Supporting information

Mesoporous Gadolino-aluminosilicate Nanoparticles as Magnetic Resonance Imaging Contrast Agents

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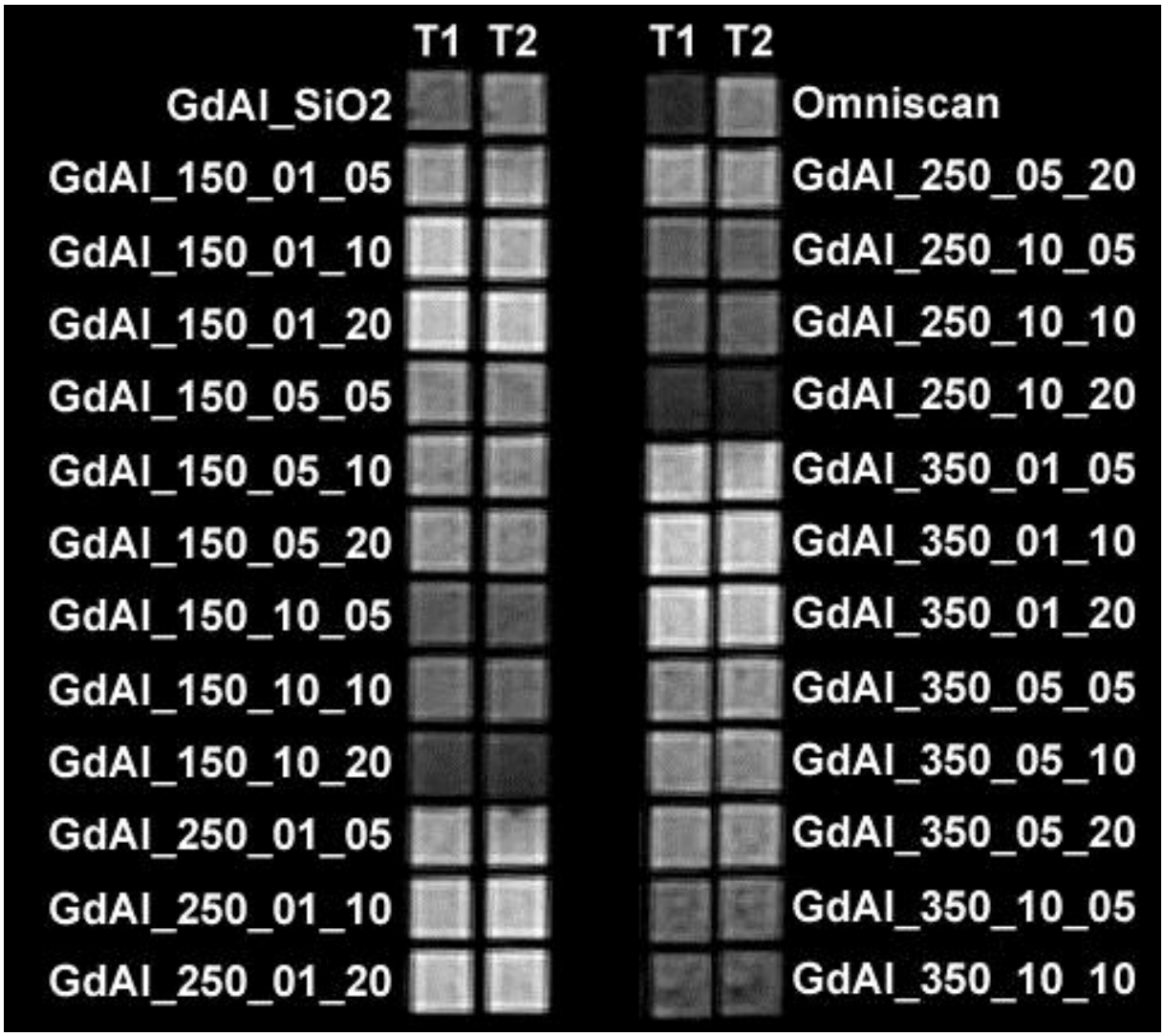
S1. Characterization results for the various Gd-Al-SiO_2 samples.

