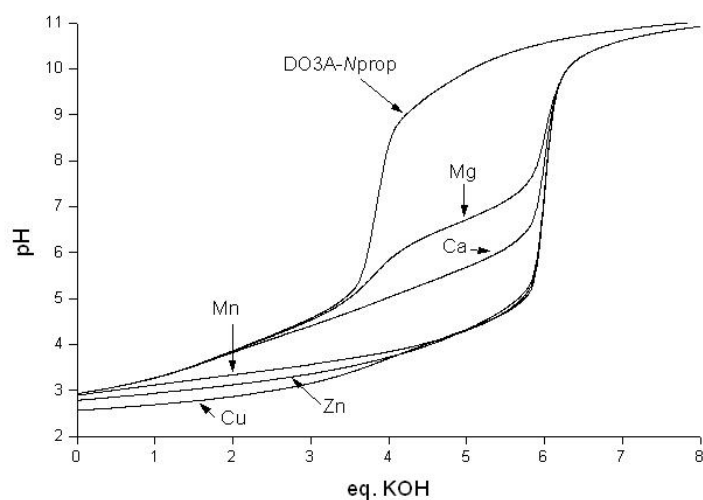


# Monopropionate analogues of DOTA<sup>4-</sup> and DTPA<sup>5-</sup>: kinetics of formation and dissociation of their lanthanide(III) complexes

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Fig. S1. Titration curves of H<sub>4</sub>DO3A-*N*prop in the absence and in the presence of various metal ions at 25°C, 0.1 M KCl; c<sub>lig</sub> = 0.003 M



**Table S1.** Formation rate constants of (CeDO3A-*N*prop)<sup>-</sup> obtained from UV-Vis measurements at different pH, 0.1 M KCl, 25°C.

	4.26	4.6	4.92	5.21	5.01	5.45
[Ce <sup>3+</sup> ] (mM)	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )
0.1	2.47 × 10 <sup>-3</sup>	5.70 × 10 <sup>-3</sup>	1.04 × 10 <sup>-2</sup>	1.55 × 10 <sup>-2</sup>	1.17 × 10 <sup>-2</sup>	2.79 × 10 <sup>-2</sup>
0.2	3.02 × 10 <sup>-3</sup>	6.19 × 10 <sup>-3</sup>	1.08 × 10 <sup>-2</sup>	1.64 × 10 <sup>-2</sup>	1.21 × 10 <sup>-2</sup>	3.29 × 10 <sup>-2</sup>
0.4	3.85 × 10 <sup>-3</sup>	6.64 × 10 <sup>-3</sup>	1.11 × 10 <sup>-2</sup>	1.83 × 10 <sup>-2</sup>	1.30 × 10 <sup>-2</sup>	3.51 × 10 <sup>-2</sup>
0.6	4.02 × 10 <sup>-3</sup>	7.11 × 10 <sup>-3</sup>	1.15 × 10 <sup>-2</sup>	2.04 × 10 <sup>-2</sup>	1.39 × 10 <sup>-2</sup>	3.72 × 10 <sup>-2</sup>
1	4.18 × 10 <sup>-3</sup>	7.04 × 10 <sup>-3</sup>	1.20 × 10 <sup>-2</sup>	2.00 × 10 <sup>-2</sup>	1.63 × 10 <sup>-2</sup>	3.60 × 10 <sup>-2</sup>
1.5	4.19 × 10 <sup>-3</sup>	7.81 × 10 <sup>-3</sup>	1.30 × 10 <sup>-2</sup>	2.10 × 10 <sup>-2</sup>	1.64 × 10 <sup>-2</sup>	3.79 × 10 <sup>-2</sup>
2	4.32 × 10 <sup>-3</sup>	7.85 × 10 <sup>-3</sup>	1.21 × 10 <sup>-2</sup>	2.07 × 10 <sup>-2</sup>	1.81 × 10 <sup>-2</sup>	3.87 × 10 <sup>-2</sup>

**Table S2.** Formation rate constants of  $(\text{GdDO3A-Nprop})^-$  obtained from UV-Vis measurements at different pH, 0.1 M KCl, 25°C.

	<b>3.92</b>	<b>4.17</b>	<b>4.09</b>	<b>4.26</b>
$[\text{Gd}^{3+}]$ (mM)	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )
0.6	$1.49 \times 10^{-3}$	$3.25 \times 10^{-3}$	$2.88 \times 10^{-3}$	$4.04 \times 10^{-3}$
1.0	$2.06 \times 10^{-3}$	$3.46 \times 10^{-3}$	$3.12 \times 10^{-3}$	$4.41 \times 10^{-3}$
2.0		$4.03 \times 10^{-3}$	$3.40 \times 10^{-3}$	$4.54 \times 10^{-3}$
3.0	$2.33 \times 10^{-3}$	$4.03 \times 10^{-3}$	$3.50 \times 10^{-3}$	$4.99 \times 10^{-3}$
4.0	$2.64 \times 10^{-3}$	$3.95 \times 10^{-3}$	$3.60 \times 10^{-3}$	$4.86 \times 10^{-3}$
5.0	$2.54 \times 10^{-3}$	$3.85 \times 10^{-3}$	$3.67 \times 10^{-3}$	$4.92 \times 10^{-3}$
6.0	$2.54 \times 10^{-3}$	$3.85 \times 10^{-3}$	$3.71 \times 10^{-3}$	$4.92 \times 10^{-3}$

