Protonation and Lanthanide(III) Complexation Equilibria of a New Tripodal Polyaza-Polycatechol-amine.

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Table S1. Acidity of STRENCAT secondary ammonium in $LnH_{-n}L^{(3+n)-}$ and $H_{-n}L^{(6-n)-}$ (n = 0-2). Stability constants for the reported deprotonation reactions:

Acidity of secondary ammonium of STRENCAT

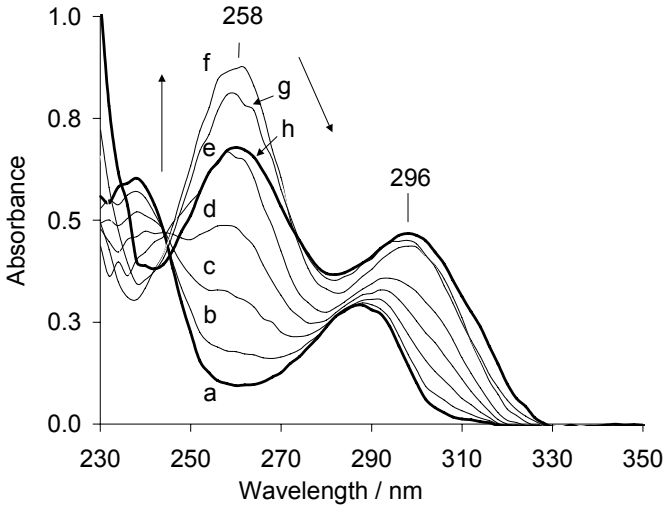
Reaction (4)	-log K'$_a$ La	Gd	Yb
n = 0 $LnL^{3-} \leftrightarrows LnH_{-1}L^{4-} + H^+$	10.44	10.58	10.56
n = 1 $LnH_{-1}L^{4-} \leftrightarrows LnH_{-2}L^{5-} + H^+$	11.46	11.16	12.77
n = 3 $LnH_{-2}L^{5-} \leftrightarrows LnH_{-3}L^{6-} + H^+$	---	11.74	12.40

Reaction (5)	-log K$_a$
n = 0 $H_3L^{3-} \leftrightarrows H_2L^{4-} + H^+$	9.80
n = 1 $H_2L^{4-} \leftrightarrows HL^{5-} + H^+$	10.54
n = 2 $HL^{5-} \leftrightarrows L^{6-} + H^+$	11.42

Table S2. Experimental conditions of potentiometry for Ln(III)/STRENCAT complexation at 25 °C. I = 0.100 mol dm^{-3} ($NaClO_4$). C_L, C_{Ln} and C_H: stoichiometric concentrations of STRENCAT (L^{6-}), lanthanide(III) and proton.

	Cup solution				Titrant NaOH
Ln(III)	V^0 mL	C_L mmol dm^{-3}	C_{Ln} mmol dm^{-3}	C_H mmol dm^{-3}	C_{OH} mmol dm^{-3}
La	20.13	1.270	1.232	8.480	100.8
La	20.13	1.238	0.618	9.399	100.8
Gd	20.13	1.627	1.503	10.12	101.0
Gd	20.13	1.609	0.805	9.866	101.0
Yb	20.13	1.671	1.666	10.09	101.0
Yb	20.13	1.606	0.799	9.826	101.0

FIGURE S1. Electronic spectra of a solution of STRENCAT $4.1 \cdot 10^{-5}$ mol dm^{-3} at different $p[H^+]$: a) $p[H^+] = 4.03$; b) $p[H^+] = 5.46$; c) $p[H^+] = 6.07$; d) $p[H^+] = 6.65$; e) $p[H^+] = 7.17$ f) $p[H^+] = 9.43$; g) $p[H^+] = 10.23$; h) $p[H^+] = 11.8$.



