Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for:

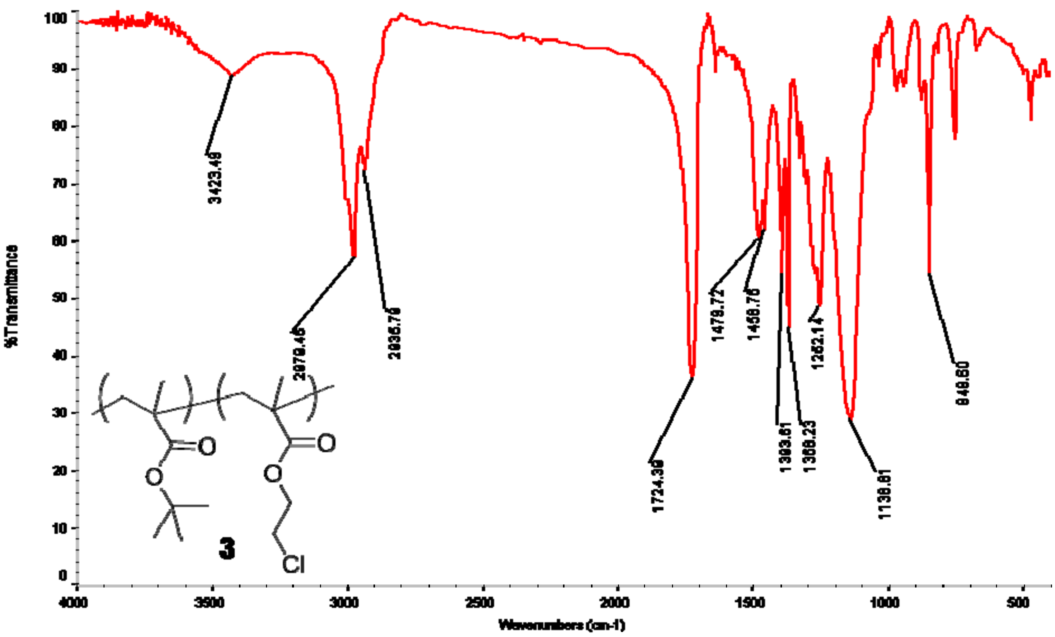
Single-chain polyacrylic nanoparticles with multiple Gd(III) centres as potential MRI contrast agents

Irma Perez-Baena,[a] Iraida Loinaz,[a] Daniel Padro,[b] Ignacio García,[a] Hans J. Grande[a] and Ibon Odriozola[a]*

[a] *CIDETEC Center for Electrochemical Technologies, New Materials Department, Paseo Miramón 196, 20009 Donostia-San Sebastián, Spain and* [b] *CIC biomaGUNE, Center for Cooperative Research in Biomaterials, Paseo Miramón 182, 20009 Donostia-San Sebastián, Spain*

