Supporting Information

Methodology for the Calibration of pH electrode for potentiometry

Electromotive force (*EMF*, in millivolts) was measured with a Metrohm pH meter (Model 713) equipped with a Metrohm combination pH glass electrode. The original electrode filling solution (3.0 mol·dm^{-3} KCl) was replaced with 1.0 mol dm^{-3} NaCl. The *EMF* in acidic and basic regions can be expressed by Eq. (1) and (2), respectively.

$$E = E^0 + RT/F \ln[H^+] + \gamma_H[H^+] \quad (1)$$

$$E = E^0 + RT/F \ln(K_w/[OH^-]) + \gamma_{OH}[OH^-] \quad (2)$$

where R is the gas constant, F is the Faraday constant and T is the temperature in K. $K_w = [H^+][OH^-]$. The last term is the electrode junction potential for the hydrogen ion or the hydroxide ion ($\Delta E_{j,H+}$ or $\Delta E_{j,OH-}$), assumed to be proportional to the concentration of the hydrogen or hydroxide ions. Prior to each titration, an acid/base titration with standard HCl and tetramethylammonium hydroxide was performed to obtain the electrode parameters of E^0, γ_H and γ_{OH}. These parameters allowed the calculation of hydrogen ion concentrations from the *EMF* in the subsequent titration.

Table S1 Thermodynamic parameters for the protonation of DTPA, I = 1.05 mol·kg^{-1} $NaClO_4$. H_5A stands for DTPA. $\log\beta_{H,M}$ and $\log\beta_{H,m}$ represent the protonation constants in molarity and molality, respectively.

Reaction	t °C	$\log\beta_{H,M}$	$\log\beta_{H,m}$	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}
$H^+ + A^{5-} = HA^{4-}$	10	9.73 ± 0.02	9.71 ± 0.02		
	25	9.43 ± 0.02	9.41 ± 0.02	-26.2 ± 1.4	93 ± 5
	40	9.29 ± 0.03	9.27 ± 0.03		
	55	9.00 ± 0.04	8.98 ± 0.04		
	70	8.91 ± 0.06	8.89 ± 0.06		
$2H^+ + A^{5-} = H_2A^{3-}$	10	18.23 ± 0.03	18.19 ± 0.03		
	25	17.69 ± 0.02	17.65 ± 0.02	-52.6 ± 1.6	162 ± 5
	40	17.34 ± 0.03	17.30 ± 0.03		
	55	16.97 ± 0.04	16.93 ± 0.04		
	70	16.75 ± 0.07	16.71 ± 0.07		
$3H^+ + A^{5-} = H_3A^{2-}$	10	22.61 ± 0.03	22.55 ± 0.03		
	25	21.92 ± 0.03	21.86 ± 0.03	-64.2 ± 2.0	204 ± 7
	40	21.54 ± 0.04	21.48 ± 0.04		
	55	21.19 ± 0.05	21.13 ± 0.05		
	70	21.01 ± 0.08	20.95 ± 0.08		
$4H^+ + A^{5-} = H_4A^-$	10	25.14 ± 0.06	25.06 ± 0.06		
	25	24.48 ± 0.04	24.40 ± 0.04	-65.0 ± 4.6	250 ± 16
	40	24.14 ± 0.06	24.06 ± 0.06		
	55	23.86 ± 0.08	23.78 ± 0.08		
	70	23.68 ± 0.15	23.60 ± 0.15		
$5H^+ + A^{5-} = H_5A(aq)$	10	27.65 ± 0.05	27.55 ± 0.05		
	25	26.85 ± 0.04	26.75 ± 0.04	-63.6 ± 5.7	301 ± 19
	40	26.46 ± 0.07	26.36 ± 0.07		
	55	26.21 ± 0.09	26.11 ± 0.09		
	70	26.16 ± 0.14	26.06 ± 0.14		