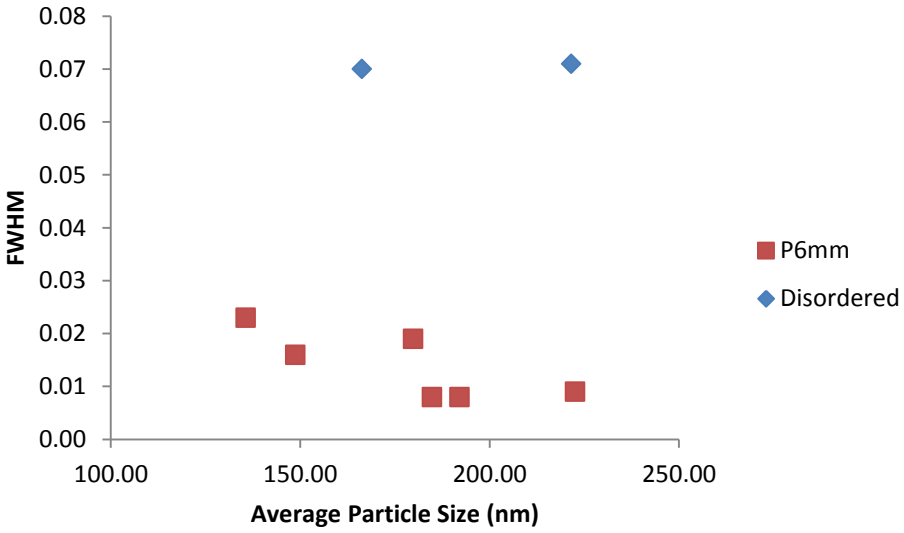
Sample Name	Composition				SAXS		Ordered Domain Size		MRI		
	Gd	Al	SiO_2	Al/Gd	d-spacing	P6mm Lattice Parameter	FWHM	Domain size [e]	r_1	r_2	r_2/r_1
	wt%	wt%	wt%	w/w	(nm)	(nm)	at (100)	(nm)	$mM^{-1}s^{-1}$	$mM^{-1}s^{-1}$	
CTB200	6.85	0	93.15	-	3.94	-	-	-	2.02	6.5	3.21
CTB250	5.93	0	94.07	-	4.49	-	-	-	3.83	7.37	1.92
CTB400	5.92	0	94.08	-	3.97	4.59	-	-	2.78	6.15	2.21
Omniscan	-	-	-	-	-	-	-	-	5.53	4.64	0.84
GdAl_150_01_05	0.67	0.10	99.23	7.0	3.33	3.85	0.013 [a]	24.60	18.77	4.81	0.26
GdAl_150_01_10	0.54	0.18	99.28	3.0	3.29	3.79	0.018 [b]	17.28	38.98	12.6	0.32
GdAl_150_01_20	2.65	0.18	97.17	15.0	3.29	3.79	0.024 [b]	13.34	5.5	1.77	0.32
GdAl_150_05_05	2.65	0.31	97.04	8.5	3.36	3.88	0.024 [b]	12.68	13.04	2.72	0.21
GdAl_150_05_10	2.74	0.58	96.68	4.7	3.36	3.88	0.028 [b]	11.14	7.71	1.48	0.19
GdAl_150_05_20	7.16	0.35	92.49	20.8	3.41	3.93	0.024 [b]	12.62	3.38	0.8	0.24
GdAl_150_10_05	5.52	0.51	93.97	10.8	3.62	-	0.035 [c]	8.28	7.09	0.96	0.13
GdAl_150_10_10	6.64	1.33	92.03	5.0	3.53	-	0.023 [b]	12.32	4.72	0.75	0.16
GdAl_150_10_20	0.36	0.05	99.59	6.7	3.47	-	0.036 [c]	7.78	212.02	10.62	0.05
GdAl_250_01_05	0.66	0.09	99.24	7.0	3.48	4.02	0.008 [a]	36.67	20.32	5.25	0.26
GdAl_250_01_10	0.48	0.19	99.33	2.5	3.51	4.05	0.008 [a]	35.82	28.97	7.37	0.25
GdAl_250_01_20	2.74	0.18	97.08	15.5	3.48	4.02	0.009 [a]	32.42	4.73	1.57	0.33
GdAl_250_05_20	6.75	0.36	92.89	18.8	3.46	3.99	0.074 [d]	4.08	2.47	0.61	0.25
GdAl_250_10_05	5.47	0.58	93.95	9.4	3.62	-	0.073 [d]	3.99	5.65	0.69	0.12
GdAl_250_10_10	6.21	1.26	92.53	4.9	3.59	-	0.022 [b]	13.32	4.7	0.61	0.13
GdAl_250_10_20	0.63	0.07	99.3	8.8	3.48	-	0.083 [d]	3.45	143.11	4.48	0.03
GdAl_350_01_05	0.70	0.04	99.25	16.0	3.51	4.05	0.008 [a]	38.81	19.08	4.6	0.24
GdAl_350_01_10	0.74	0.08	99.18	9.0	3.51	4.05	0.009 [a]	33.86	20.9	6.05	0.29
GdAl_350_01_20	0.75	0.19	99.06	4.0	3.48	4.02	0.008 [a]	36.62	24.2	7.82	0.32
GdAl_350_05_05	3.26	0.17	96.57	19.5	3.48	4.02	0.016 [b]	18.13	6.5	0.96	0.15
GdAl_350_05_10	2.98	0.35	96.67	8.5	3.46	3.99	0.019 [b]	16.06	8.61	1.49	0.17
GdAl_350_05_20	3.20	0.56	96.24	5.7	3.41	3.93	0.023 [b]	13.14	7.35	1.16	0.16
GdAl_350_10_05	6.13	0.37	93.5	16.8	3.48	-	0.070 [d]	4.18	4.95	0.69	0.14
GdAl_350_10_10	6.15	0.42	93.43	14.6	3.56	-	0.071 [d]	4.09	6.64	0.98	0.15

