Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting informations for

The time-resolved fluorescence study of kinetics and thermodynamics of Eu(III) and Tb(III) complexes with the do2a macrocyclic ligand

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Table S1. Consecutive protonation constants of H_2do2a and their stability constant of their Ln(III) complexes (25 °C).

Constant	Ref. [1] [a]	Ref. [2] [a]	Ref. [2] [a]	Ref. [3] [a,b]	Ref. 4] [d]
$\log K_{\mathrm{HL}}$	11.45	11.38	10.91	10.94	10.91;10.94
$\log K_{\mathrm{H2L}}$	9.54	9.62	9.45	9.55	9.45; 9.54
$\log K_{\mathrm{H3L}}$	4.00	3.95	4.09	3.85	4.09; 3.85
$\log K_{\mathrm{H4L}}$	2.36	2.62	3.18	2.55	3.18; 2.55
$\log K_{\mathrm{H5L}}$	<2.3	---	---	---	---
$\log K_{\mathrm{H6L}}$	<2.3	---	---	---	---
Ionic strength	0.1 M $(NMe_4)ClO_4$	0.1 M $(NMe_4)Cl$	0.1 M KCl	0.1 M $(NMe_4)Cl$	0.1 M KCl
$\log K_{\mathrm{LaL}}$	---	16.6		10.94	---
$\log K_{\mathrm{CeL}}$	---	---		11.31	11.3
$\log K_{\mathrm{EuL}}$	---	---		12.99	---
$\log K_{\mathrm{GdL}}$	---	19.4; 19.1		13.06	---
$\log K_{\mathrm{TbL}}$	---	---		12.93	---
$\log K_{\mathrm{YbL}}$	---	20.6		13.26	13.4
$\log K_{\mathrm{CaL}}$	---	7.8		7.16	---

[a] Potentiometry, [b] Capillary zone electrophoresis, [c] Spectrophotometry

References:

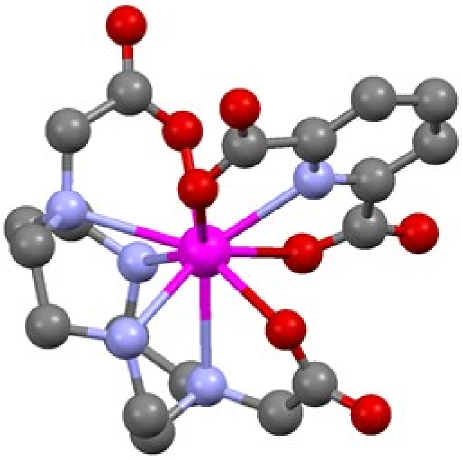
[1] J. Weeks, M.R. Taylor, K.P. Wainwright, *Dalton Trans* **1997**, 317 – 322.

[2] J. Huskens, D.A. Torres, Z. Kovacs, J.P.Andre, C.F.G.C. Geraldes, A.D. Sherry, *Inorg. Chem.* **1997,** 36, 1495-1503.

[3] C.A. Chang, Y.H. Chen, H.Y. Chen, F.K.Shieh, *Dalton Trans.* **1998**, 3243-3248.

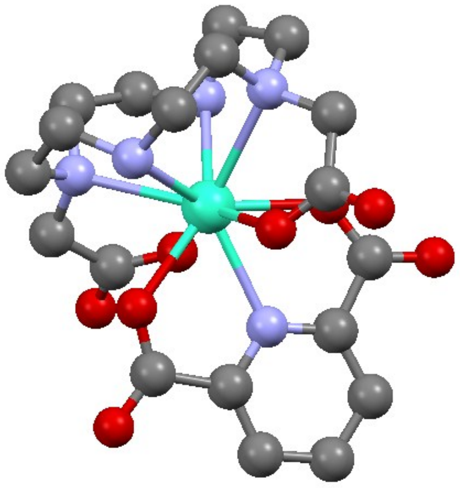
[4] E. Szilagi, E. Toth, Z. Kovacs, J. Platzcek, B. Raduchel, E. Brucher, *Inorg. Chim. Acta* **2000,** 298, 226-234.

