Supplementary Information (SI) for Journal of Materials Chemistry B.

Exploring the influence of internal surface modification of paramagnetic mesoporous silica nanoparticles on MRI relaxation dynamics

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Supporting Information

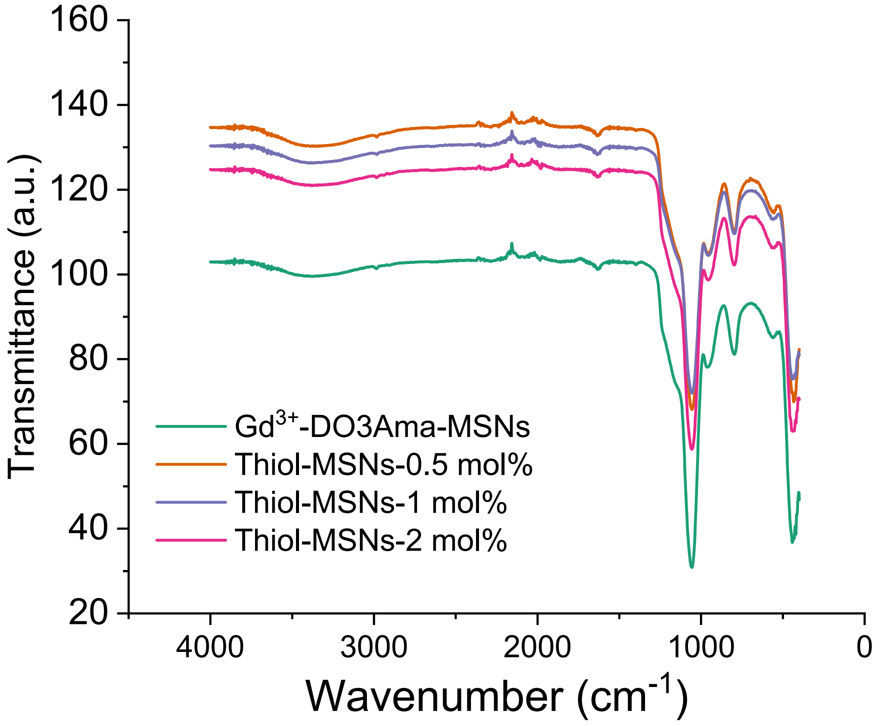

Figure S1. FTIR spectra of MSNs, as labelled.

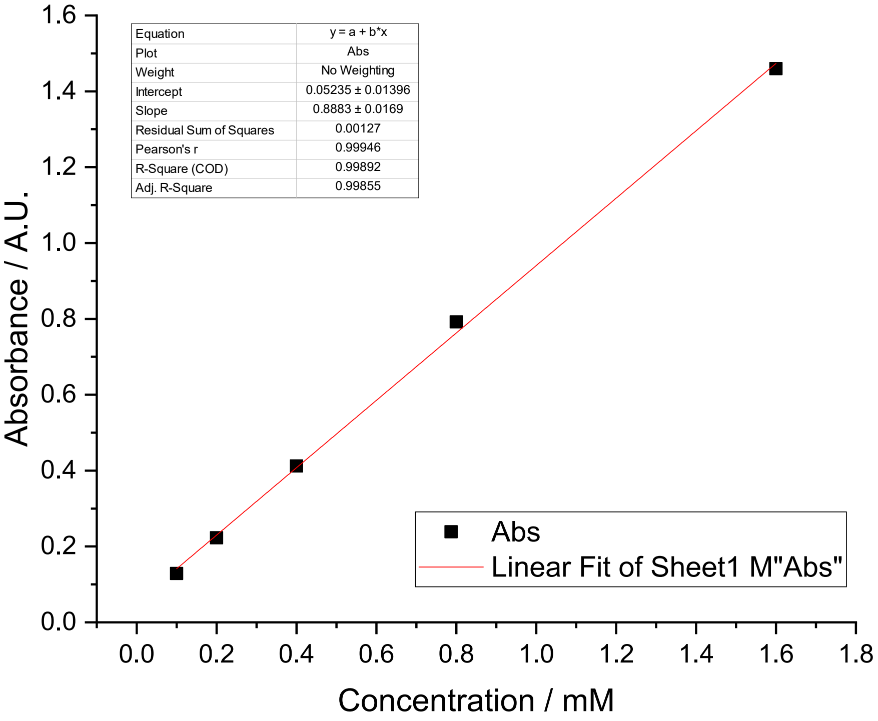

Figure S2. Calibration curve of L-cysteine hydrochloride standards dissolved in reaction buffer, measured at 412 nm.