[a] peak fitted to a Lorentzian curve function.
[b] peak fitted to a Gaussian curve function.
[c] peak fitted to a exponential Gaussian function.
[d] peak fitted to a Pearson IV curve function with the variable parameter v = 30.
[e] calculated using the Scherrer equation with K=0.93.[1, 2]

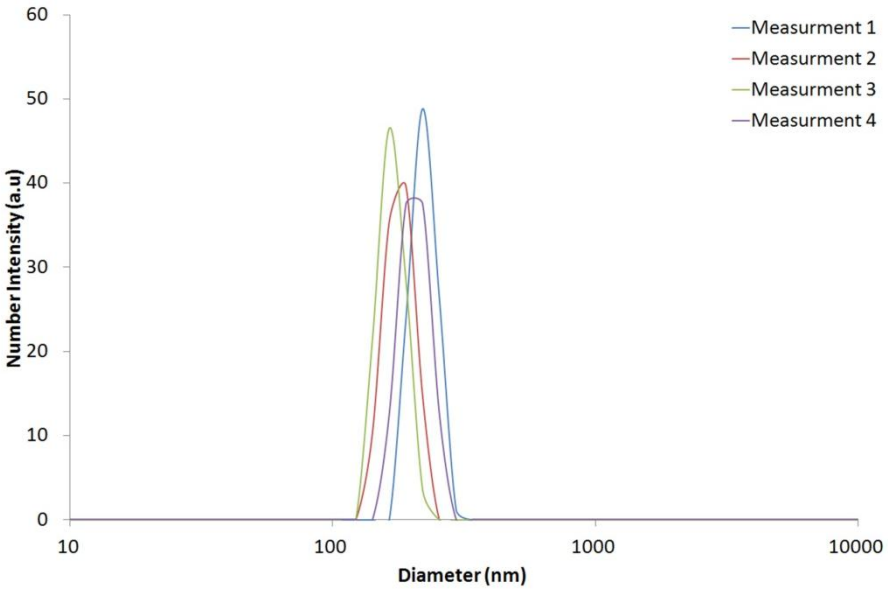
S2: Phantom MRI images of the T_1 and T_2 contrast for the series of reported materials.