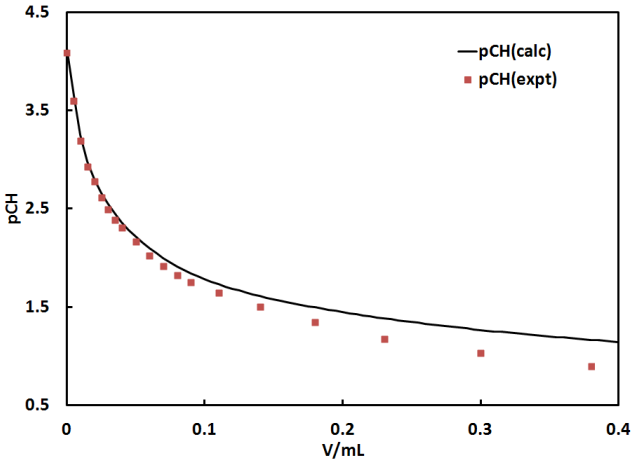


Fig. S1 Potentiometric titration of Cm(III)-DTPA at 25 ^{o}C, I = 1.0 M $NaClO_4$. Initial solution: 1.14 ml, $C_H^0/C_{Cm}^0/C_L^0$ (in mM): 0.015/1.14/6.14; titrant: 0.37 M $HClO_4$/0.63 M $NaClO_4$.

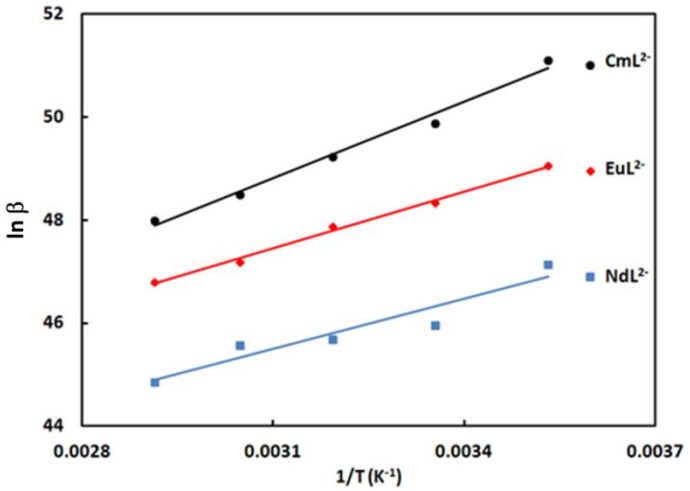


Fig. S2 Van't Hoff plot of the stability constants of M(III)-DTPA. I = 1.0 M $NaClO_4$, M stands for Cm, Nd, or Eu, and L stands for DTPA. Data for Nd and Eu are from ref.[12].