*To whom correspondence should be addressed: iodriozola@cidetec.es

FT-IR Spectra



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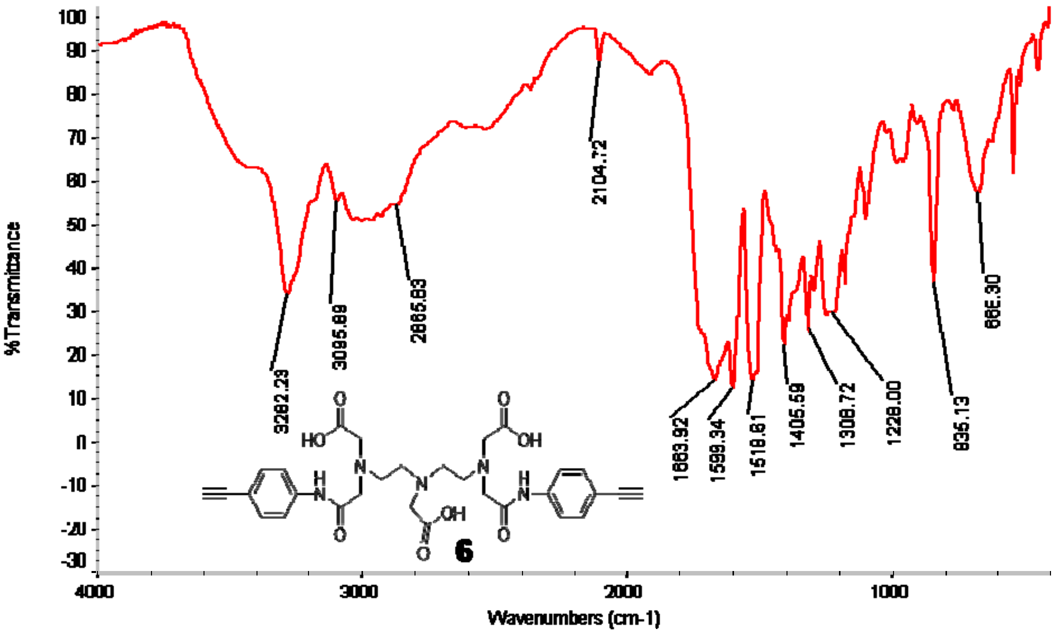