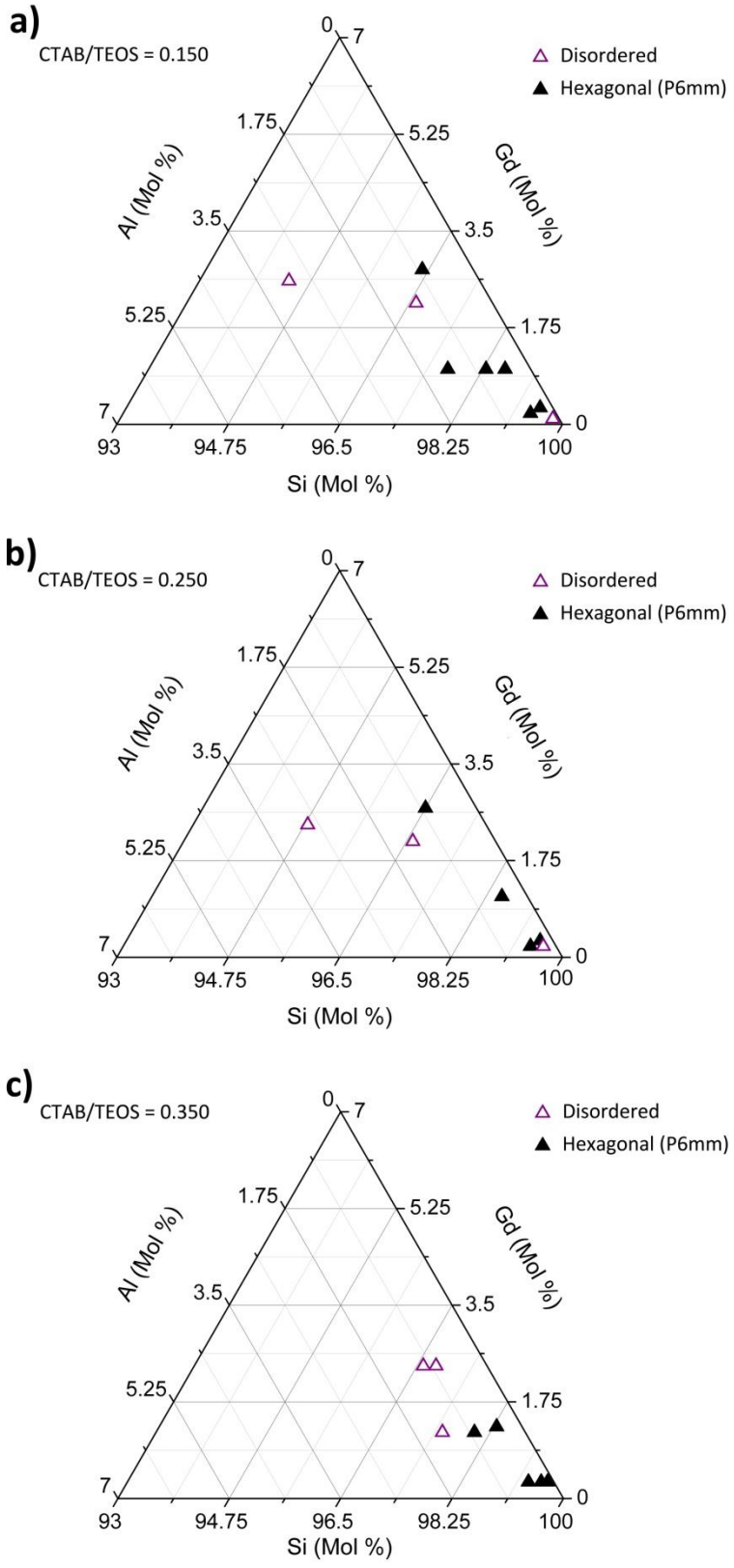
S3. Average particle size measured using DLS plotted against the FWHM of the first correlation peak for the various CTAB/TEOS = 0.350 silicate sample.



