

Supporting information to “Simplified speciation and improved phosphodiesterolytic activity of hydroxo complexes of trivalent lanthanides in aqueous DMSO” by Irma Sánchez-Lombardo and Anatoly K. Yatsimirsky

Table 1S. Results of potentiometric titrations of lanthanides in 80% vol DMSO. The mean values of $\log\beta_{pq}$ are given with standard errors calculated by averaging of β values obtained in independent titration experiments. Errors in $\log\beta_{pq}$ values as fitting parameters in each titration experiment were less than ± 0.05 .

Titrations in the presence of 0.01 M NaClO₄

[La(ClO ₄) ₃], mM	sigma ^a	log β_{pq}		
		2-1	1-1	1-3
0.5	3.07	-5.48	-8.59	-28.48
1.0	3.58	-5.68	-8.74	-28.61
1.5	4.0	-5.80	-8.44	-28.03
mean		-5.65±0.09	-8.59±0.09	-28.4±0.2

for an alternative model with binuclear species:

[La(ClO ₄) ₃], mM	sigma ^a	2-1	2-2	2-6
0.5	5.05	-5.11	-13.61	-54.02
1.0	7.3	-5.38	-14.15	-53.76
1.5	6.49	-5.4	-13.78	-52.36
mean		-5.30±0.09	-13.8±0.2	-53.4±0.5

[Eu(ClO ₄) ₃], mM	sigma ^a	2-1	1-1	1-3
0.5	0.60	- ^b	-8.13	-24.55
1.0	1.39	-5.10	-8.28	-25.83
1.5	4.02	-5.00	-8.2	-24.64
2.0	2.62	-4.63	-8.22	-25.21
mean		-4.9±0.1	-8.21±0.03	-25.1±0.3

for alternative model with binuclear species:

[Eu(ClO ₄) ₃], mM	sigma	2-1	2-2	2-6
0.5	5.08		-10.69	-45.99
1.0	2.44		-13.12	-48.56
1.5	2.82		-12.39	-46.15
2.0	3.34	-6.31	-12.94	-47.77
mean			-12.3±0.6	-47.1±0.6

Titrations in the absence of added NaClO₄

[La(ClO ₄) ₃], mM	sigma ^a	2-1	1-1	1-2	1-3
0.5	5.0	-5.70	-8.87	-19.20	-29.66
1.0	6.65	-5.4	-8.97	-19.02	-29.42
1.5	14.9	-6.04	-9.39	-19.33	-29.58

mean		-5.7±0.2	-9.1±0.1	-19.18±0.09	-29.55±0.07
[Nd(ClO₄)₃], mM	sigma^a	2-1	1-1	1-2	1-3
0.5	10.15	- ^b	-8.05	-17.31	-26.19
0.8	6.45	-5.20	-8.80	-18.90	-27.80
1.0	8.11	-5.82	-8.22	- ^b	-27.55
1.0	3.47	-5.55	-8.34	-17.69	-27.65
1.5	12	-5.23	-8.54	-17.80	-27.56
mean		-5.5±0.1	-8.5±0.1	-17.9±0.3	-27.64±0.06^c
[Eu(ClO₄)₃], mM	sigma^a	1-1	1-2	1-3	
1.0	3.32	-7.60	-16.13	-24.60	
1.0	12.38	-7.70	-15.69	-24.46	
1.2	9.00	-7.90	-16.2	-24.22	
2.0	3.39	-7.36	-15.12	-23.62	
mean		-7.6±0.1	-15.8±0.2	-24.2±0.2	

^a Goodness of fit is measured in Hyperquad by *sigma*, the value of the scaled sum of squares, which is given in the table together with log β_{pq} values for each titration. When *sigma* is close to 1 it can be said that the data has been fitted within experimental error. However, even with large *sigma* values the fitting quality may be still acceptable. Thus with *sigma* equal e.g. 20 the program typically calculates the fitting parameters with errors less than 0.05 in the logarithmic scale (the relative error $\pm 10\%$). In addition the *sigma* value depends on weighting scheme, which in Hyperquad is automatic and ignores any systematic errors. It seems therefore difficult to assign a definite meaning to the absolute value of *sigma*, but this parameter is certainly appropriate for comparison of fitting qualities to different models.

^b Hyperquad assigned “excessive” or “negative” value to respective β , which was ignored in the calculation of the mean value.

^c The value -26.19 excluded.

Table 2S. Mean values of hydrolysis constants of trivalent lanthanides in 80% vol. DMSO at 25°C obtained by joint fitting of all titration plots for each cation and respective sigma values calculated by Hyperquad.