Table S2. Overview of molecular structures of ternary [Ln(do2a)(dpa)]$^-$ and binary [Eu(do2a)]$^+$ complexes.



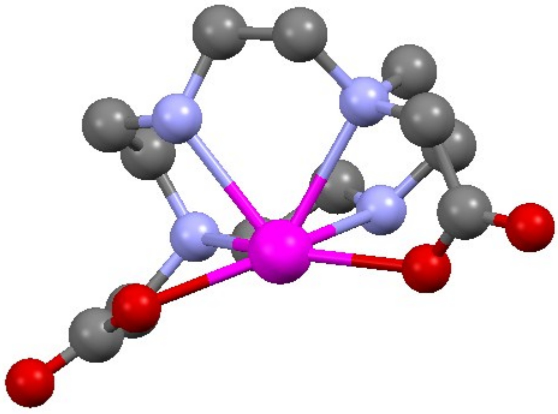
[Eu(do2a)(dpa)]$^-$ complex [Ref. 1]

Eu-N1$^{\mathrm{macro}}$	2.67 Å
Eu-N2$^{\mathrm{macro}}$	2.59 Å
Eu-N3$^{\mathrm{macro}}$	2.67 Å
Eu-N4$^{\mathrm{macro}}$	2.58 Å
Eu-O1$^{\mathrm{macro}}$	2.38 Å
Eu-O2$^{\mathrm{macro}}$	2.37 Å
Eu-O1^{DPA}	*2.40 Å*
Eu-O2^{DPA}	*2.41 Å*
Eu-N^{DPA}	*2.51 Å*



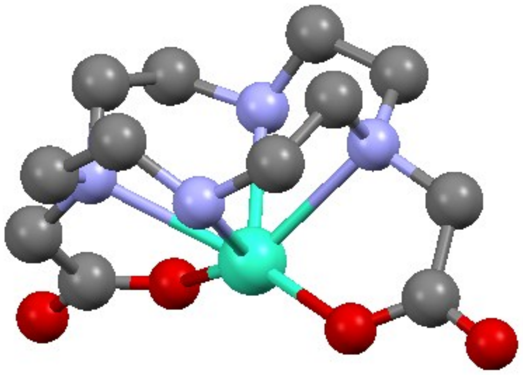
[Tb(do2a)(dpa)]$^-$ complex [Ref. 2]

Tb-N1$^{\mathrm{macro}}$	2.64 Å
Tb-N2$^{\mathrm{macro}}$	2.57Å
Tb-N3$^{\mathrm{macro}}$	2.66 Å
Tb-N4$^{\mathrm{macro}}$	2.56 Å
Tb-O1$^{\mathrm{macro}}$	2.36 Å
Tb-O2$^{\mathrm{macro}}$	2.35 Å
Tb-O1^{DPA}	*2.39 Å*
Tb-O2^{DPA}	*2.40 Å*
Tb-N^{DPA}	*2.49 Å*



[Eu(do2a)]$^+$ complex[Ref. 3]

Eu-N1$^{\mathrm{macro}}$	2.70 Å $^{\mathrm{LC}}$; 2.71 Å $^{\mathrm{SC}}$
Eu-N2$^{\mathrm{macro}}$	2.61 Å $^{\mathrm{LC}}$; 2.62 Å $^{\mathrm{SC}}$
Eu-N3$^{\mathrm{macro}}$	2.72 Å $^{\mathrm{LC}}$; 2.73 Å $^{\mathrm{SC}}$
Eu-N4$^{\mathrm{macro}}$	2.61 Å $^{\mathrm{LC}}$; 2.62 Å $^{\mathrm{SC}}$
Eu-O1$^{\mathrm{macro}}$	2.35 Å $^{\mathrm{LC}}$; 2.34 Å $^{\mathrm{SC}}$
Eu-O2$^{\mathrm{macro}}$	2.30 Å $^{\mathrm{LC}}$; 2.29 Å $^{\mathrm{SC}}$



