.3	1.75 (2)	1.63 (2)
Gd-Boeh pH 4.3 + NaCl 0.9%	1.33 (2)	1.06 (2)
Gd-Boeh pH 7.5	1.49 (2)	1.04 (2)
Gd-Boeh pH 7.5 + NaCl 0.9%	1.32 (2)	1.21 (2)

In parenthesis the q value measured