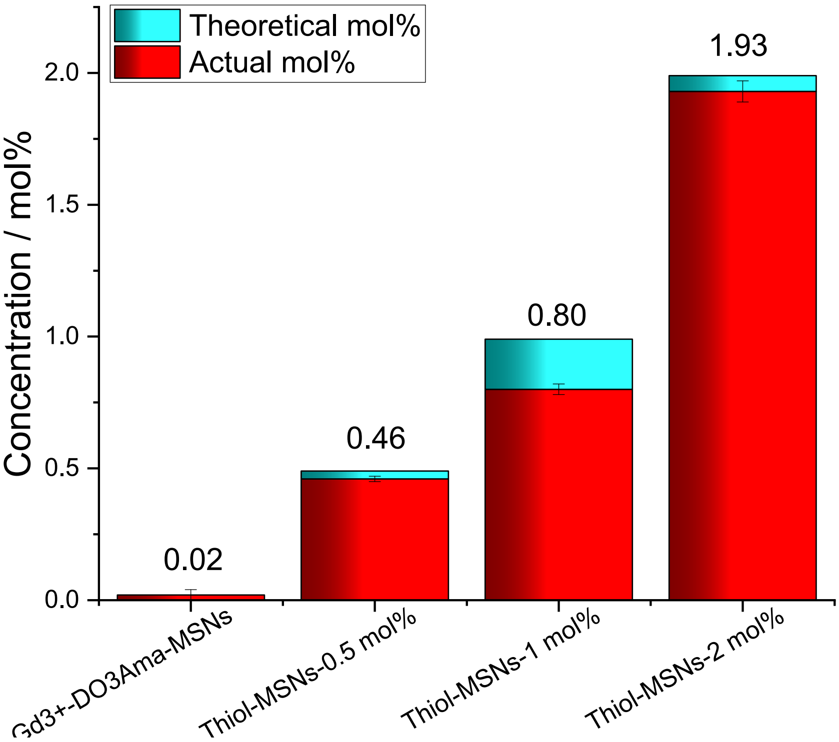

Figure S3. Thiol assays determining the quantity of thiol groups attached to the pores of the MSNs in molar percentage (n = 3 independent measurements). Blue strip at the top represents the difference from actual (red) to theoretical (blue) molar percentages.

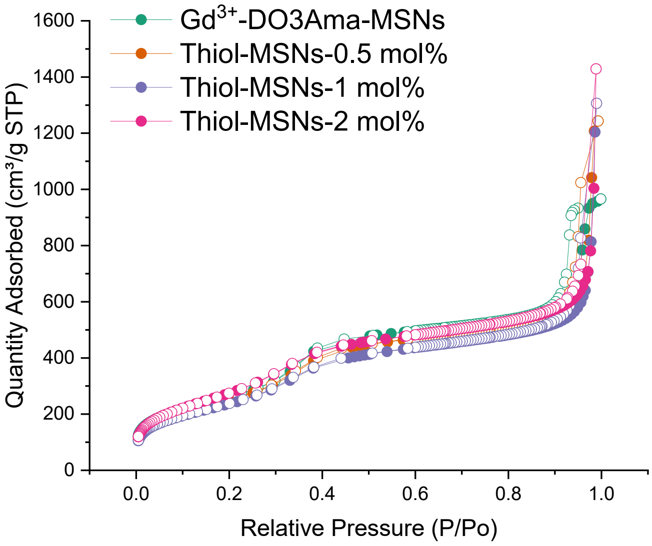

Figure S4. Nitrogen sorption porosimetry curves (adsorption solid shapes, desorption empty shapes).

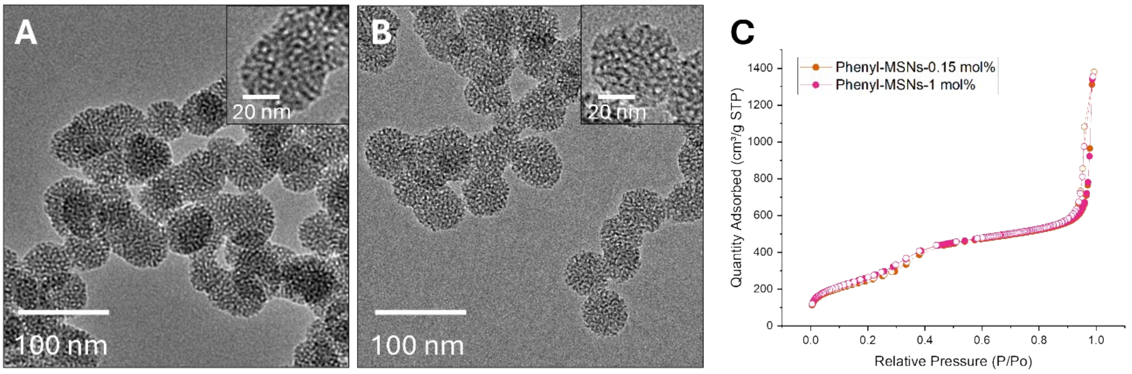

Figure S5. TEM of a) Phenyl-MSNs-0.15 mol% and b) Phenyl-MSNs-1 mol% and c) gas sorption porosimetry of Phenyl-MSNs-0.15 mol% and Phenyl-MSNs-1 mol% (adsorption solid shapes, desorption empty shapes).