**Table S3.** Formation rate constants of  $(\text{YbDO3A-Nprop})^-$  obtained from UV-Vis measurements at different pH, 0.1 M KCl, 25°C.

pH	<b>4.27</b>	<b>4.35</b>	<b>4.17</b>	<b>3.91</b>
$[\text{Yb}^{3+}]$ (mM)	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )	$k$ ( $\text{s}^{-1}$ )
0.6	$6.27 \times 10^{-3}$	$7.22 \times 10^{-3}$	$5.26 \times 10^{-3}$	$4.14 \times 10^{-3}$
1.0	$6.61 \times 10^{-3}$	$8.00 \times 10^{-3}$	$5.53 \times 10^{-3}$	$4.41 \times 10^{-3}$
2.0	$7.18 \times 10^{-3}$	$8.19 \times 10^{-3}$	$5.95 \times 10^{-3}$	$5.08 \times 10^{-3}$
3.0	$7.53 \times 10^{-3}$	$8.63 \times 10^{-3}$	$6.25 \times 10^{-3}$	
4.0	$7.60 \times 10^{-3}$	$8.76 \times 10^{-3}$	$6.23 \times 10^{-3}$	$5.28 \times 10^{-3}$
5.0	$7.69 \times 10^{-3}$	$8.24 \times 10^{-3}$	$6.51 \times 10^{-3}$	$5.66 \times 10^{-3}$
6.0	$7.65 \times 10^{-3}$	$8.46 \times 10^{-3}$	$6.48 \times 10^{-3}$	

**Table S4.** Dissociation rate constants of (GdDTTA-*Nprop*)<sup>2-</sup> in the presence of Eu<sup>3+</sup> following the changes of <sup>1</sup>H-relaxivity at 200 MHz, at different pH, 0.1 M KCl, 25°C.

pH	4.92	5.01	5.24	5.19	5.43
[Eu <sup>3+</sup> ] (mM)	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )
0.03	2.57 × 10 <sup>-3</sup>	2.17 × 10 <sup>-3</sup>	1.01 × 10 <sup>-3</sup>	1.62 × 10 <sup>-3</sup>	5.38 × 10 <sup>-4</sup>
0.02	3.49 × 10 <sup>-3</sup>	2.41 × 10 <sup>-3</sup>	9.64 × 10 <sup>-4</sup>	1.72 × 10 <sup>-3</sup>	7.16 × 10 <sup>-4</sup>
0.01	5.72 × 10 <sup>-3</sup>	2.92 × 10 <sup>-3</sup>	1.41 × 10 <sup>-3</sup>	2.50 × 10 <sup>-3</sup>	5.83 × 10 <sup>-4</sup>
0.005	1.00 × 10 <sup>-2</sup>	5.20 × 10 <sup>-3</sup>	1.94 × 10 <sup>-3</sup>	3.30 × 10 <sup>-3</sup>	8.50 × 10 <sup>-4</sup>

**Table S5.** Dissociation rate constants of (GdDTTA-*Nprop*)<sup>2-</sup> in the presence of Zn<sup>2+</sup> following the changes of <sup>1</sup>H-relaxivity at 200 MHz, at different pH, 0.1 M KCl, 25°C.

pH	4.85	5.14	4.96	5.5
[Zn <sup>2+</sup> ] (mM)	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )	k (s <sup>-1</sup> )
0.03	5.88 × 10 <sup>-3</sup>	5.72 × 10 <sup>-3</sup>	6.41 × 10 <sup>-3</sup>	6.26 × 10 <sup>-3</sup>
0.02	5.25 × 10 <sup>-3</sup>	5.53 × 10 <sup>-3</sup>	5.12 × 10 <sup>-3</sup>	5.97 × 10 <sup>-3</sup>
0.01	3.73 × 10 <sup>-3</sup>	3.18 × 10 <sup>-3</sup>	3.46 × 10 <sup>-3</sup>	3.53 × 10 <sup>-3</sup>
0.005	2.60 × 10 <sup>-3</sup>	2.43 × 10 <sup>-3</sup>	2.10 × 10 <sup>-3</sup>	2.99 × 10 <sup>-3</sup>

**Table S6.** Observed dissociation rate constants of  $(\text{CeDO3A-Nprop})^{2-}$  as a function of proton concentration, determined from the changes in UV-Vis absorption.

$[\text{H}^+]$ (M)	$k_d$ ( $\text{s}^{-1}$ )
0.1999	0.0742
0.1803	0.0664
0.1499	0.0647
0.1245	0.0471
0.1147	0.0429
0.1000	0.0416
0.0902	0.0364
0.0794	0.0320
0.0706	0.0287
0.0631	0.0262
0.0550	0.0267
0.0446	0.0225
0.0300	0.0182
0.0200	0.0143
0.0158	0.0121
0.0126	0.0097
0.0099	0.0082
0.0059	0.0047
0.0030	0.0018