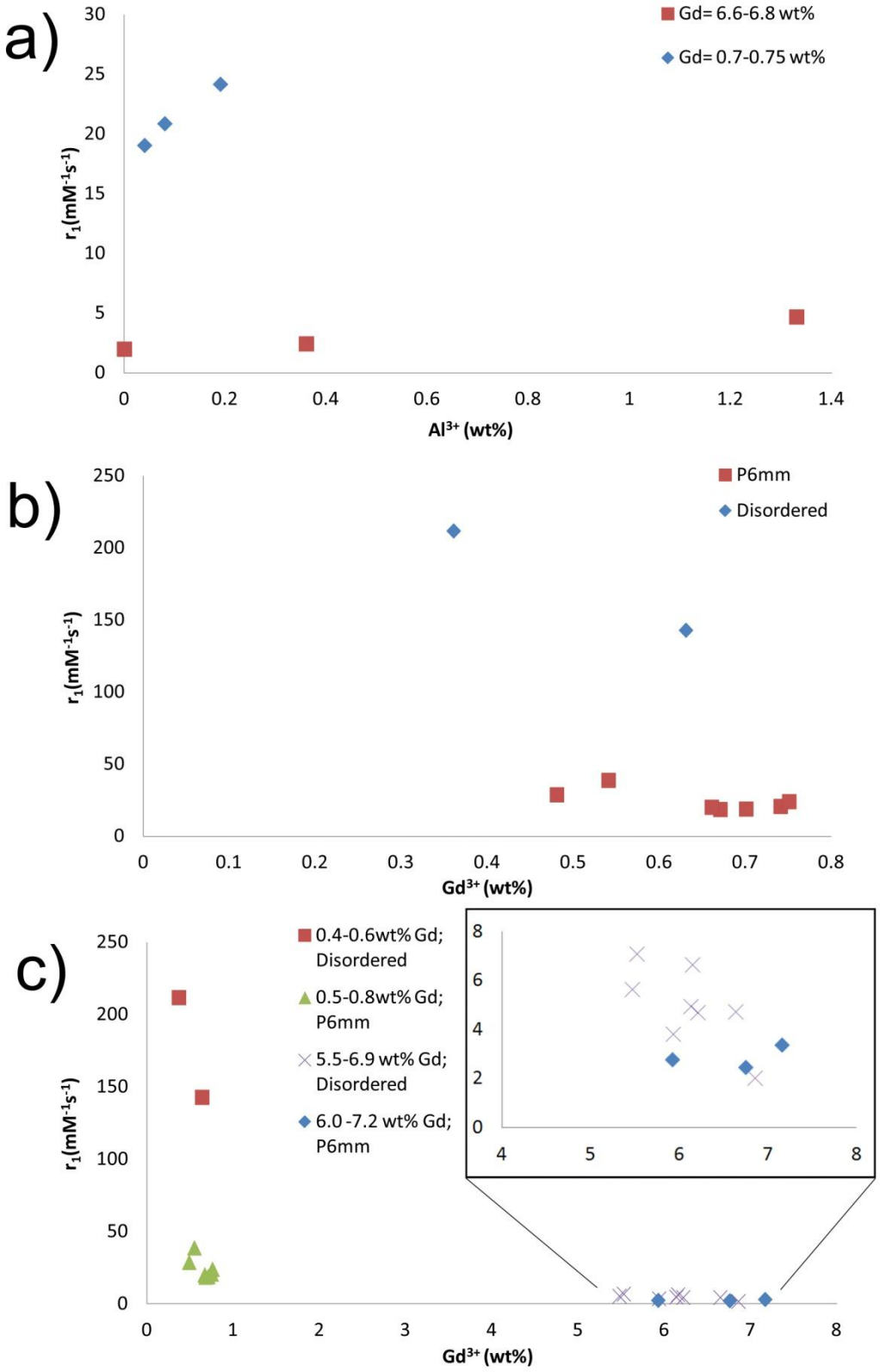
S4. Dynamic light scattering of *GdAl_150_01_20*.