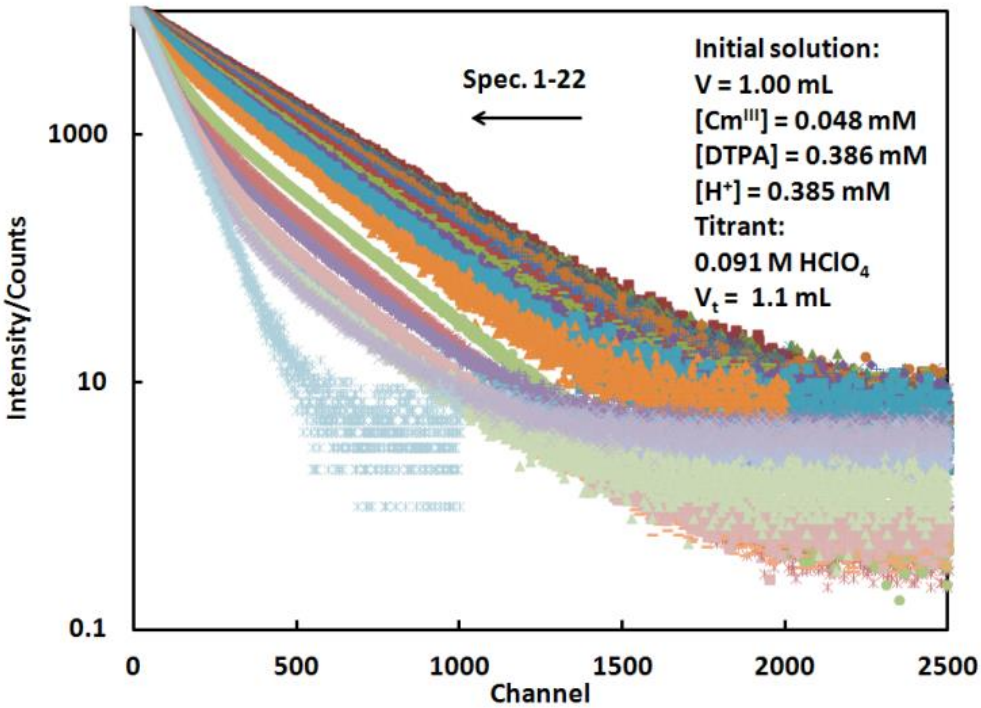


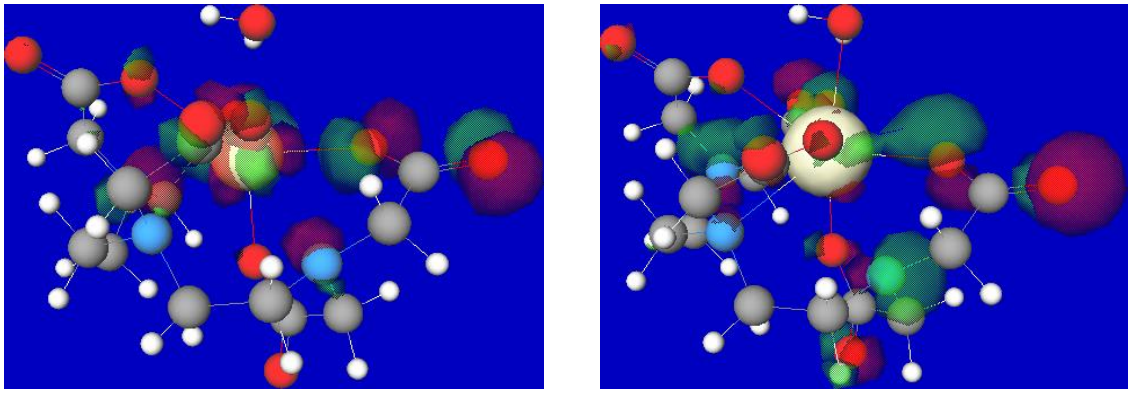
Fig. S3 Luminescence decay of Cm(III)/DTPA solutions.

Note: The kinetic trances in this figure are best viewed in conjunction with the Cm speciation plot in Fig.S7 (top figure, Fig.S7).

The first trace (Spec #1) represent 100% $Cm(aq)^{3+}$, a single exponential decay with τ = 67 μs.

The last trace (Spec# 22) represent 100% CmL^{2-}, a single exponential decay with τ = 268 μs.

The traces in between (Spec # 2 -21) were fitted with two components (Component 1 with τ = 67 μs and Component 2 with τ = 268 μs). From Spec # 2 to #21, the percentage of Component 1 decreased from nearly 100% to 0%, while the percentage of Component 2 increased from 10% to nearly 100%.



(a) Cm-dtpa (b) Eu-dtpa

Fig. S4. Molecular orbitals of Cm-dtpa and Eu-dtpa. Only a HOMO is shown in this case. Other orbitals show similar characteristics in terms of bonding interaction between the central metal atom and the ligand oxygen and nitrogen atoms.