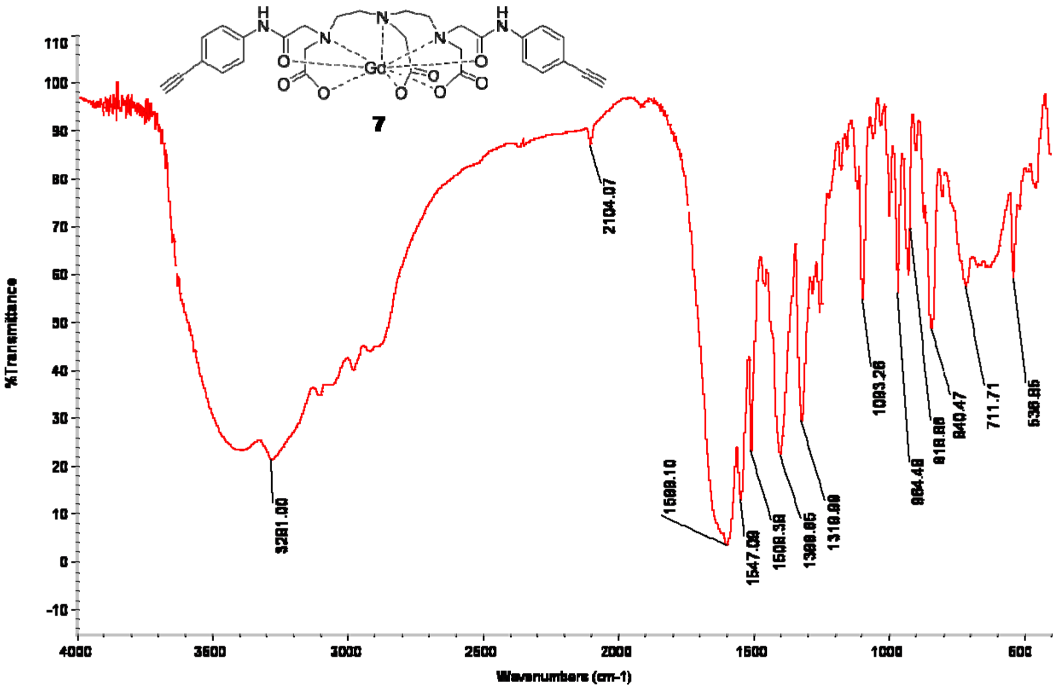
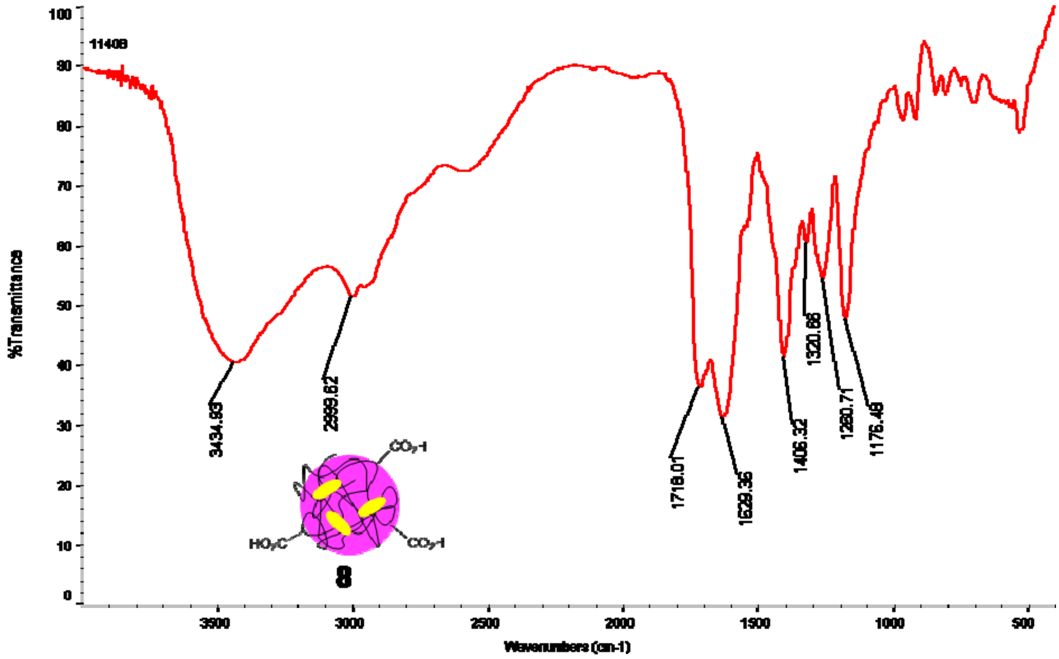
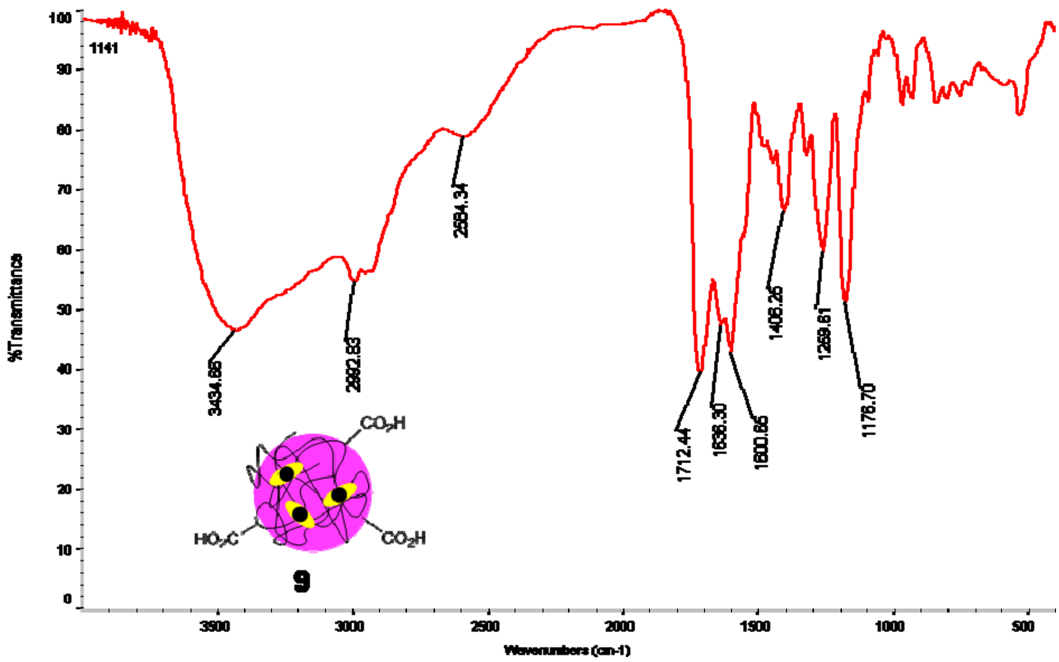
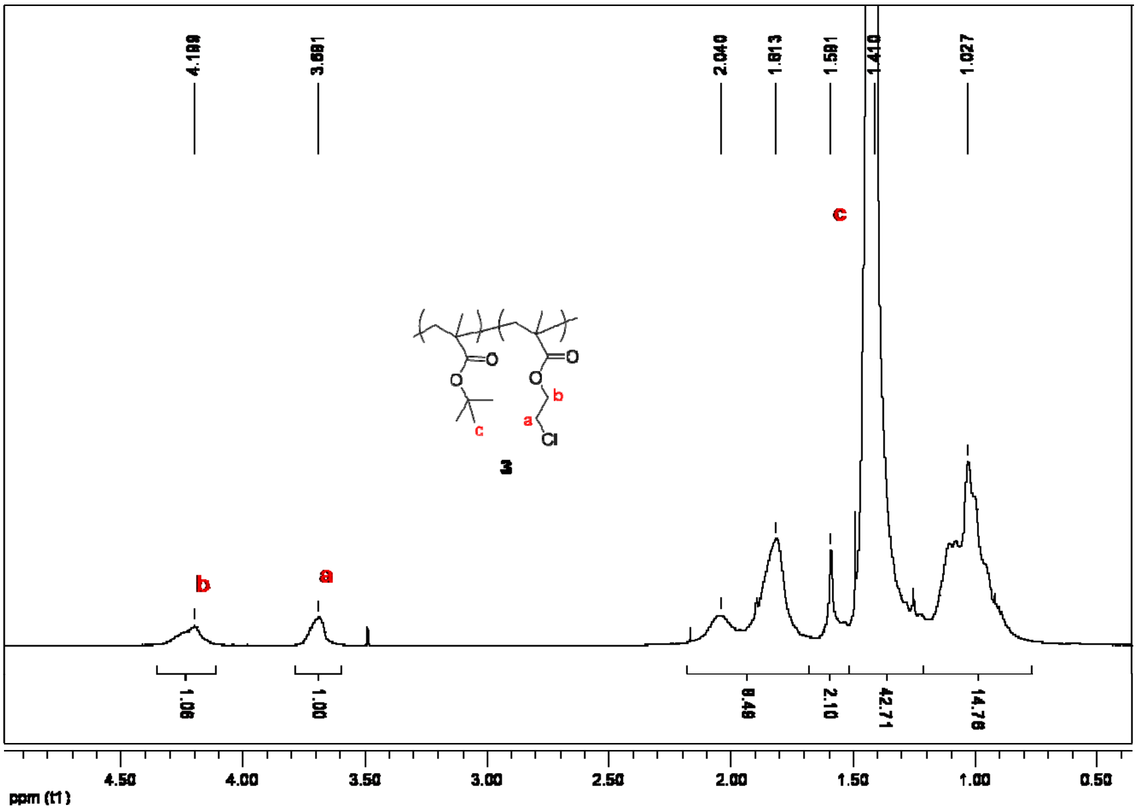