[Tb(do2a)]$^+$ complex

Eu-O1^{water}	$2.70\,\text{Å}^{LC}$; $2.63\,\text{Å}^{SC}$
Eu-O2^{water}	$2.63\,\text{Å}^{LC}$; $2.72\,\text{Å}^{SC}$
Eu-O3^{water}	$2.59\,\text{Å}^{LC}$; $2.59\,\text{Å}^{SC}$

Quasi-relativistic effective core potentials: Large Core- LC and Small Core-SC, employed for quantum-chemical calculations (see Ref. 3)

[Ref. 1] J.P. Kirby, M.L. Cable, D.J. Levine, H.B. Gray and A, Ponce, *Anal. Chem.,* 2008, 80, 5750-5754.

[Ref. 2] M.L. Cable, J.P. Kirby, K. Sorasaenee, H.B. Gray and A, Ponce, *J. Am. Chem. Soc.,* 2007, 129, 1474-1475.

[Ref. 3] C.A.Chang, H.Y. Lee and Ch.-L. Chen, *Dalton Trans.*, 2013, 42, 6397-6409.

The calculation of stability constants from TRFS experimental data

Generally, the number of water molecules coordinated to Eu(III) complex was estimated by simplified equation [ref. 1] as

$$q_{\mathrm{H_2O\text{-}EuL}} = 1.05 \times k_{\mathrm{H_2O}} - 0.70 \qquad \text{(S1)}$$

and/or other form was obtained after rearrangement

$$k_{\mathrm{H_2O\text{-}EuL}} = \frac{q_{\mathrm{H_2O\text{-}EuL}} + 0.70}{1.05} \qquad \text{(S2)}$$

The equilibrium constant for the following reaction at given pH

$$[\mathrm{Eu(H_2O)_9}]^{3+} + \mathrm{L} \xleftrightarrow{K_{\mathrm{eff,EuL}}} [\mathrm{EuL(H_2O)_3}]^{+} + 6\,\mathrm{H_2O} \qquad \text{(Eq\_A)}$$

is defined as

$$K_{\mathrm{eff,EuL}} = \frac{[\mathrm{EuL}]}{[\mathrm{Eu}] \times [\mathrm{L}]} \qquad \text{(S3)}$$

and the mass-balance equations are valid

$$c_{\mathrm{Eu}} = [\mathrm{EuL}] + [\mathrm{Eu}] \qquad \text{(S4A)}$$

$$c_{\mathrm{L}} = [\mathrm{EuL}] + [\mathrm{L}] \qquad \text{(S4B)}$$

The following equation related to rate constant of luminescence decay of Eu(III) complex in presence of free Eu(III) ion was derived elsewhere [ref. 1]

$$k_{\mathrm{H_2O,\,EuL\text{-}Eu}} = k_{\mathrm{H_2O,\,EuL}} \times \delta_{\mathrm{EuL}} + k_{\mathrm{H_2O,\,Eu}} \times (1 - \delta_{\mathrm{EuL}}) \qquad \text{(S5)}$$

where the relative concentration of Eu(III) complex is $\delta_{\mathrm{EuL}} = \dfrac{[\mathrm{EuL}]}{\mathrm{c_{Eu}}}$

Combining Eqs (S3) and (S4A and S4B), the following equation is derived

$$K_{\mathrm{eff,EuL}} = \frac{[\mathrm{EuL}]}{[\mathrm{Eu}] \times [\mathrm{L}]} = \frac{\delta_{\mathrm{EuL}} \times c_{\mathrm{Eu}}}{(1 - \delta_{\mathrm{EuL}}) \times c_{\mathrm{Eu}} \times (c_{\mathrm{L}} - \delta_{\mathrm{EuL}} \times \mathrm{c_{Eu}})} = \frac{\delta_{\mathrm{EuL}}}{(1 - \delta_{\mathrm{EuL}}) \times (c_{\mathrm{L}} - \delta_{\mathrm{EuL}} \times \mathrm{c_{Eu}})} \qquad \text{(S6)}$$