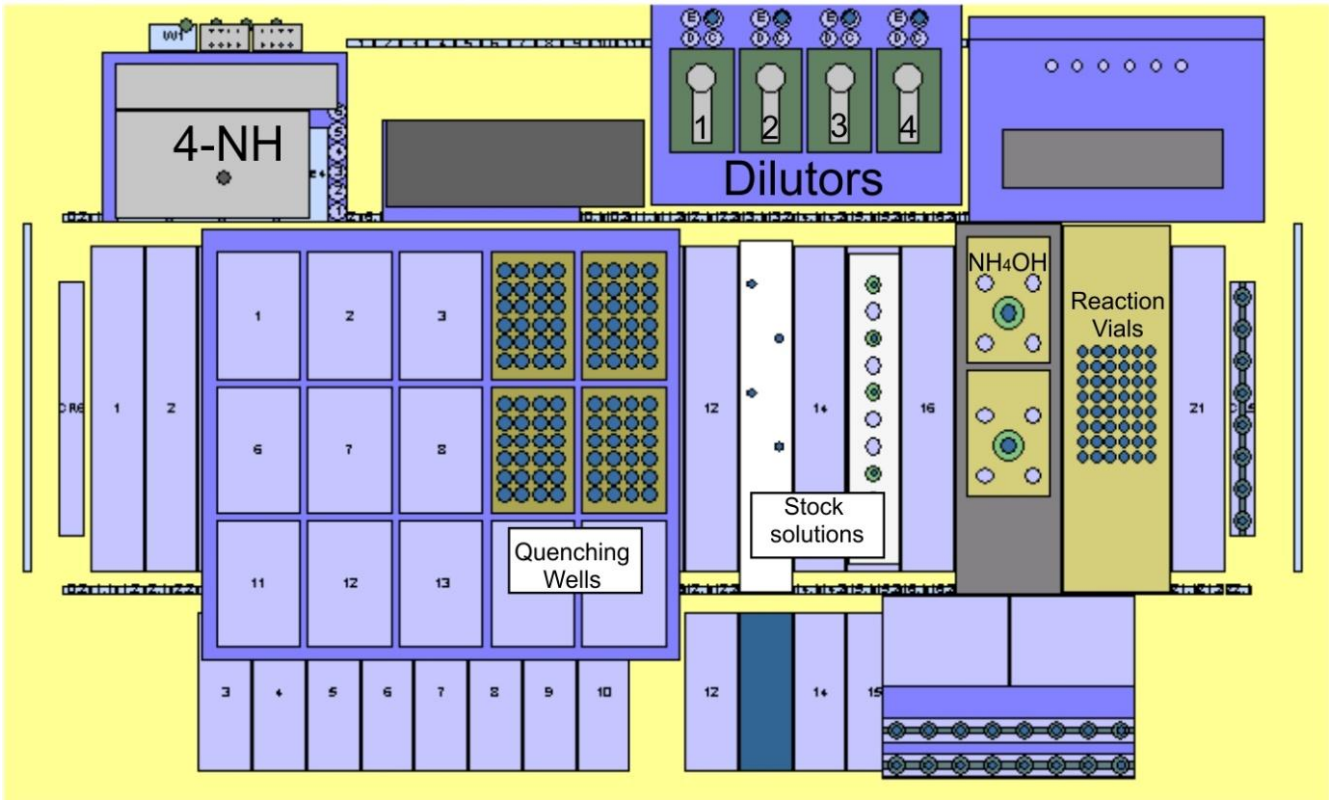
S5. Ternary phase diagrams for various GdAl SiO_2 samples. The three ternary phase diagrams a), b) and c) are for samples with a CTAB/TEOS ratio of 0.150, 0.250 and 0.350, respectively.



S6. Longitudinal relaxivity verses a) Al^{3+}, b) Gd^{3+} and c) pore ordering for the various silicate samples.



S7. Screen capture of the experimental setup used in this work on the Chemspeed Accelerator™ SLTII robotic synthesis platform.

