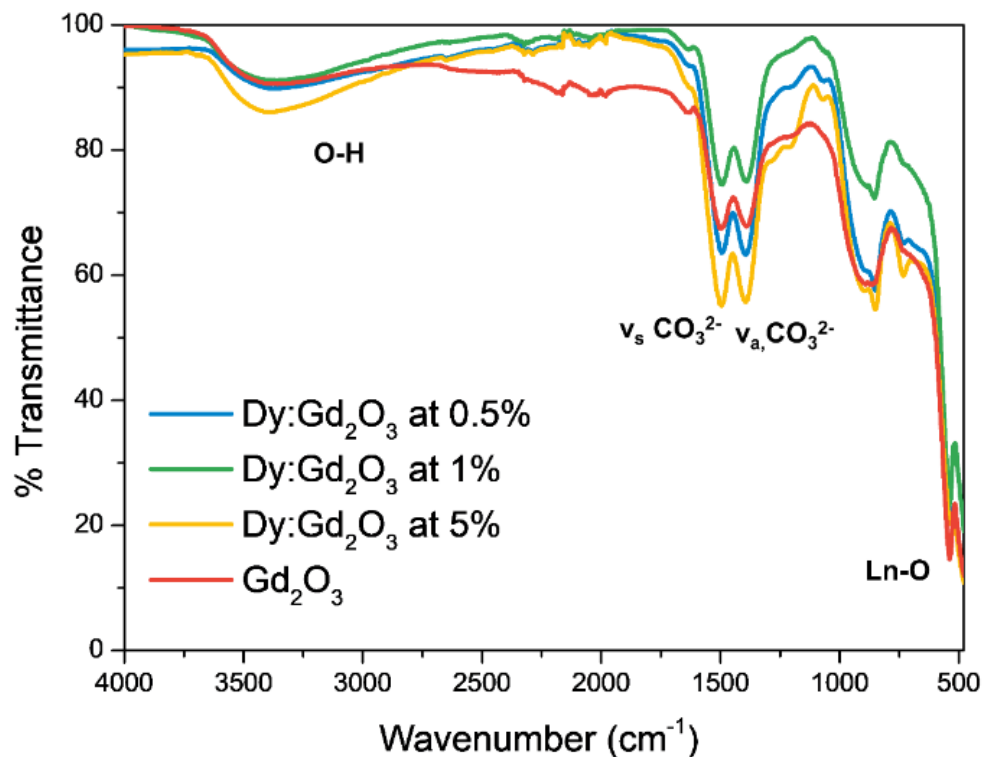


Supplementary Material

Attenuated Total reflectance Infrared Spectra



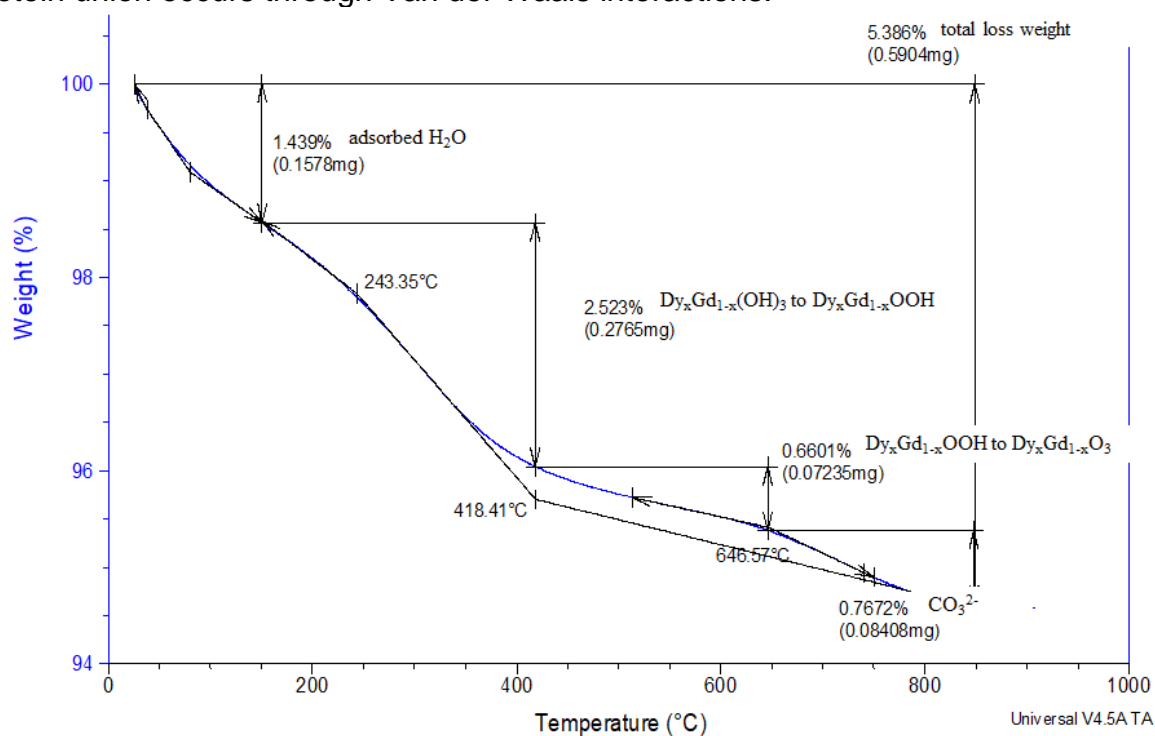
S1. Infrared spectra for the gadolinium oxide (matrix) and its Dy³⁺-doped oxides. All of them show the hydrated molecules and carbonate ions on their surfaces.

Thermogravimetric analysis

The thermal stability of the Dy: Gd₂O₃ at 1% sample was studied from 25 to 1000 °C at a heating rate of 10 °C / min. The following slopes were observed corresponding to a total loss of 5% w: The first slope, which goes up to 180 °C was assigned to adsorbed water molecules losses (1.4%) on the oxide surface. The second (2.5% w) up to 418 °C and the third losses (0.6%) at 646 °C, are attributed to the hydroxide formation and its subsequent hydrolysis during