

Electronic Supporting Information

Rapid hydrolysis of phosphate diester promoted by Ce(IV) conjugating with β -cyclodextrin monomer and dimer

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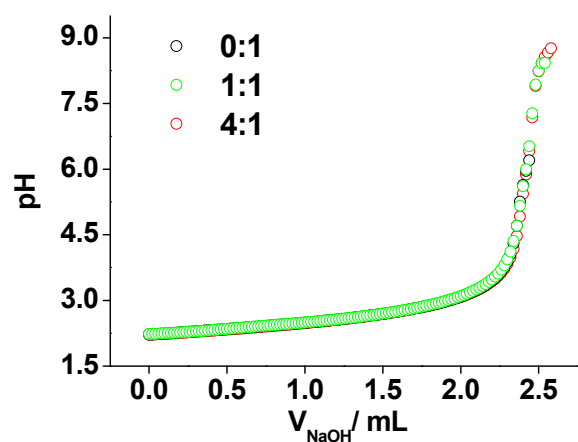


Fig. S1 Titration curves of 1 mM $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ by NaOH in aqueous solution ($I = 0.1 \text{ M NaNO}_3$) at $298 \pm 0.1 \text{ K}$. Conditions: black, $[\beta\text{CD}]:[\text{Ce}(\text{IV})] = 0:1$; green, $[\beta\text{CD}]:[\text{Ce}(\text{IV})] = 1:1$; red, $[\beta\text{CD}]:[\text{Ce}(\text{IV})] = 4:1$.

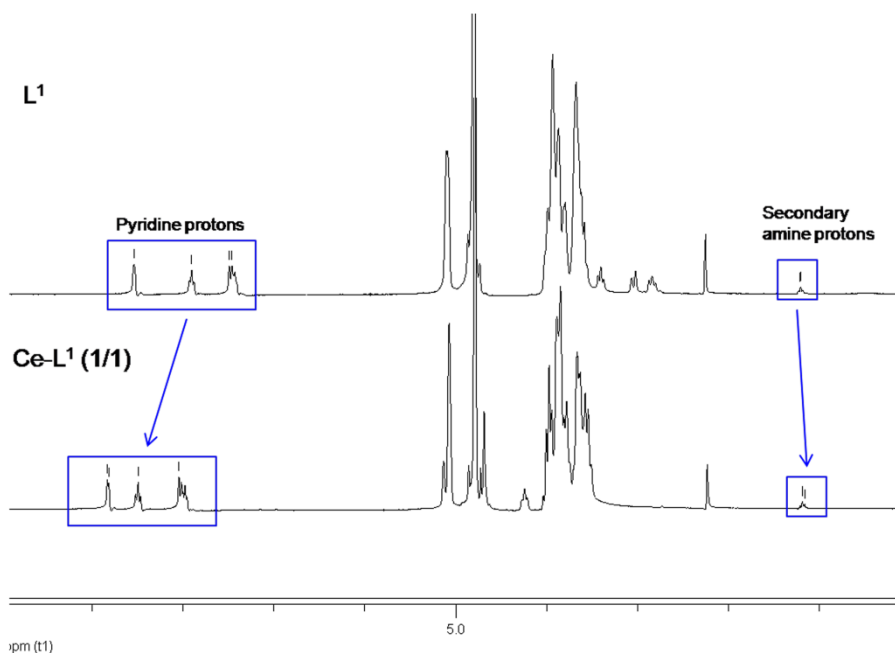


Fig. S2 ^1H NMR spectra of L^1 (upper) and $\text{Ce}(\text{IV})\text{-L}^1$ (bottom) in D_2O .

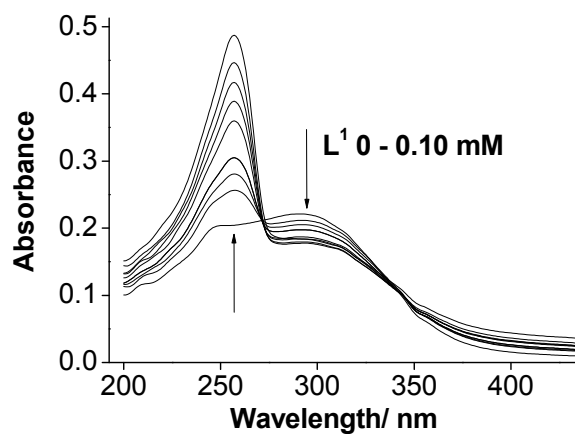


Fig. S3 UV-vis spectra of 0.06 mM $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ at increasing concentrations of L^1 from 0 to 0.10 mM at $298 \pm 0.1\text{K}$.