Figures S2, S3 and S4. Potentiometric titration curves of STRENCAT and lanthanides(III) in 1:1 (curve a) and 2:1 (curve b) molar ratios. Full lines: calculated with concentrations given in Table S2 and stability constants of Tables 1 and 2. Symbols represent only some experimental values.

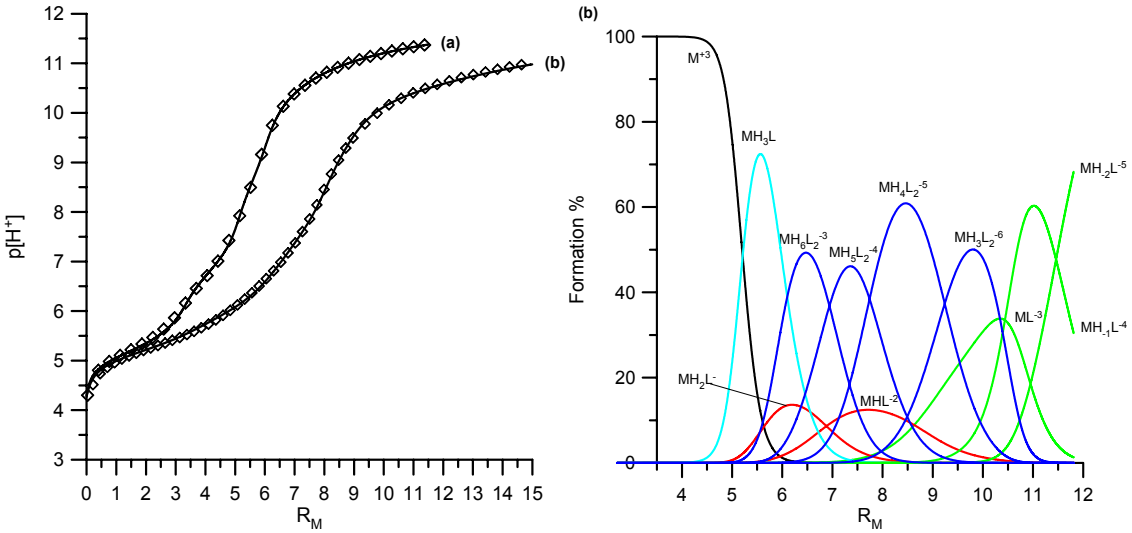


Figure S2. M = La. Plot on the right was calculated for 2:1 ligand-metal ratio.