the sol-gel process. The above indicates a remnant of hydroxide precursor due to a low calcination time. Finally, the

fourth loss is related to the formation of CO_3^{2-} ions on the oxide surface owing to the presence of atmospheric CO_2 during the calcination process. However, these ions are found at a trace level (0.7% in weight) making them difficult to observe by XRD measurements.

The amount of remanent OH^- , particularly on the oxide surfaces, enhanced their silanisation process and the subsequent biomolecules binding. Previous work has also reported successful silanisation without previous surface activation, where the protein union occurs through Van der Waals interactions.



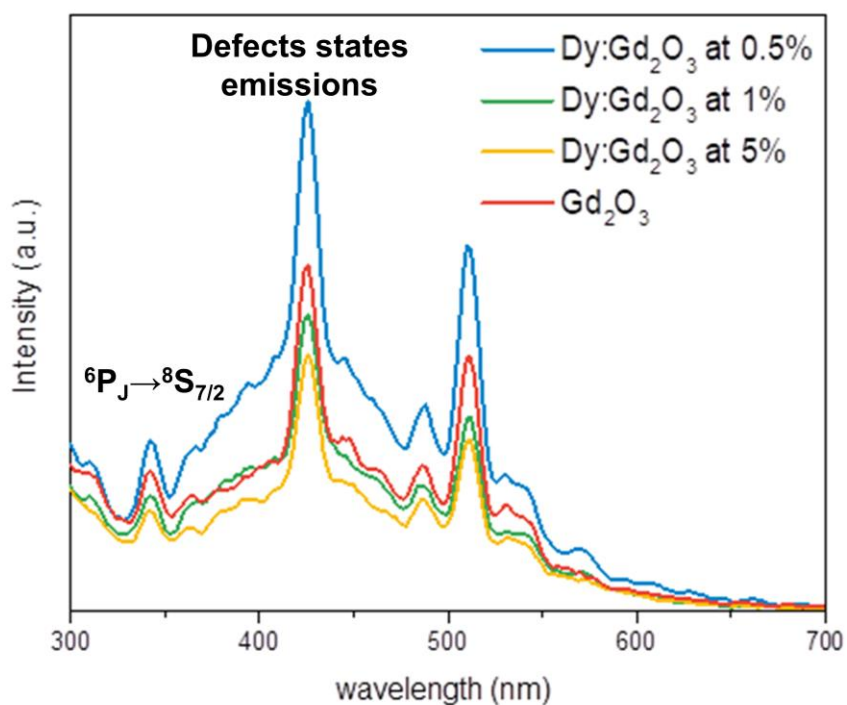
S2. Thermogram for sample $\text{Dy@Gd}_2\text{O}_3$ (at 5%)