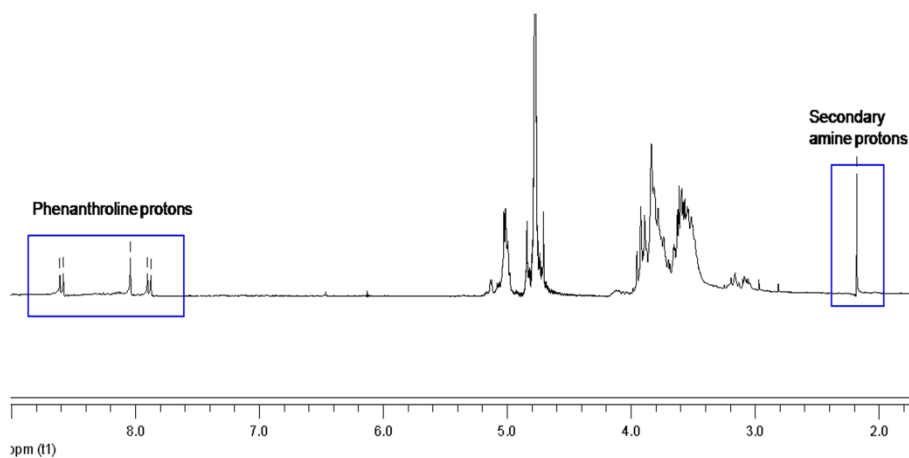


Fig. S4 ¹H NMR spectrum of $\text{Ce}(\text{IV})\text{-L}^2$ (ratio 1:1) in D_2O .

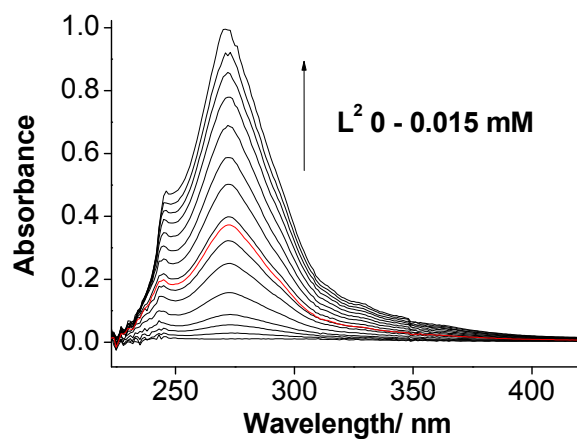


Fig. S5 UV-vis spectra at $298 \pm 0.1\text{K}$ of $2.5\ \mu\text{M}\ \text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ at increasing concentrations of L^2 from 0 to 0.015 mM (black lines); the red line represents the free L^2 at 0.015 mM. Enhanced absorption observed for $\text{Ce}(\text{IV})\text{-L}^2$ compared with free L^2 approved coordination between L^2 and $\text{Ce}(\text{IV})$ ion.

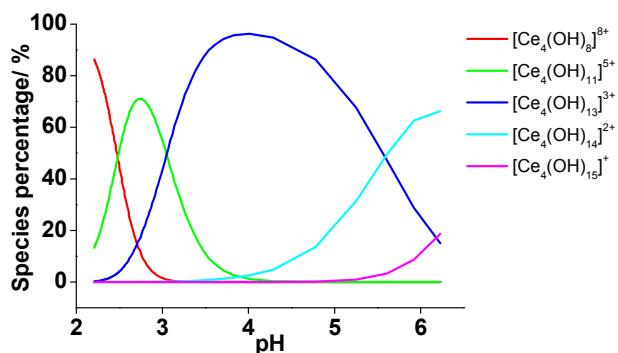


Fig. S6 Species distribution of 1.0 mM $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ in aqueous solution at 0.1 M NaNO_3 and 298 ± 0.1 K.