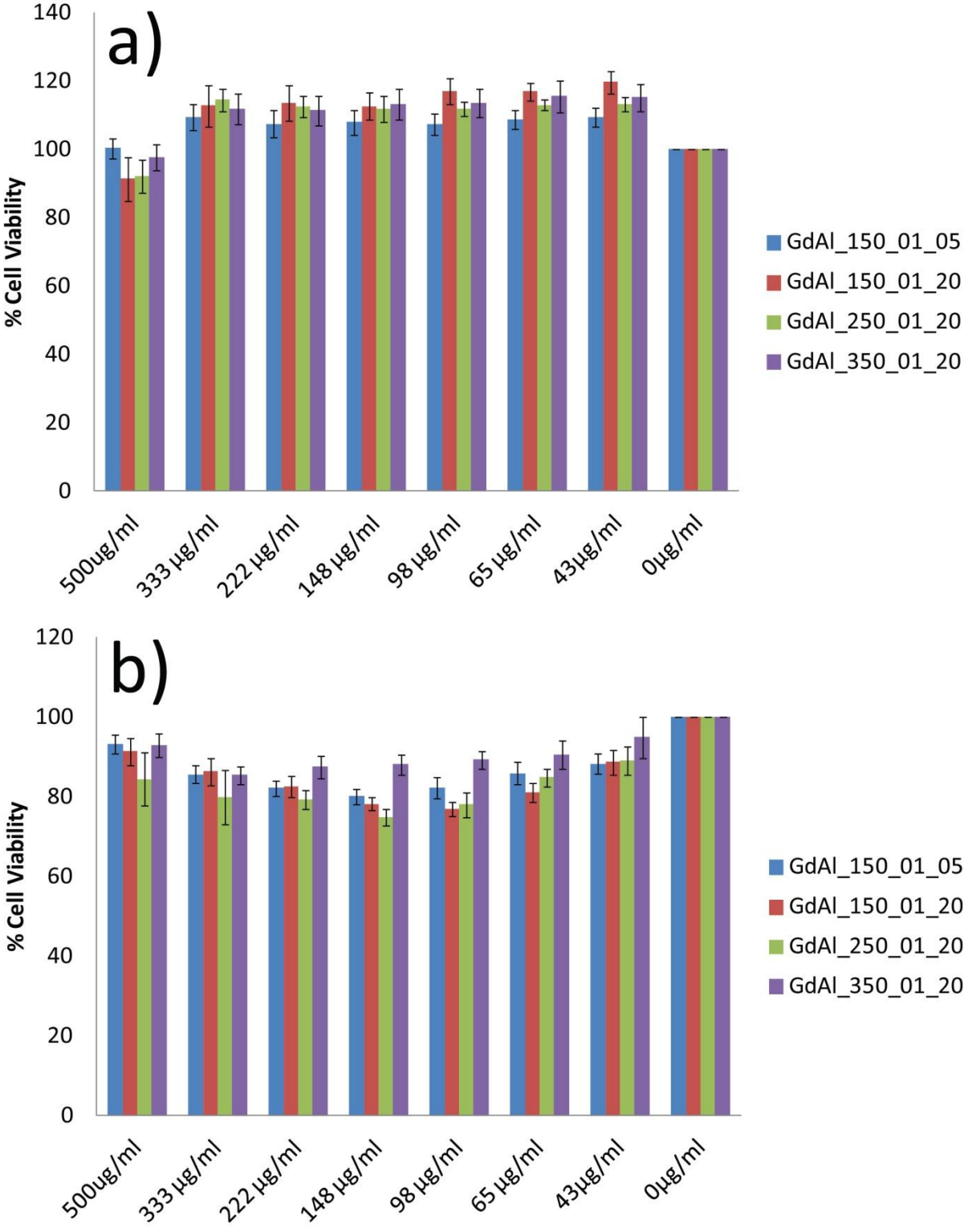


S8. Reagent amounts for the synthesis of Gd-Al-SiO_2

Exp #	Sample name	CTAB mg	TEOS mL	EtOH mL	HCl [a] mL	Gd^{3+} [b] mL	Al^{3+} [c] mL	H_2O mL	Total mL
1	GdAl_150_01_05	71.4	0.285	0.787	0.238	0.024	0.006	0.446	1.786
2	GdAl_150_01_10	71.4	0.285	0.787	0.238	0.024	0.012	0.440	1.786
3	GdAl_150_01_20	71.4	0.285	0.787	0.238	0.024	0.024	0.428	1.786
4	GdAl_150_05_05	71.4	0.285	0.787	0.238	0.119	0.030	0.327	1.786
5	GdAl_150_05_10	71.4	0.285	0.787	0.238	0.119	0.060	0.298	1.786
6	GdAl_150_05_20	71.4	0.285	0.787	0.238	0.119	0.119	0.238	1.786
7	GdAl_150_10_05	71.4	0.285	0.787	0.238	0.238	0.060	0.179	1.786
8	GdAl_150_10_10	71.4	0.285	0.787	0.238	0.238	0.119	0.119	1.786
9	GdAl_150_10_20	71.4	0.285	0.787	0.238	0.238	0.238	0.000	1.786
10	GdAl_250_01_05	118.3	0.285	0.787	0.238	0.024	0.006	0.446	1.786
11	GdAl_250_01_10	118.3	0.285	0.787	0.238	0.024	0.012	0.440	1.786
12	GdAl_250_01_20	118.3	0.285	0.787	0.238	0.024	0.024	0.428	1.786
13	GdAl_250_05_20	118.3	0.285	0.787	0.238	0.119	0.119	0.238	1.786
14	GdAl_250_10_05	118.3	0.285	0.787	0.238	0.238	0.060	0.179	1.786
15	GdAl_250_10_10	118.3	0.285	0.787	0.238	0.238	0.119	0.119	1.786
16	GdAl_250_10_20	118.3	0.285	0.787	0.238	0.238	0.238	0.000	1.786
17	GdAl_350_01_05	166.6	0.285	0.787	0.238	0.024	0.006	0.446	1.786
18	GdAl_350_01_10	166.6	0.285	0.787	0.238	0.024	0.012	0.440	1.786
19	GdAl_350_01_20	166.6	0.285	0.787	0.238	0.024	0.024	0.428	1.786
20	GdAl_350_05_05	166.6	0.285	0.787	0.238	0.119	0.030	0.327	1.786
21	GdAl_350_05_10	166.6	0.285	0.787	0.238	0.119	0.060	0.298	1.786
22	GdAl_350_05_20	166.6	0.285	0.787	0.238	0.119	0.119	0.238	1.786
23	GdAl_350_10_05	166.6	0.285	0.787	0.238	0.238	0.060	0.179	1.786
24	GdAl_350_10_10	166.6	0.285	0.787	0.238	0.238	0.119	0.119	1.786

a: HCl was diluted to a concentration of 2.25 M HCl.
b: Gd^{3+} aqueous solution was made using $GdCl_3.6H_2O$ to a concentration of 209 mM in MilliQ water.