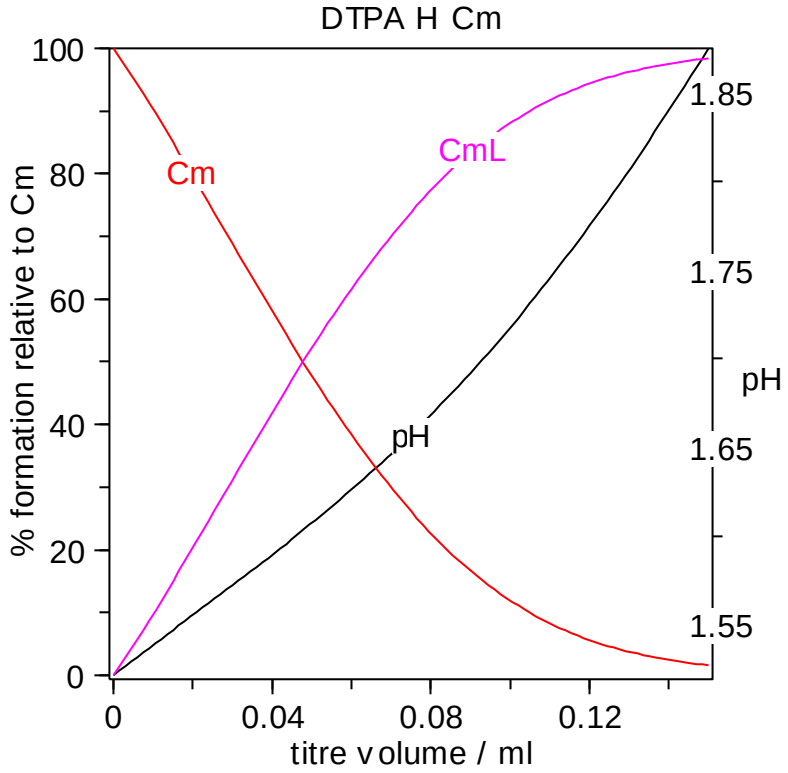


Fig. S5 Speciation plot (% of Cm) corresponding to the spectrophotometric titration shown in Fig.1 of the paper. $t = 25^{o}C$, $I = 1.00$ M $NaClO_4$. Initial solution in cuvette: 1.00 mL, 1.15 mM Cm(III)/30.1 mM H^+; titrant: 0.050 M Na_3H_2DTPA in 1 M $NaClO_4$, totally added 0.15 mL. pCH in the cup ranges from 1.52 to 1.875.