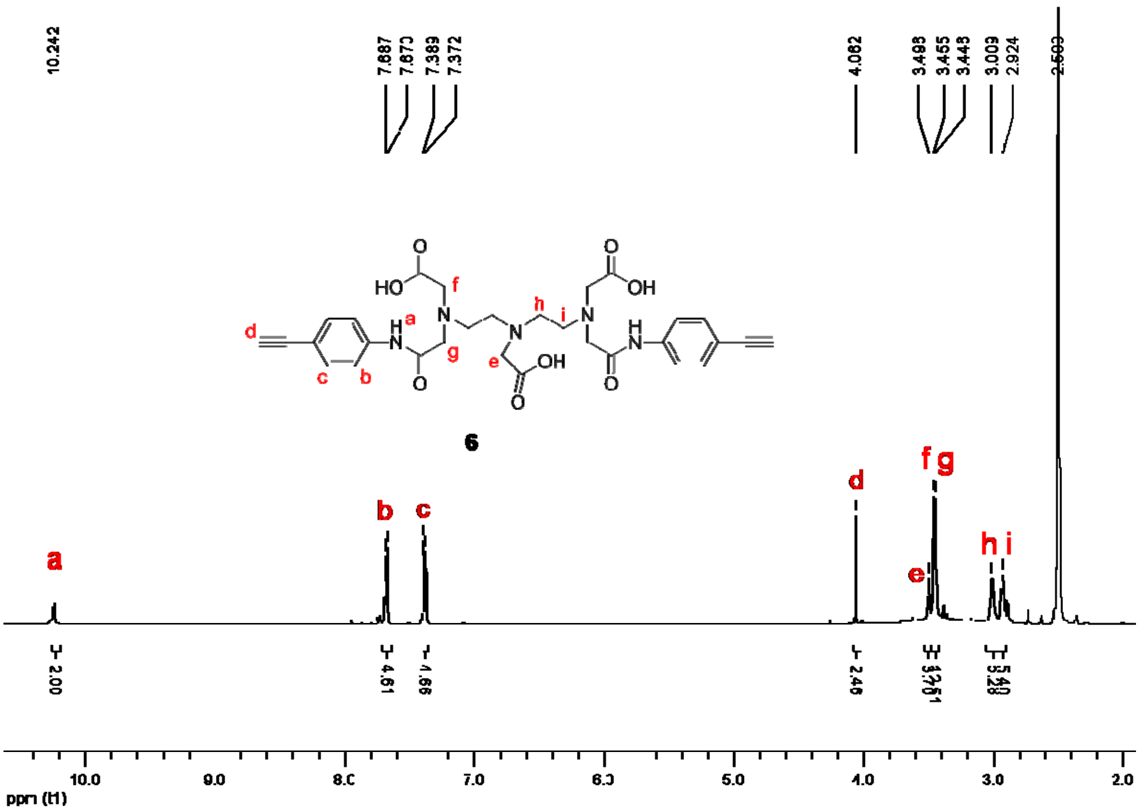



11408
%Transmittance
Wavenumbers (cm-1)
3434.83
2999.62
1718.01
1629.36
1406.32
1320.88
1260.71
1176.48
CO2H
HO2C
CO2H
8

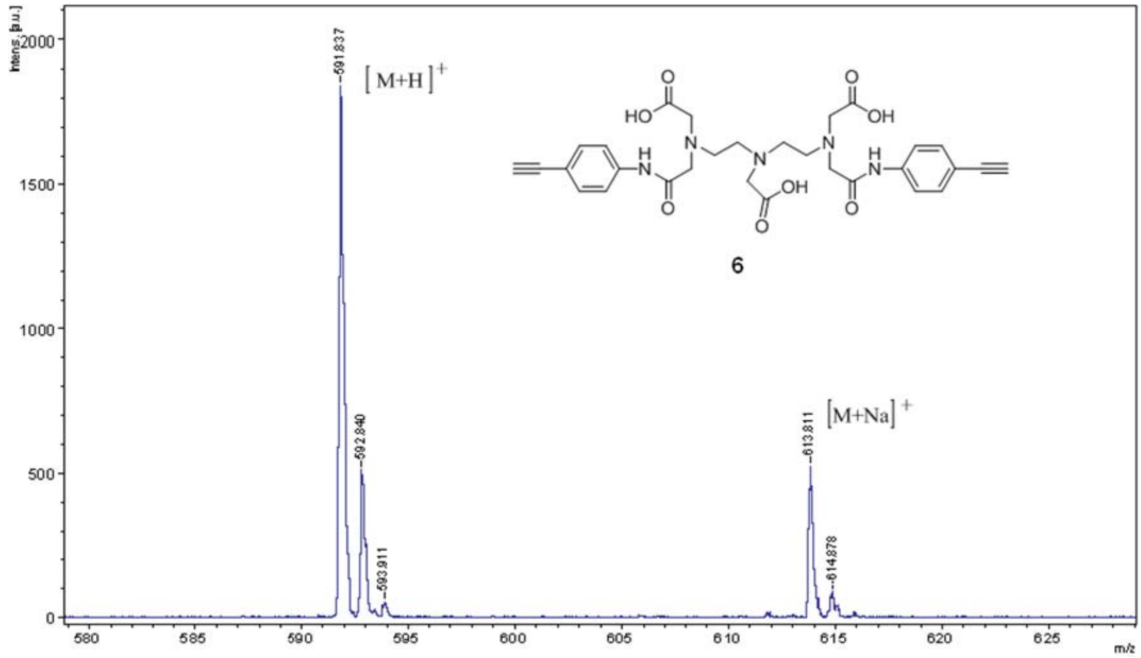

1141
%Transmittance
Wavenumbers (cm-1)
3434.85
2992.83
2594.34
1712.44
1636.30
1600.85
1406.25
1259.61
1178.70
CO2H
HO2C
CO2H
9

