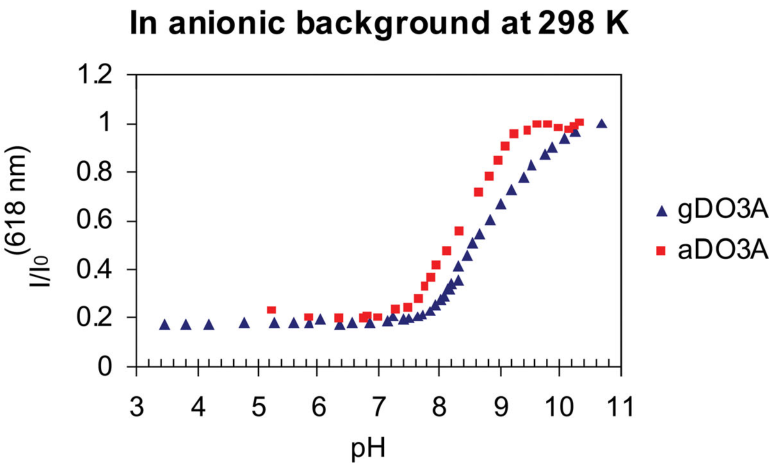
Electronic Supplementary Information

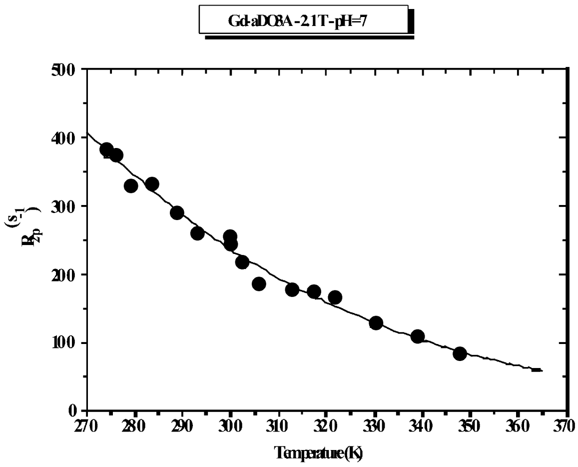


Anionic background:
CO_3^{2-}: 30mM,
Cl^-: 100mM,
$H_2PO_4^-$: 0.9 mM
lactate: 2.3 mM
citrate: 0.13 mM
(i.e. simulating an extracellular environment).

S1 Variation of emission intensity at 618nm for $[EugDO3A]^{3-}$ and $[EuaDO3A]^{3-}$ in the presence of a simulated extracellular anionic background (298K). The observed inflection above pH 7.5 corresponds to the onset of binding by carbonate, displacing the water molecules that quench the Eu excited state.

Exchange lifetime τ_M

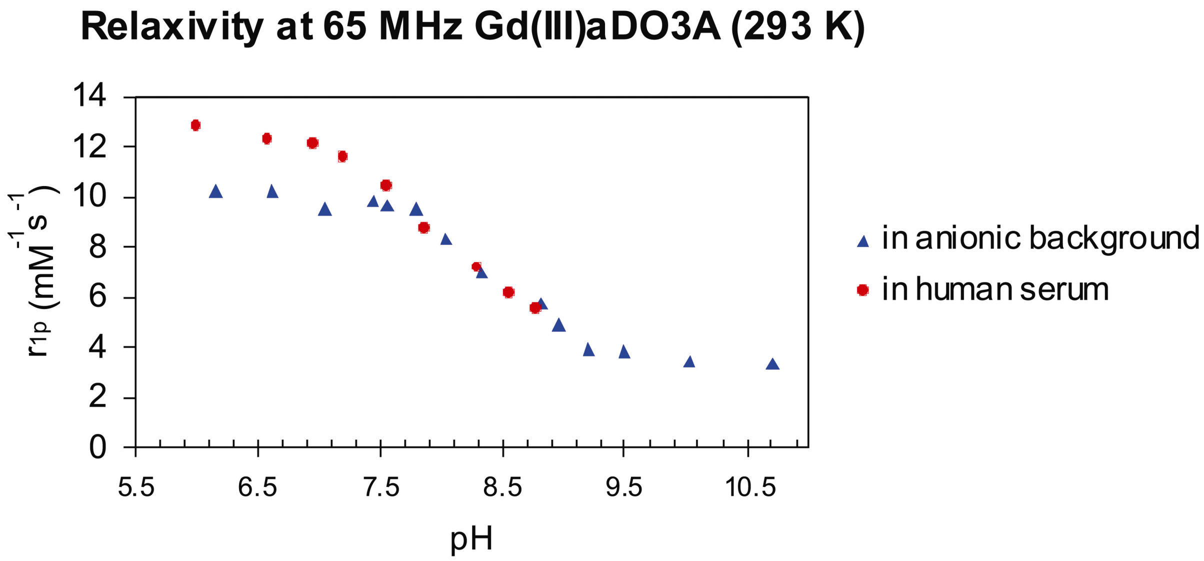
Measurements of the transverse ^{17}O relaxation time at variable temperature.