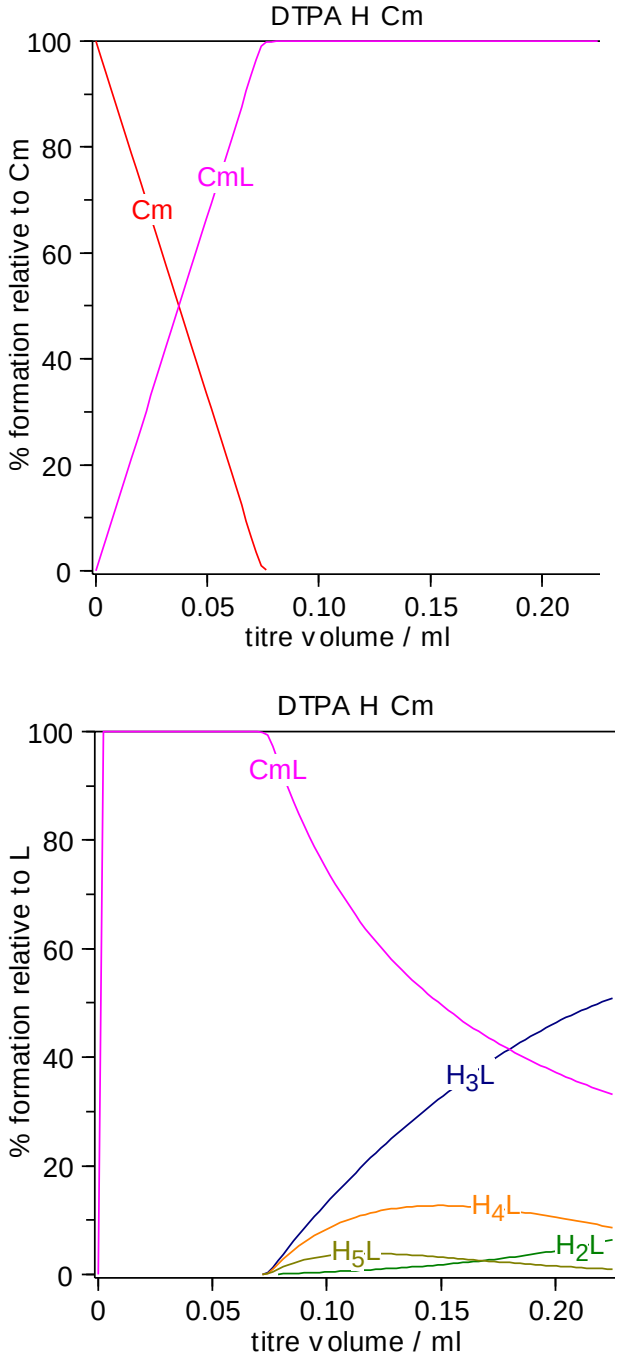


Fig. S6 Speciation plots (top, % of Cm; lower, % of L) corresponding to the calorimetric titration shown in Fig.2 of the paper. $t = 25^{o}C$, $I = 1.00$ M $NaClO_4$. Initial solution in titration cell: 0.900mL, 0.845 mM Cm(III)/0.708 mM H^+; titrant 0.0102 M Na_3H_2DTPA in 1M $NaClO_4$. pCH in the cup ranges from 3.15 to 3.33.