Energy Dispersive Spectroscopy

Element	Line Type	k Factor	k Factor type	Absorption Correction	Wt%	Wt% Sigma	Atomic %
O	K series	2.020	Theoretical	1.00	23.58	2.66	75.22
Gd	L series	2.111	Theoretical	1.00	73.07	3.21	23.72
Dy	L series	2.121	Theoretical	1.00	3.35	2.48	1.05
Total					100.00		100.00

S3. Atomic Composition chart for sample Dy: Gd₂O₃ (at 1%).

Photoluminescence in aqueous dispersion

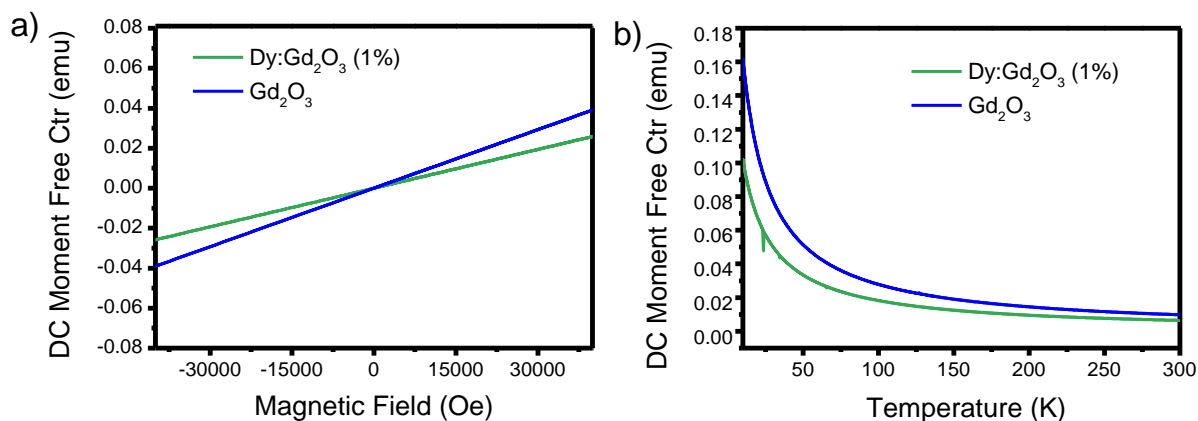


S4. Photoluminescence measurements exciting at 340 nm for Dy-doped Gd₂O₃ nanoparticles dispersed in water.

Magnetisation measurements

To know if there is a new magnetic ordering upon decreasing particle size, we measured the magnetisation behaviour of the Dy@Gd₂O₃ (5%) and parent Gd₂O₃ samples by registering the hysteresis loops at 300 K. Results from these measurements are presented in **S 5a** and show a clear paramagnetic response in both samples. Furthermore, 1 T field cooled (FC) temperature dependent

magnetisation measurements confirmed that this paramagnetic behaviour extends down to low temperatures (see **S5 b**).