Fitting the curve to the Swift-Connick equations

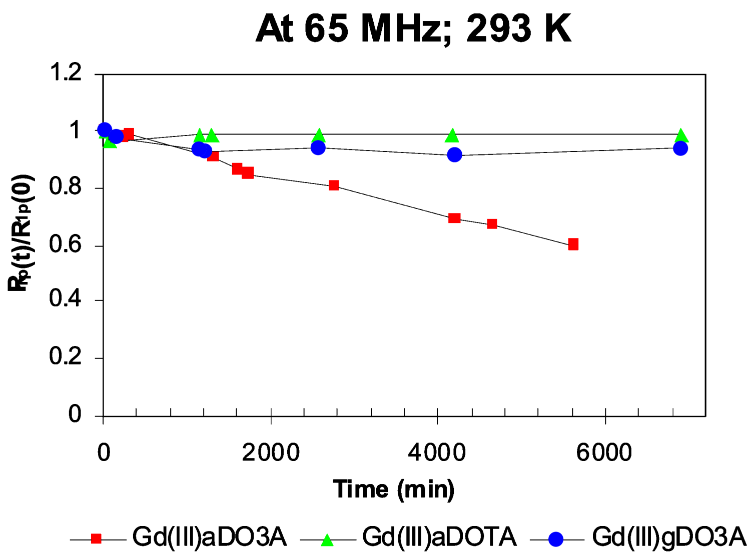
τ_M **= 30 ns** (*i.e. very fast)*

S2 Variation of the transverse 17-O relaxation rate of water as a function of temperature, showing the (Swift-Connick) fit to the experimental data (2.1T, pH = 7).



S3 Variation of the relaxivity of $[GdaDO3A]^{3-}$ with pH (293K) in a simulated extracellular ionic background (triangles) and in human serum solution.

1 mM Gd complex
1 mM $ZnCl_2$
pH = 7.0 in phosphate buffer ([KH_2PO_4] =0.026 mol/L, [Na_2HPO_4] = 0.041mol/L).



$$GdL \rightarrow L^{(n+3)-} + Gd^{+3}$$
$$L^{(n+3)-} + Zn^{+2} \rightarrow ZnL^{(n+1)-}$$
$$Gd^{+3} + PO^{3-} \rightarrow Gd(PO_4)_{ins}$$

Laurent S. and co-worker *Investigative Radiology* **2001,** *36*, 115.

Thermodynamic (T.I.) and kinetic (K.I.) index

Complex	T.I.	K.I.
GdaDO3A	**0.69**	**2760**
GdgDO3A	0.95	¥
GdaDOTA	0.99	¥
GdDOTA	0.99	¥
GdDTPA	0.49	260

T.I. R_{1p}(3days)/R_{1p}(0); **S.I.** Time for $R_{1p}(t)/R_{1p}(0)$ = 0.80

S4 and S-5 Empirical screen of complex stability by monitoring the change in the relaxivity of the stated Gd complexes as a function of time, following the methods of Laurent and Muller. Note the high kinetic and thermodynamic stability indices with respect to $[GdDTPA]^{2-}$