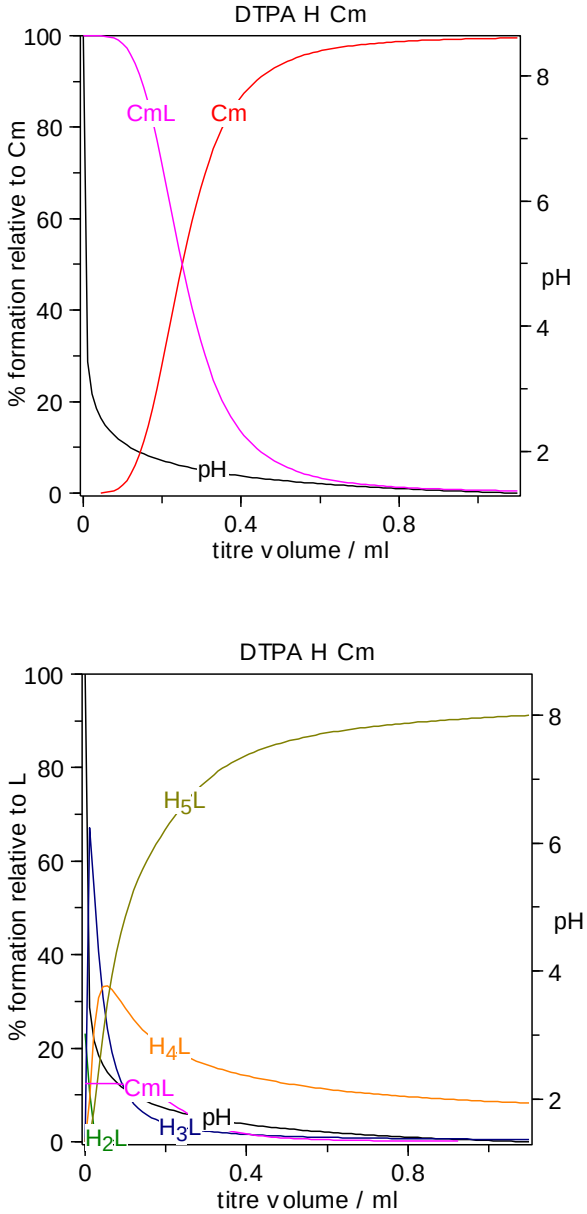
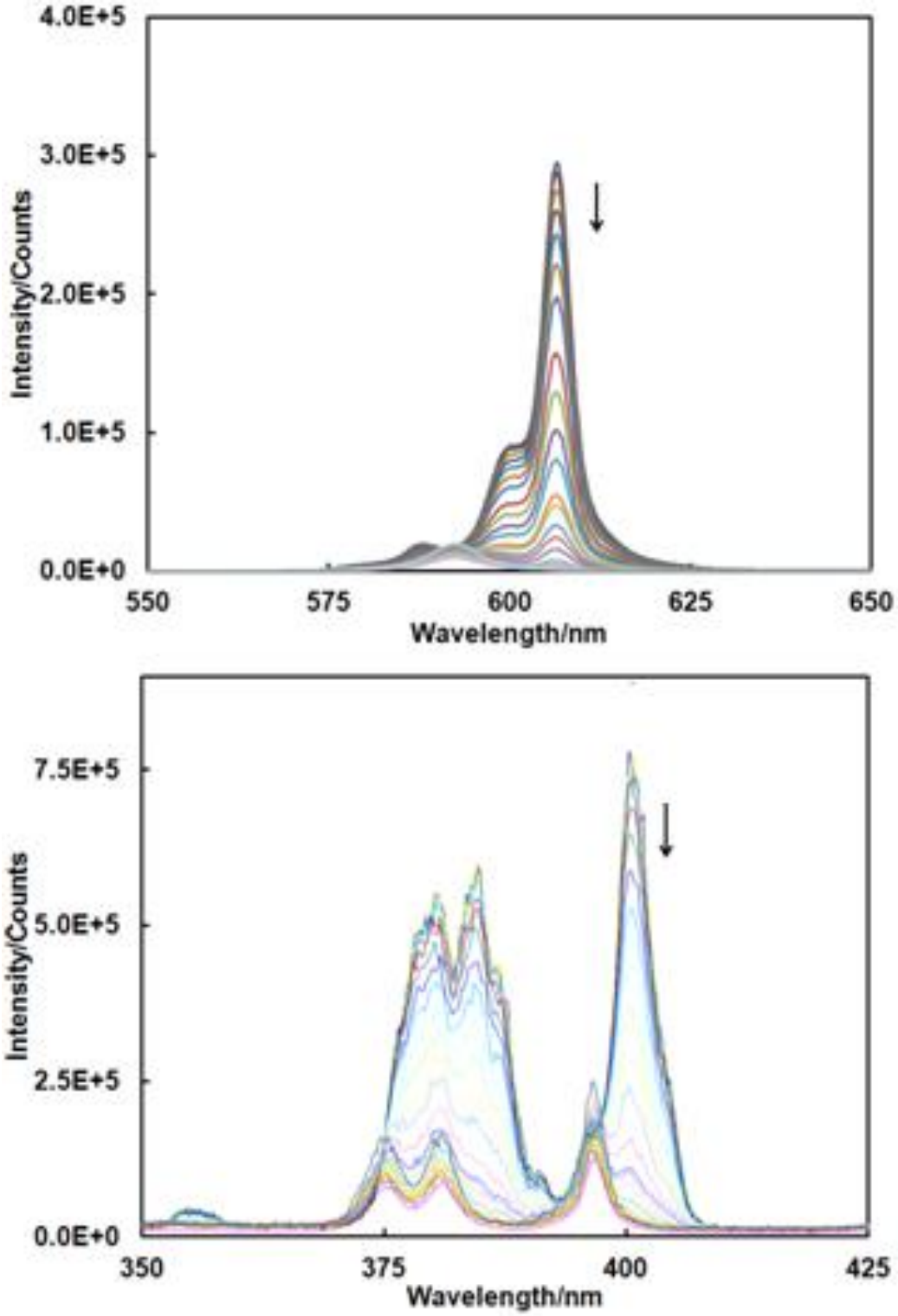


Fig. S7 Speciation plots (top, % of Cm; lower, % of L) corresponding to the luminescence titration shown in Fig.3 of the paper. $t = 25^{o}C$, $I = 1.00$ M $NaClO_4$. $V^0 = 1.0$ mL, $C_H^0 = 0.385$ mM, $C_{Cm}^0 = 0.048$ mM, $C_{DTPA}^0 = 0.386$ mM; titrant: 0.091 M $HClO_4$, total added 1.10 mL, pCH ranges from 8.64 to 1.33.

(Fig.3 enlarged for better viewing)