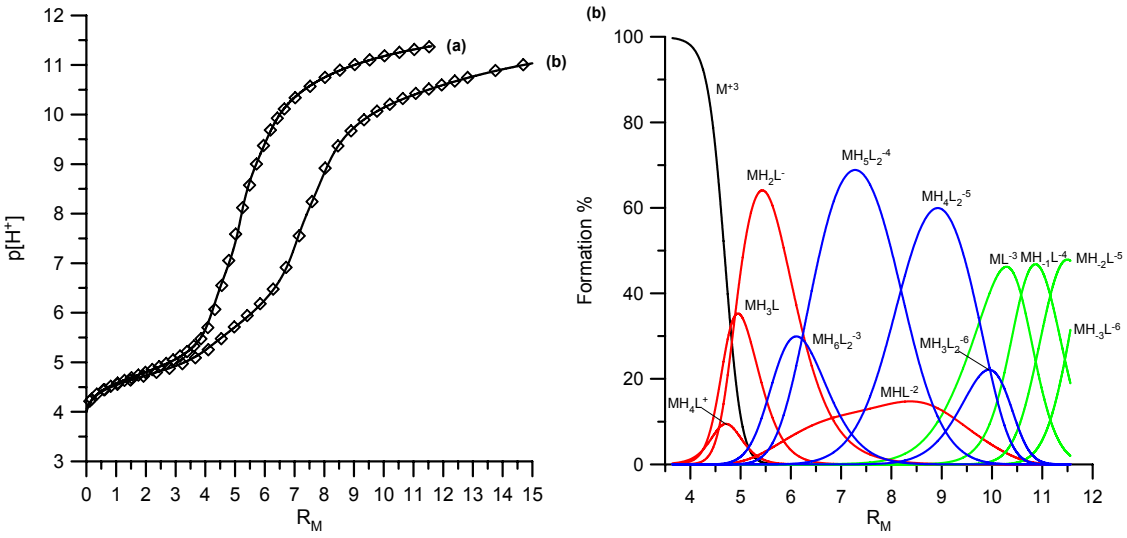


Figure S3. M = Gd. Plot on the right was calculated for 2:1 ligand-metal ratio.

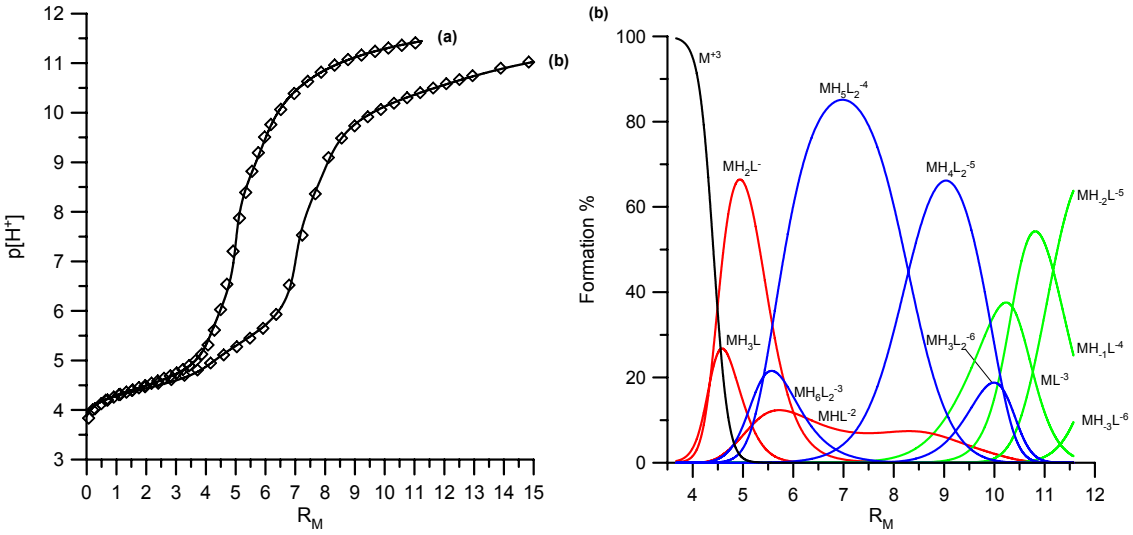


Figure S4. M = Yb. Plot on the right was calculated for 2:1 ligand-metal ratio.

Figure S5. Electronic spectra changes during titration of Gd^{3+}/STRENCAT. (L = STRENCAT, $C_L = 4.0 \cdot 10^{-5}$ mol dm^{-3}, $C_L/C_{Gd} = 1$).