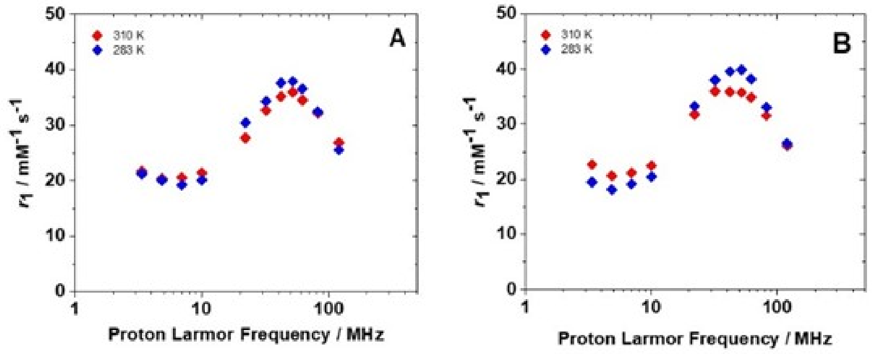

Figure S6. ^{1}H NMRD profiles (at 10 °C and 37 °C) of a) Thiol-MSNs-2 mol% and b) Phenyl-MSNs-1 mol%.

Table S1. Gadolinium concentrations of the different modified samples, as determined by ICP-OES (n = 3), given in mM and converted to weight percent relative to SiO_2.

Sample	**[Gd] (mM)**	**Gd : Si (wt%)**
Gd^{3+}-DO3Ama-MSNs	0.24 ± 0.04	2.7
Thiol-MSNs-0.5 mol%	0.19 ± 0.05	2.1
Thiol-MSNs-1 mol%	0.19 ± 0.05	2.1
Thiol-MSNs-2 mol%	0.21 ± 0.01	2.3
Phenyl-MSNs-0.15 mol%	0.24 ± 0.09	2.7
Phenyl-MSNs-1 mol%	0.24 ± 0.06	2.7

Table S2. Surface areas, pore volumes and pore diameters of the modified MSNs as determined by nitrogen adsorption-desorption porosimetry using BET and BJH methods.

Sample	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore diameter (nm)**
Gd^{3+}-DO3Ama-MSNs	985 ± 9	0.81	3.0
Thiol-MSNs-0.5 mol%	946 ± 10	0.76	3.1
Thiol-MSNs-1 mol%	888 ± 9	0.72	3.1
Thiol-MSNs-2 mol%	1080 ± 18	0.76	3.0
Phenyl-MSNs-0.15 mol%	941 ± 11	0.79	3.2
Phenyl-MSNs-1 mol%	1018 ± 12	0.78	3.0

Relaxometric data treatment

Relaxivity is described by three contributions, depending on the type of interaction:

$$r_i = r_i^{IS} + r_i^{SS} + r_i^{OS} \tag{1}$$

The relaxivity of a paramagnetic probe is governed by three distinct mechanisms that depend on the proximity and interaction of water molecules with the metal center. The inner-sphere (IS) contribution involves water molecules directly coordinated to the metal. Beyond this immediate coordination, the second-sphere (SS) contribution involves water molecules that interact with the complex through hydrogen bonding; these molecules contribute significantly only if they remain near the metal for a residence time long enough to facilitate relaxation. Finally, the outer-sphere (OS) contribution accounts for the influence of bulk water molecules as they diffuse close to paramagnetic center. In the case of hydrated systems, the enhancement of relaxation rates is typically dominated by the inner-sphere component. This contribution is described by the following equation:

$$\left(\frac{1}{T_1}\right)^{IS} = \frac{1}{1000}\cdot\frac{C \times q}{55.56}\cdot\frac{1}{T_{1M}+\tau_M} = \frac{p_m}{T_{1M}+\tau_M} \tag{2}$$

Where p_m is the mole fraction of the bound water molecules, q is the number of inner-sphere water molecules; t_M is the residence lifetime of an inner-sphere water molecule and T_{1M} is the longitudinal proton relaxation time of bound water.

For nanosystems in slow tumbling motion:

$$\frac{1}{T_{1M}} = \frac{K}{r_H^6}\left[\frac{3S^2\tau_{CG}}{1+\omega_H^2\tau_{CG}^2} + \frac{3(1-S^2)\tau_{CL}}{1+\omega_H^2\tau_{CL}^2}\right] \tag{3}$$

$$\frac{1}{\tau_{CG}} = \frac{1}{\tau_{RG}} + \frac{1}{\tau_M} + \frac{1}{T_{1e}}; \quad \frac{1}{\tau_{CL}} = \frac{1}{\tau_{CG}} + \frac{1}{\tau_{RL}} \tag{4}$$

where K combines a series of constants and assumes a value of 5.18 $\times 10^{-31}$ (cm^6/s^2; CGS unit) for Gd^{3+}. r_H is the distance between the metal and water protons and ω_H is the proton Larmor frequency. The model distinguish the global rotation of the nanosized system (τ_{RG})

from the local motion of the chelate units (τ_{RL}). The degree of correlation between the two types of motions is given by the parameter S^2.