Electronic Supplementary Information

Variation of emission intensity at 618nm for \([\text{EugDO3A}]^{3-}\) and \([\text{EuaDO3A}]^{3-}\) 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.

**In anionic background at 298 K**

Anionic background:
- \(\text{CO}_3^{2-}: 30\, \text{mM},\)
- \(\text{Cl}^-: 100\, \text{mM},\)
- \(\text{H}_2\text{PO}_4^-: 0.9\, \text{mM}\)
- lactate: 2.3 mM
- citrate: 0.13 mM
(i.e. simulating an extracellular environment).
Exchange lifetime $t_M$

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

Fitting the curve to the Swift-Connick equations

$t_M = 30 \text{ ns (i.e. very fast)}$

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 $[\text{Gd(III)DO3A}]^-$ with pH (293K) in a simulated extracellular ionic background (triangles) and in human serum solution.
1 mM Gd complex
1 mM ZnCl₂
pH = 7.0 in phosphate buffer ([KH₂PO₄] = 0.026 mol/L, [Na₂HPO₄] = 0.041 mol/L).

At 65 MHz; 293 K


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

<table>
<thead>
<tr>
<th>Complex</th>
<th>T.I.</th>
<th>K.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd(DO)₃A</td>
<td>0.69</td>
<td>2760</td>
</tr>
<tr>
<td>Gd(DO)₃A</td>
<td>0.95</td>
<td>¥</td>
</tr>
<tr>
<td>Gd(DOTA)</td>
<td>0.99</td>
<td>¥</td>
</tr>
<tr>
<td>Gd(DOTA)</td>
<td>0.99</td>
<td>¥</td>
</tr>
<tr>
<td>GdDTPA</td>
<td>0.49</td>
<td>260</td>
</tr>
</tbody>
</table>

T.I. \( R_{1p(3\text{days})}/R_{1p(0)} \); 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⁻.