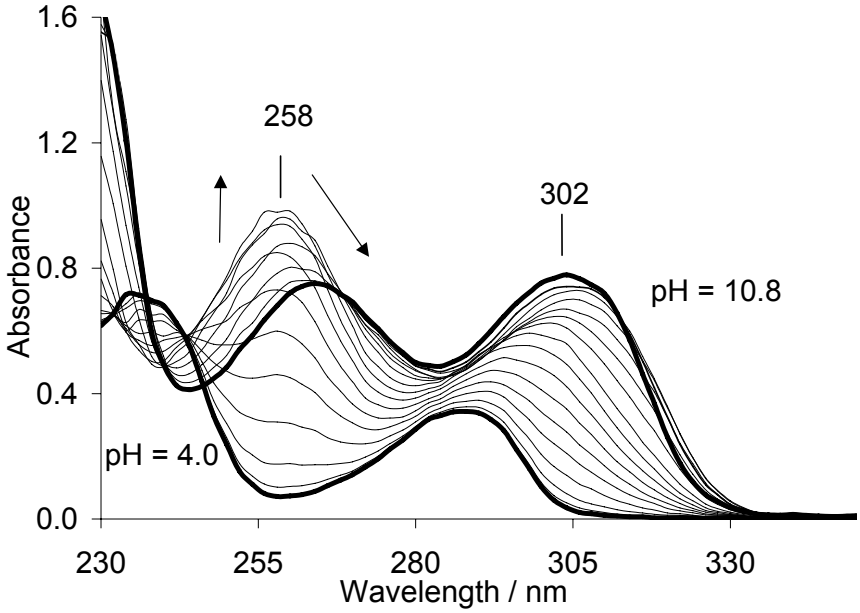
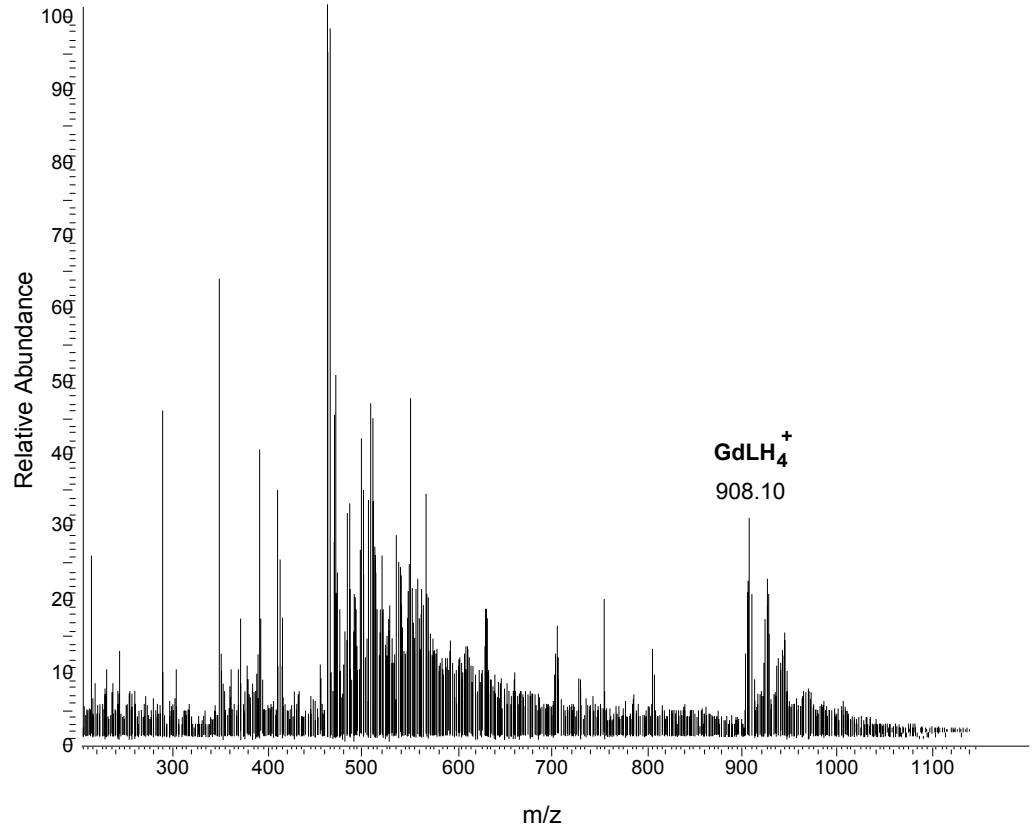


Figure S6. ESI-MS spectra of Gd(III)/STRENCAT solution prepared at pH = 6.1. $C_{Gd} = 4\ 10^{-5}$ mol dm^{-3}, $C_{Gd}/C_L = 1$: a) positive mode ; b) negative mode.

a)



b)