Table S1 Thermodynamic parameters for species of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ in solution at 298 ± 0.1 K with estimated errors in parentheses.

Species formula	$\text{Log } \beta$	$\text{p}K_a$
OH^-	-13.80	-
$[\text{Ce}_4(\text{OH})_8]^{8+}$	20.29(1)	-
$[\text{Ce}_4(\text{OH})_{11}]^{5+}$	12.85(1)	-
$[\text{Ce}_4(\text{OH})_{13}]^{3+}$	6.75(1)	-
$[\text{Ce}_4(\text{OH})_{14}]^{2+}$	1.17(1)	5.58
$[\text{Ce}_4(\text{OH})_{15}]^+$	-5.62(1)	6.79

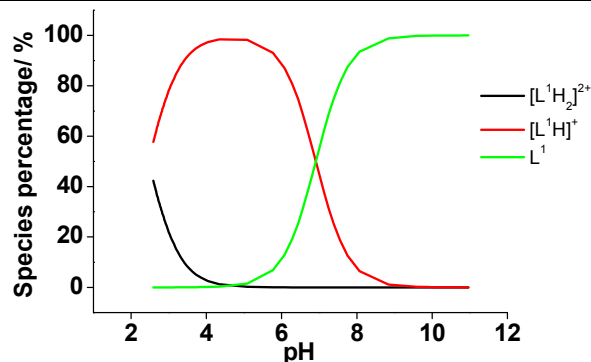


Fig. S7 Species distributions of 1.0 mM L^1 in aqueous solutions at 0.1 M NaNO_3 and 298 ± 0.1 K.

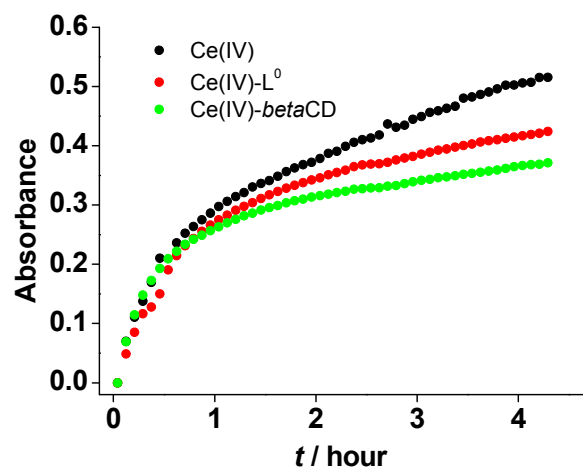


Fig. S8 BNNP (0.01 mM) hydrolysis at pH 7.2 (50 mM HEPES, $I = 0.1$ M NaNO_3) and 308 ± 0.1 K. Conditions: black, $[\text{Ce}(\text{IV})] = 0.1$ mM; red, $[\text{Ce}(\text{IV})] = 0.1$ mM, $[\text{L}^0] = 0.1$ mM; green, $[\text{Ce}(\text{IV})] = 0.1$ mM, $[\beta\text{CD}] = 0.1$ mM.