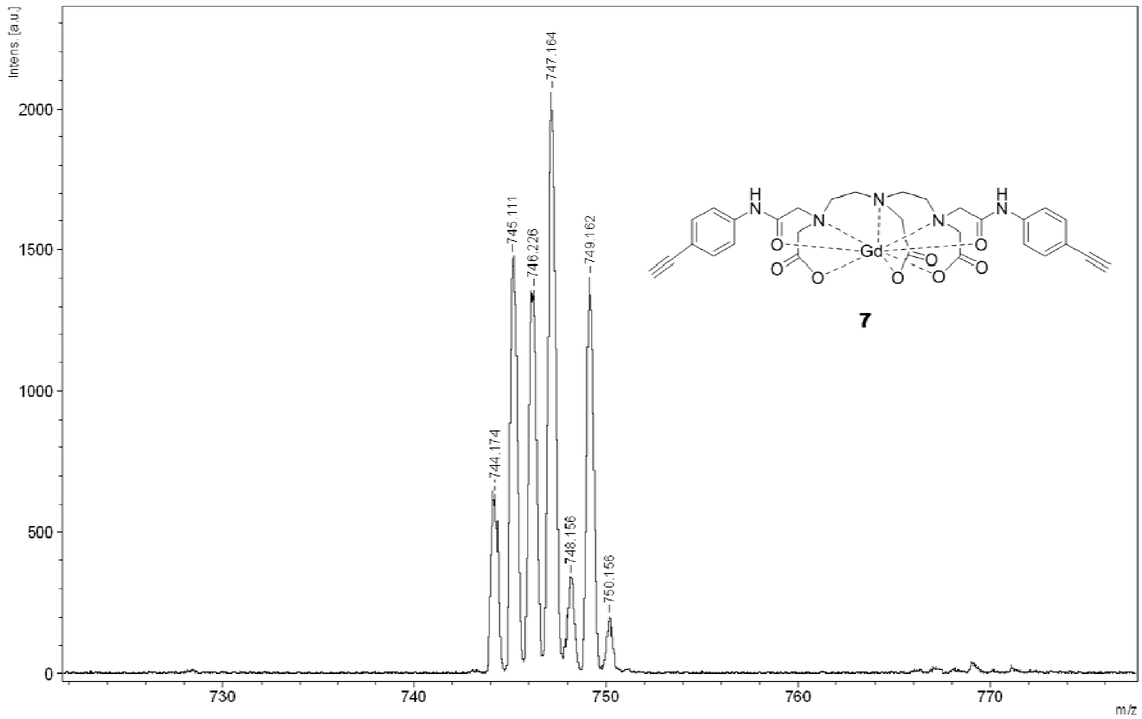
[1]H NMR Spectra

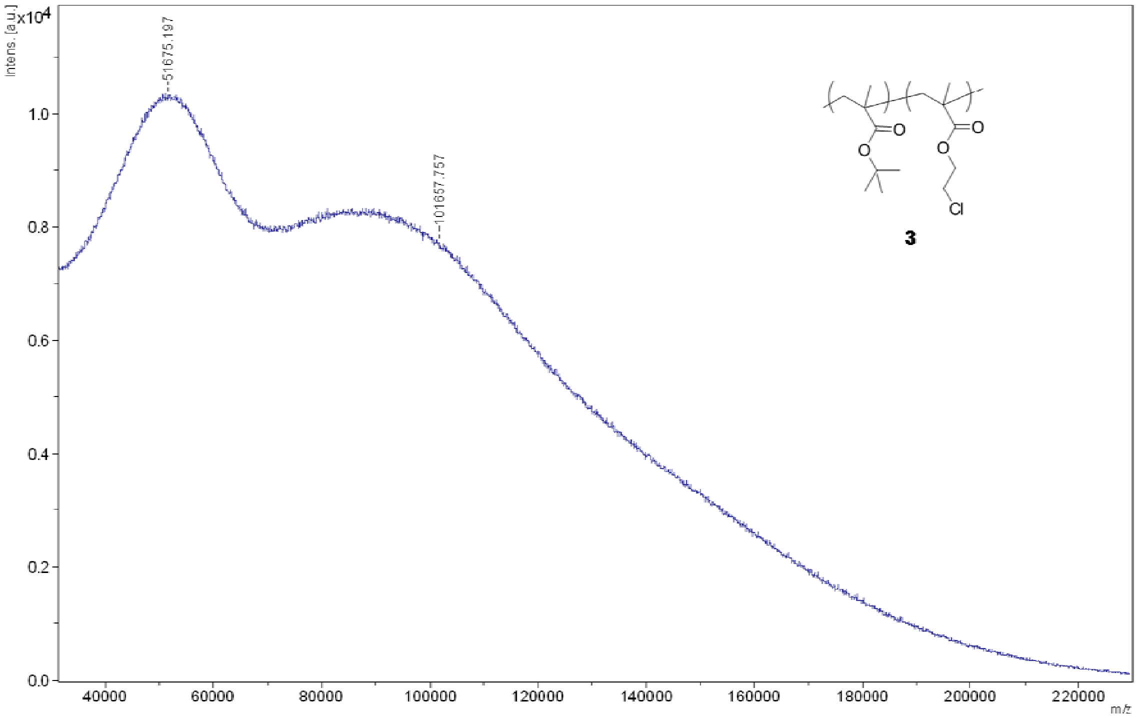




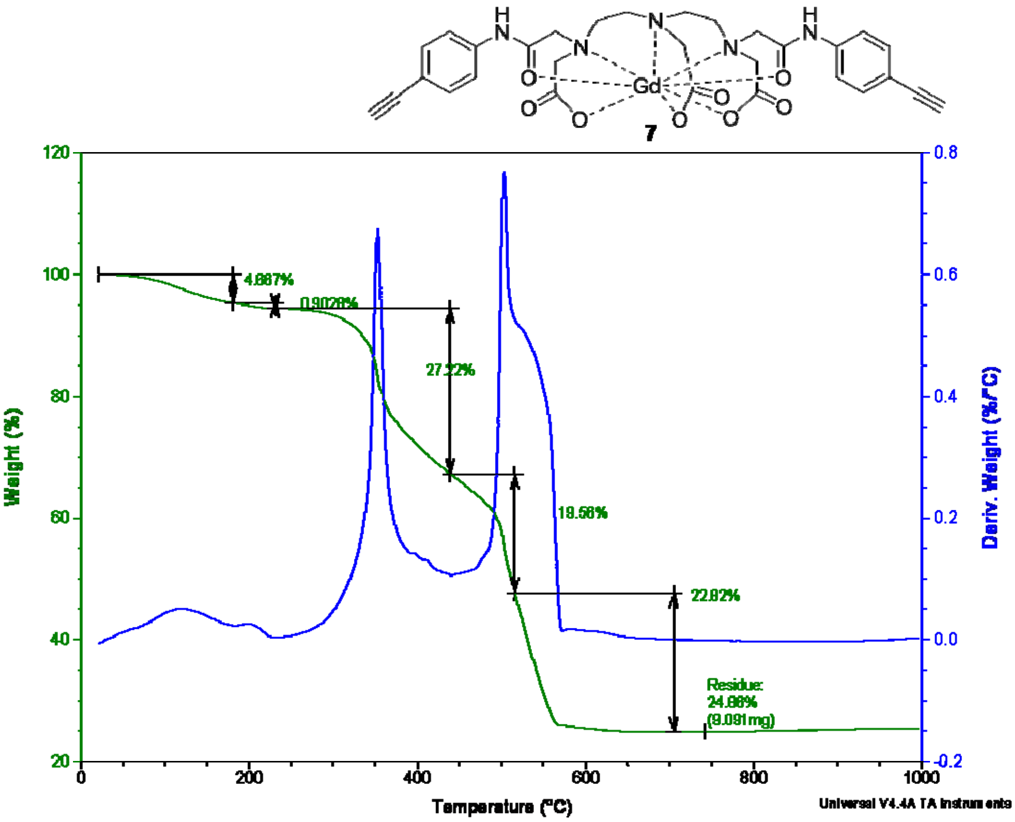
MALDI-TOF Spectra

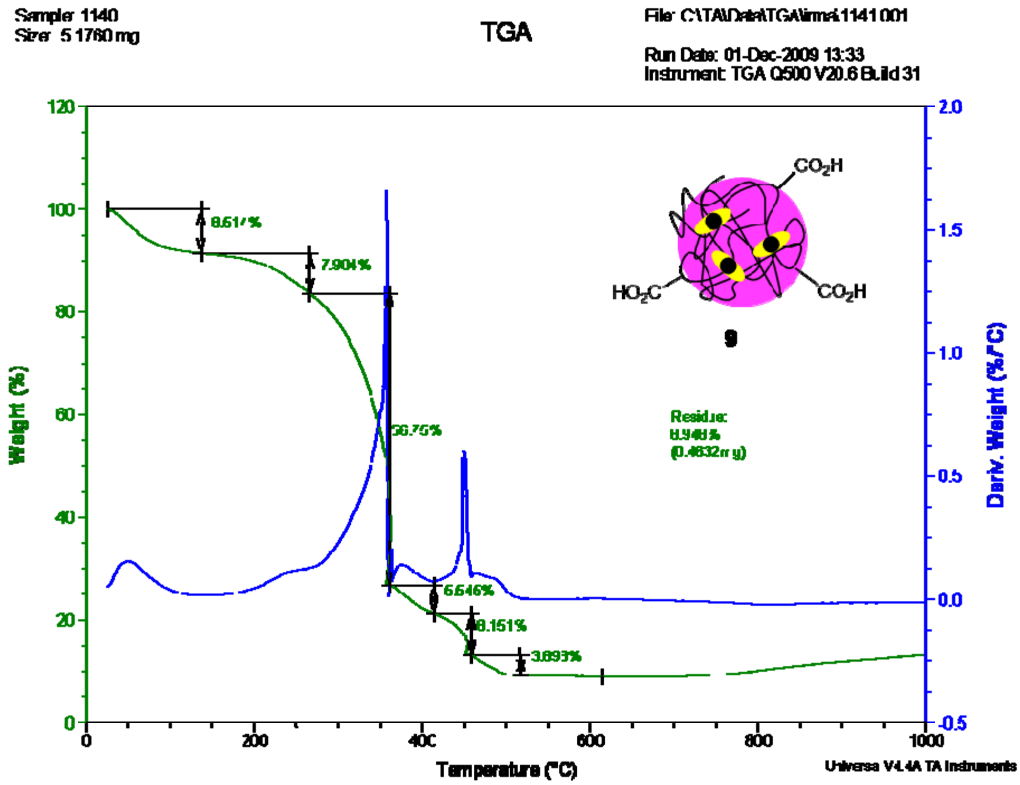





Intens. [a.u.]
x10^4
51675.197
101657.757
3
m/z

TGA spectra


7
4.687%
0.9028%
27.22%
19.56%
22.82%
Residue:
24.86%
(9.091mg)
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.4A TA Instruments



Gd content calculations for PNPs 10

TGA: TGA analyses were run in air, from room-temperature to 1000 ºC at a rate of 10 ºC min^{-1}.

Initial sample: 5.176 mg

Final residue: 0.4632 mg (8.948 %)

From the TGA curve we eliminate the 1st weight loss which corresponds to water (8.514%).

Initial PNPs weight – water = dry PNPs weight

5.176 – (5.176 x 0.08514) = 4.735 mg dry PNPs