Species	log β_{pq}				
	[NaClO ₄]=0			[NaClO ₄]=10 mM	
	La(III)	Nd(III)	Eu(III)	La(III)	Eu(III)
Ln₂(OH)⁵⁺	-5.85±0.11	-5.26±0.12		-5.76±0.12	-4.76±0.08
Ln(OH)²⁺	-9.36±0.07	-8.43±0.04	-7.76±0.03	-8.55±0.03	-7.83±0.02
Ln(OH)₂⁺	-19.22±0.06	-17.83±0.08	-16.07±0.02		
Ln(OH)₃	-29.56±0.03	-28.3±0.2	-24.80±0.02	-28.21±0.03	-24.7±0.02
sigma	20.86	13.8	25.0	11.91	18.4

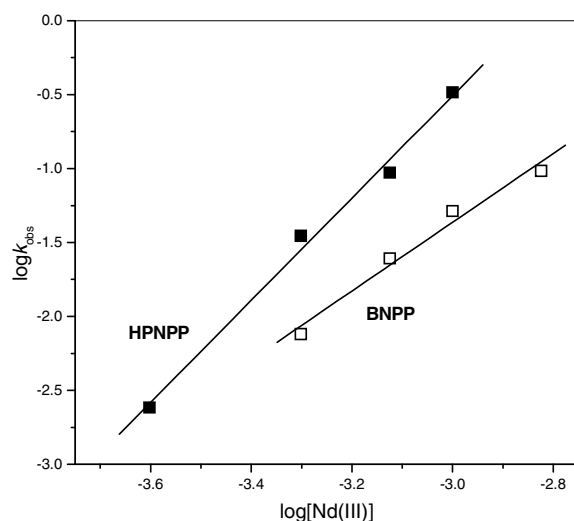


Fig. S1. Observed first-order rate constants for the hydrolysis of BNPP (open squares) and HPNPP (solid squares) by $\text{Nd}(\text{ClO}_4)_3$ at variable concentrations of $\text{Nd}(\text{ClO}_4)_3$ and Me_4NOH taken at the constant ratio $[\text{La}(\text{III})]:[\text{OH}^-]=1:2$ in 80% vol. DMSO at 25°C .

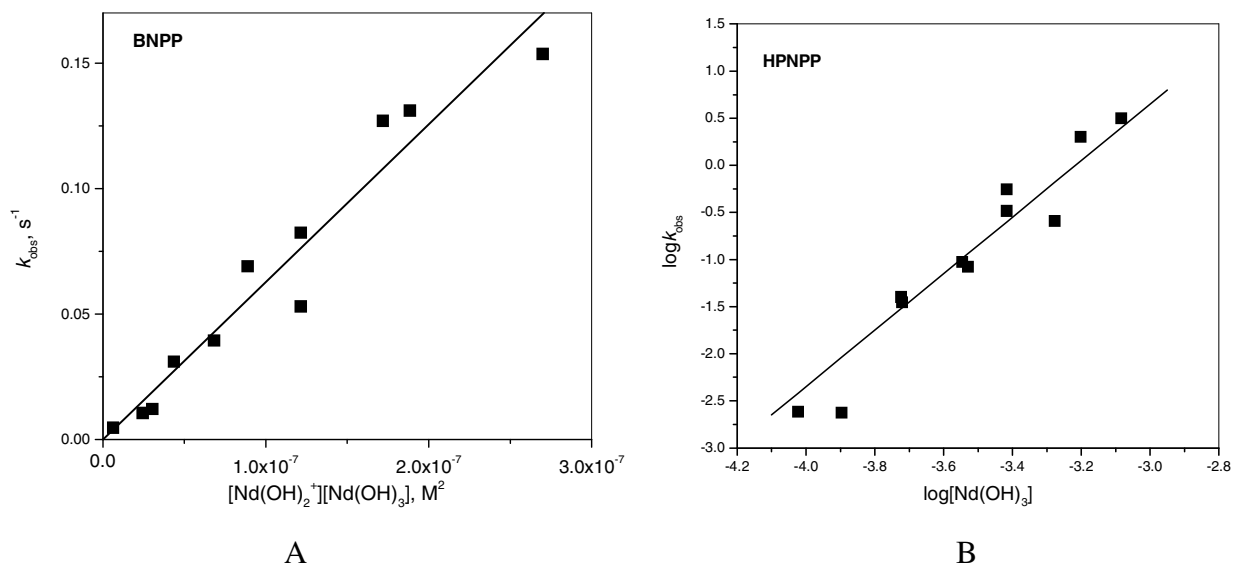


Fig. S2. Observed first-order rate constants for the hydrolysis of BNPP (A) and HPNPP (B) by $\text{Nd}(\text{ClO}_4)_3$ in 80% vol. DMSO at 25°C as a function of calculated concentrations of $\text{Nd}(\text{OH})_2^+$ and $\text{Nd}(\text{OH})_3$ in accordance with kinetic equations (6) and (7) respectively. The slope of the line in (A) equals k_3 and the slope of the line in (B) equals 3.