S5. Magnetisation measurements on Dy@Gd₂O₃ (5%) (green line) and Gd₂O₃ (blue line). a) Magnetic moment response vs external magnetic field (hysteresis loops) recorded at 300 K. b) 1T field cooled (FC) temperature dependent magnetization measurements (Is magnetic moment or susceptibility)

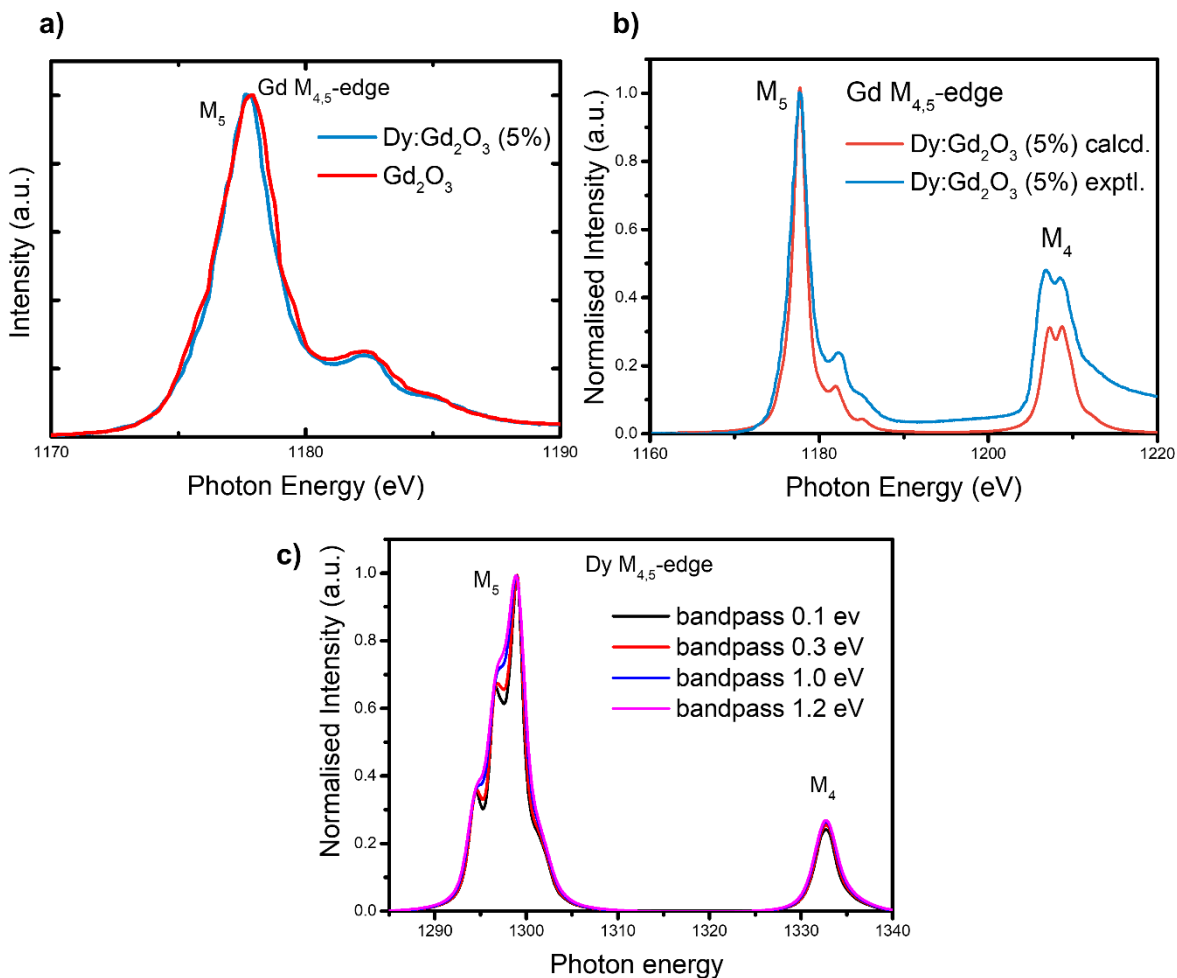
Computational details for XAS calculated spectra.