ICP: Once the samples were burned in the TGA oven to remove all the organics, the residue was dissolved in ICP grade nitric acid (50 mL, HNO_3 final concentration 0.2%), and analyzed by ICP for Gd.

Results: the concentration of Gd was found to be 5.35 ppm (= 5.35 mg Gd·L^{-1}).

As the residue was dissolved in 50 mL of nitric acid:

$$50 \text{ mL} \cdot 5.35 \text{ mg Gd}\cdot\text{L}^{-1} = 50\cdot10^{-3} \text{ L} \cdot 5.35 \text{ mg Gd}\cdot\text{L}^{-1} = 0.2675 \text{ mg Gd in total.}$$

Then Gd wt% of the initial sample:

Gd wt% = (0.2675 mg Gd / 4.735 mg PNP)·100 = 5.6 wt% Gd

To calculate how many Gd^{3+} ions are per DTPA center, first we calculate the number of DTPA mmoles that are in 4.735 mg of PNPs. For that we need to calculate the molecular weight of the PNPs **9**. Taking into account that we have started from a 9:1 ratio of *t*BMA and ClEMA monomers, the repeating unit of this compound can be envisaged as a Gd-DTPA unit attached to 18 units of methacrylic acid (Figure S1). This gives a molecular weight of 2605 g/mol DTPA.