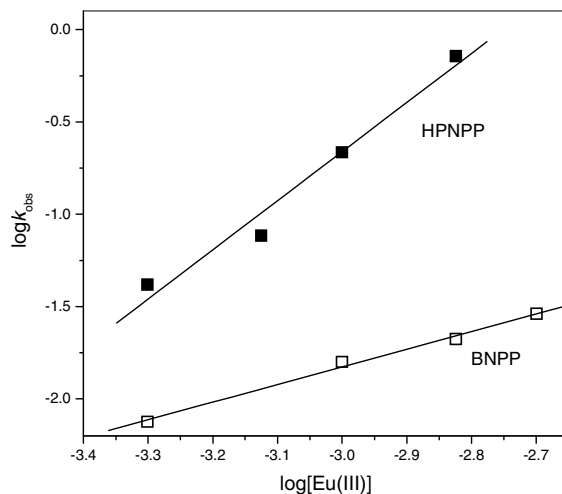


Fig. S3. Observed first-order rate constants for the hydrolysis of BNPP (open squares) and HPNPP (solid squares) by $\text{Eu}(\text{ClO}_4)_3$ at variable concentrations of $\text{Eu}(\text{ClO}_4)_3$ and Me_4NOH taken at the constant ratio $[\text{Eu(III)}]:[\text{OH}^-]=1:2$ in 80% vol. DMSO at 25°C.

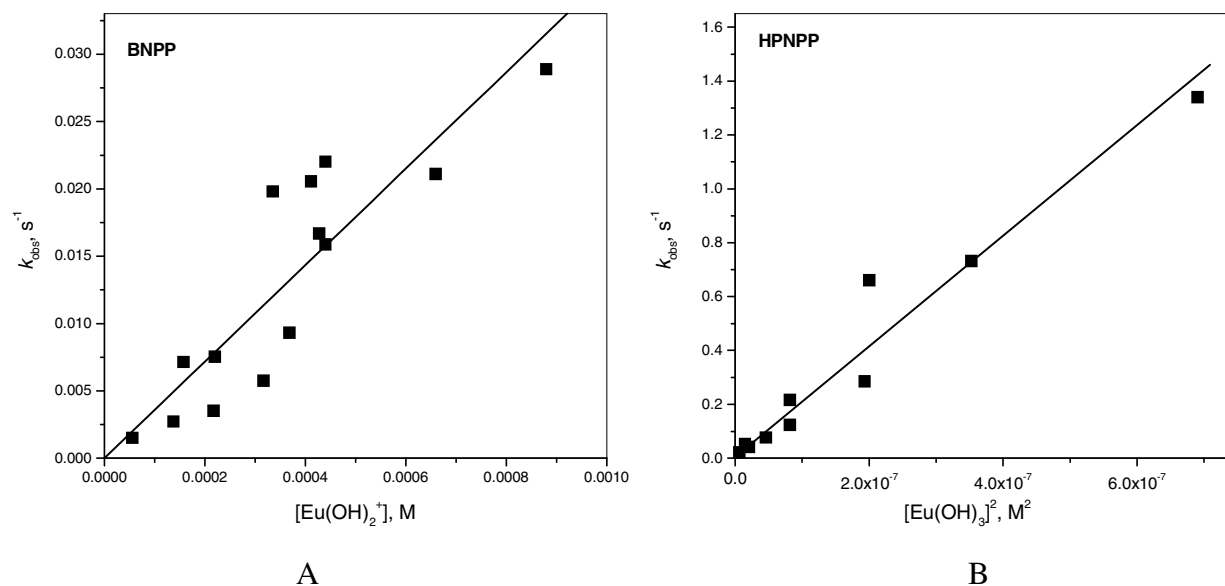


Fig. S4. Observed first-order rate constants for the hydrolysis of BNPP (A) and HPNPP (B) by $\text{Eu}(\text{ClO}_4)_3$ in 80% vol. DMSO at 25°C as a function of calculated concentrations of $\text{Eu}(\text{OH})_2^+$ and $[\text{Eu}(\text{OH})_3]^2$ respectively. The slope of the line in (A) approximately equals k_2 (see equation (8)) and the slope of the line in (B) equals k_3 (see equation (9)).