Atomic multiplet calculations for Gd³⁺ and Dy³⁺ at the M_{4,5} edges (3d-4f transitions) were done using the code Crispy (Retegan, Marius. 2019. "Crispy: V0.7.3." <https://doi.org/10.5281/zenodo.1008184>) The calculations were done for T=300 K, the Hartree-Fock integrals F_k, and G_k were scaled to 80% (0.8) of its atomic values, while the spin-orbit coupling (z) was set to 100% (1). For Dy³⁺ the values of the initial Hamiltonian were: U(4f,4f):0.0, F2(4f,4f):15.313, F4(4f,4f):9.609, F6(4f,4f):6.913, z (4f):0.246; On the other hand the values for the final Hamiltonian were: U(4f,4f):0, F2(4f,4f):15.967, F4(4f,4f):10.031, F6(4f,4f):7.221, U(3d,4f):0.0, F2(3d,4f):10.388, F4(3d,4f):4.881, G1(3d,4f):7.520, G3(3d,4f):4.411, G5(3d,4f):3.048, z (4f):0.278 y z (3d):14.441. To account for the natural broadening, the calculated spectra were broadened by Lorentzian functions with FWHM of 1.31 eV and 1.85 eV for the M_{4,5}

edges, respectively. To improve the agreement with the experimental data, the calculated Dy³⁺ spectra were also convoluted by 0.1 eV, 0.3 eV, 1.0 eV and 1.2 eV FWHM Gaussian Functions, representing the instrumental broadening. The best agreement between theory and experiment was found with the Gaussian set to 1.2 eV FWHM (see **S6 c**).

For Gd³⁺ the values of the initial Hamiltonian were: U(4*f*,4*f*):0.0, F2(4*f*,4*f*):14.502, F4(4*f*,4*f*):9.101, F6(4*f*,4*f*):6.548, z (4*f*):0.197; On the other hand the values for the final Hamiltonian were: U(4*f*,4*f*):0, F2(4*f*,4*f*):15.195, F4(4*f*,4*f*):9.550, F6(4*f*,4*f*):6.875, U(3*d*,4*f*):0.0, F2(3*d*,4*f*):9.713, F4(3*d*,4*f*):4.532, G1(3*d*,4*f*):9.946, G3(3*d*,4*f*):4.072, G5(3*d*,4*f*):2.813, z (4*f*):0.226 y z (3*d*):12.358. The calculated spectra were broadened by Lorentzian functions with FWHM of 1.19 eV and 1.59 eV for the M_{4,5} edges, respectively. To account for the instrumental broadening, the calculated Gd³⁺ spectrum was also convoluted by 0.1 eV Gaussian (see **S6 b**).

Further, to compare experimental and theoretical spectra, after normalising to one the intensity of the peak at the M₅ edge, the calculated spectra of Dy³⁺ and Gd³⁺ were shifted by -8.141 eV and -16.495 eV, respectively.



S6. Calculated atomic Gd³⁺ and Dy³⁺ $M_{4,5}$ -edge spectra. **a)** Amplification of the absorption level M_5 for the host matrix with (blue line) and without (red line) the dopant (Dy³⁺). **b)** Comparison between the calculated (red line) and experimental (blue line) XAS spectra monitoring the $M_{4,5}$ -edge absorption in Gd³⁺. **c)** Calculated XAS spectra monitoring the Dy³⁺ $M_{4,5}$ -edges absorption convoluted by 0.1 eV, 0.3 eV, 1.0 eV and 1.2 eV FWHM Gaussian Functions. All calculated spectra were generated using the code Crispy (Retegan, Marius. 2019. "Crispy: V0.7.3." <https://doi.org/10.5281/zenodo.1008184>).