Thus, the initial amount of PNPs **10** was 4.735 mg / 2605 = 1.82×10^{-3} mmol DTPA.

The amount of Gd was found to be 0.2675 mg / 157.25 = 1.70×10^{-3} mmol Gd, which means that approximately 93% of the DTPA centers are occupied with Gd^{3+} ions. If the calculations are made considering the polymer in form of sodium methacrylate salt, an occupancy of 110% is obtained. The sample for ICP was taken from a neutral freeze-dried sample, so part of the carboxylic groups are expected to be as the sodium salt form. From these results we can conclude that practically all the DTPA units are Gd-loaded.

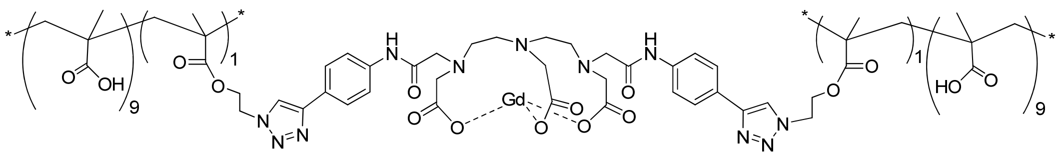


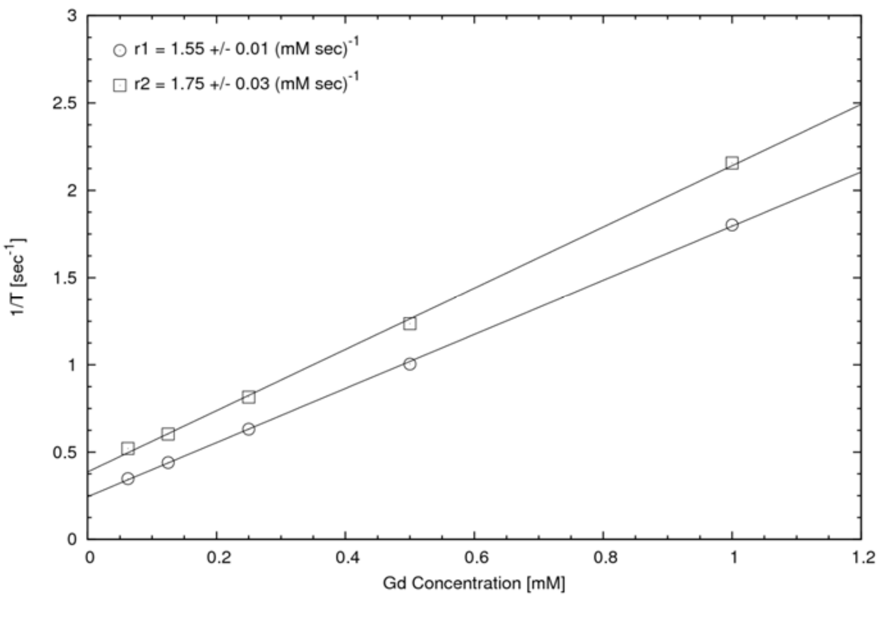
Figure S1. Chemical structure of the repeating unit of PNPs **10**.