c: Al^{3+} aqueous solution was made using $AlCl_3$ to a concentration of 247 mM in MilliQ water.

S9: Cell viability results for a) A549 and b) CHO-WT cells incubated with a the selected *GdAl* samples at varying nanoparticle concentrations. Results are presented as a percentage of viable cells compared to the control sample.



Cell toxicity study

Cells:
Chinese Hamster Ovary cells constitutively expressing Green Fluorescent Protein (CHO-GFP) (kindly received from K. Wark; CSIRO CMSE Australia) were grown in MEMα modification (Sigma, USA), and human alveolar basal epithelial cells (A549; ATCC CCL-185) were grown in DMEM (Invitrogen, USA). Both base media were supplemented with

10% foetal bovine serum, 2 mM glutamine, 10 mM Hepes, 1.5 g/L sodium bicarbonate, 0.01% penicillin and 0.01% streptomycin. Cells were grown at 37 ºC with 5% CO_2.

Toxicity assay:
CHO-GFP and A549 cells were seeded at $1x10^4$ cells per well in 96-well tissue culture plates and grown overnight at 37 ºC with 5% CO_2.
The silicate materials were added to 3 wells in the 96 well culture plates for each sample and incubated at 37 ºC and incubated for 72 h. Toxicity was measured using the Alamar Blue reagent (Invitrogen USA) according to manufacturer's instructions. Briefly, media was removed and replaced with 100 µl of standard media containing 10% Alamar Blue reagent, cells were then incubated for 2 h at 37 ºC with 5% CO_2. The assay was read on an EL808 Absorbance microplate reader (BIOTEK, USA) at 540 nm and 620 nm. Cell viability was determined by subtracting the 620 nm measurement from the 540 nm measurement. Obtained data was analysed in Microsoft Excel. Results are presented as a percentage of untreated cells and the presented data are representative of three separate experiments in triplicate.

References

[1] U. Holzwarth, N. Gibson, Nat Nano 2011, 6, 534.
[2] T. Landh, Journal of Physical Chemistry 1994, 98, 8453.