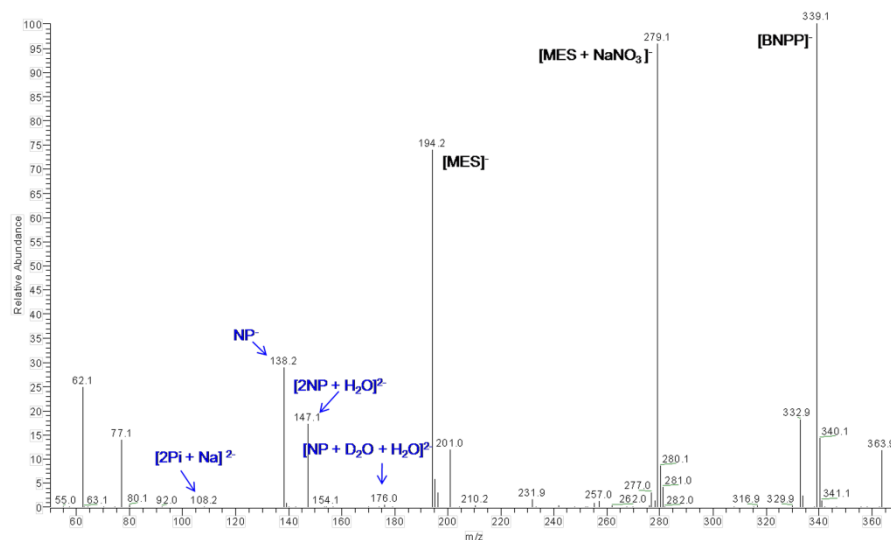


Fig. S9 Negative charge ESI MS analysis of the BNPP hydrolysis products. Conditions: [Ce(IV)] = 0.5 mM, [L¹] = 2.0 mM, [BNPP] = 1.0 mM, 10% D₂O solution buffered at pH 6.5 (50 mM MES, I = 0.1 M NaNO₃).

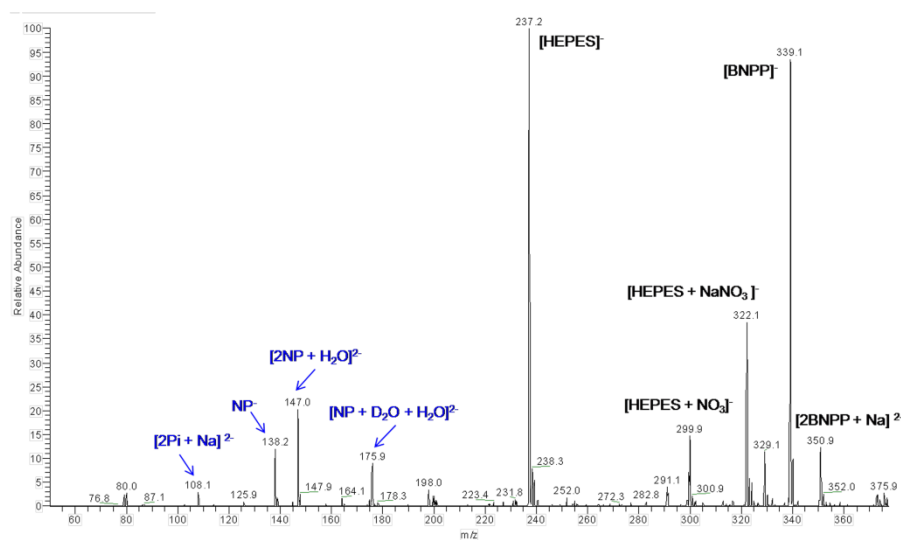


Fig. S10 Negative charge ESI MS analysis of the BNPP hydrolysis products. Conditions: [Ce(IV)] = 0.5 mM, [L²] = 2.0 mM, [BNPP] = 1.0 mM, 10% D₂O solution buffered at pH 7.2 (50 mM HEPES, I = 0.1 M NaNO₃).

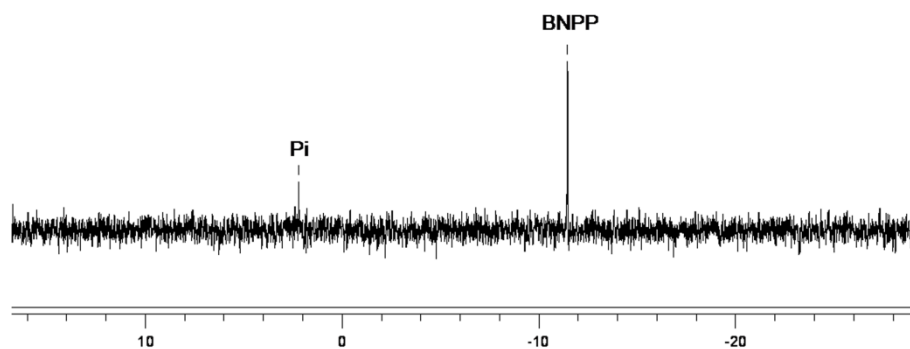


Fig. S11 ³¹P NMR analysis of BNPP hydrolysis product catalyzed by Ce-L² in 10% D₂O solution at 308 ± 0.1K: [Ce(IV)] = 0.5 mM, [L²] = 2.0 mM, [BNPP] = 1.0 mM, [HEPES buffer] = 50 mM and I = 0.1 M NaNO₃. Similar result was obtained for Ce-L¹