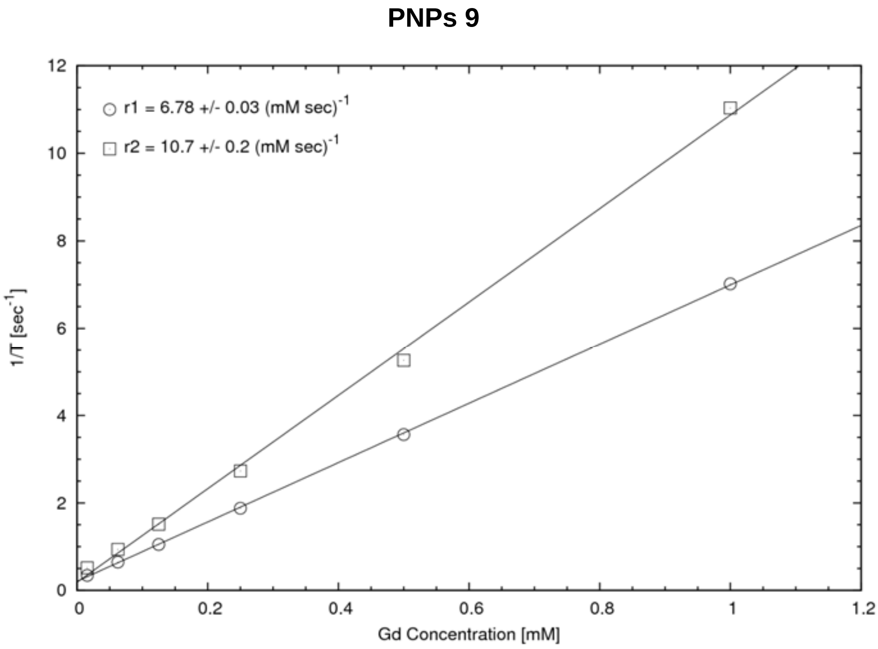
Average number of Gd^{3+} ions per nanoparticle

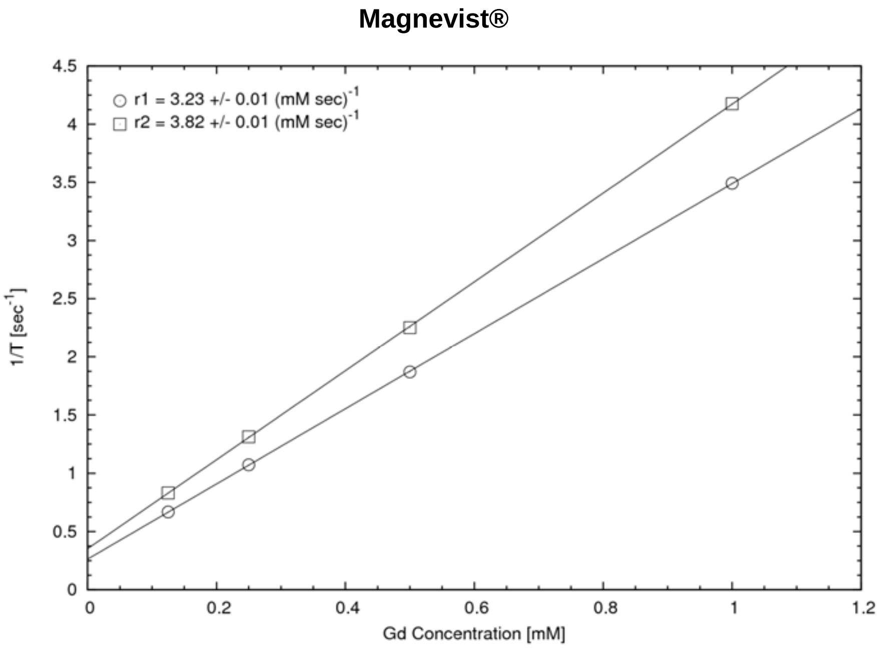
Considering a M_w of ~46 kDa and a molecular weight of 2605 g per each DTPA unit (calculated above), each nanoparticle would be loaded with an average of 46000/2605 = 18 Gd^{3+} ions.

Relaxivity values

Complex 7




PNPs 9
r1 = 6.78 +/- 0.03 (mM sec)-1
r2 = 10.7 +/- 0.2 (mM sec)-1
1/T [sec-1]
Gd Concentration [mM]
0
2
4
6
8
10
12
0.2
0.4
0.6
0.8
1
1.2


Magnevist®
r1 = 3.23 +/- 0.01 (mM sec)-1
r2 = 3.82 +/- 0.01 (mM sec)-1
1/T [sec-1]
Gd Concentration [mM]
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0.2
0.4
0.6
0.8
1
1.2