Substituting Eq. (S5) by Eq. (S2)

$$\frac{q_{\mathrm{H_2O,\,EuL\text{-}Eu}} + 0.70}{1.05} = \frac{q_{\mathrm{H_2O,EuL}} + 0.70}{1.05} \times \delta_{\mathrm{EuL}} + \frac{q_{\mathrm{H_2O,\,Eu}} + 0.70}{1.05} \times (1 - \delta_{\mathrm{EuL}}) \qquad \text{(S7)}$$

and the new Equation is obtained after arrangement:

$$q_{\mathrm{H_2O,EuL\text{-}Eu}} = q_{\mathrm{H_2O,EuL}} \times \delta_{\mathrm{EuL}} + q_{\mathrm{H_2O,Eu}} \times (1 - \delta_{\mathrm{EuL}}) \qquad \text{(S8)}$$

Thus, the relative concentration of Eu(III) complex can be calculated as

$$\delta_{\mathrm{EuL}} = \frac{q_{\mathrm{H_2O,\,Eu}} - q_{\mathrm{H_2O,\,EuL\text{-}Eu}}}{q_{\mathrm{H_2O,\,Eu}} - q_{\mathrm{H_2O,\,EuL}}} \qquad \text{(S9)}$$

Assuming the chemical reaction (A), the Eq. (S9) can be simplified as

$$\delta_{\mathrm{EuL}} = \frac{9 - q_{\mathrm{H_2O,\,EuL\text{-}Eu}}}{6} \qquad \text{(S10)}$$

and this relationship can be used for calculation of equilibrium constant (see Eq. (S6)). To get stability constant which is independent on pH:

$$\log \beta_{\mathrm{EuL}} = \log K_{\mathrm{eff,EuL}} - \log\ \alpha_{\mathrm{L(H)}} \qquad \text{(S11)}$$

where the term is calculated as

$$\alpha_{\mathrm{L(H)}} = 1 + K_{\mathrm{p1}} \times [\mathrm{H^+}] + K_{\mathrm{p1}} \times K_{\mathrm{p2}} \times [\mathrm{H^+}]^2 + \ldots \qquad \text{(S12)}$$

Analogously, the equilibrium constant for the following reaction at given pH

$$[\mathrm{Tb(H_2O)_8}]^{3+} + \mathrm{L} \xleftrightarrow{K_{\mathrm{eff,TbL}}} [\mathrm{TbL(H_2O)_2}]^{+} + 6\,\mathrm{H_2O} \qquad \text{(Eq\_B)}$$

is defined as

$$K_{\mathrm{eff,TbL}} = \frac{[\mathrm{TbL}]}{[\mathrm{Tb}]\times[\mathrm{L}]} \qquad \text{(S13)}$$

as well as

$$q_{\mathrm{H_2O,TbL\text{-}Tb}} = q_{\mathrm{H_2O,TbL}} \times \delta_{\mathrm{TbL}} + q_{\mathrm{H_2O,Tb}} \times (1-\delta_{\mathrm{TbL}}) \qquad \text{(S14)}$$

Thus the relative concentration of Tb(III) complex can be calculated as

$$\delta_{\mathrm{TbL}} = \frac{q_{\mathrm{H_2O,\,Tb}} - q_{\mathrm{H_2O,\,TbL\text{-}Tb}}}{q_{\mathrm{H_2O,\,Tb}} - q_{\mathrm{H_2O,\,TbL}}} \qquad \text{(S15)}$$

Assuming the chemical reaction (B), the Eq. (14) can be simplified as

$$\delta_{\mathrm{TbL}} = \frac{8 - q_{\mathrm{H_2O,\,TbL\text{-}Tb}}}{6} \qquad \text{(S16)}$$

and this relationship can be used for calculation of equilibrium constant (see Eq. (S13)).

To get stability constant independent on pH:

$$\log \beta_{\mathrm{EuL}} = \log K_{\mathrm{eff,EuL}} - \log\ \alpha_{\mathrm{L(H)}} \qquad \text{(S17)}$$

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1 P.P. Barthelemy and G.R. Choppin, *Inorg. Chem.*, 1989, **28**, 3354-3357.

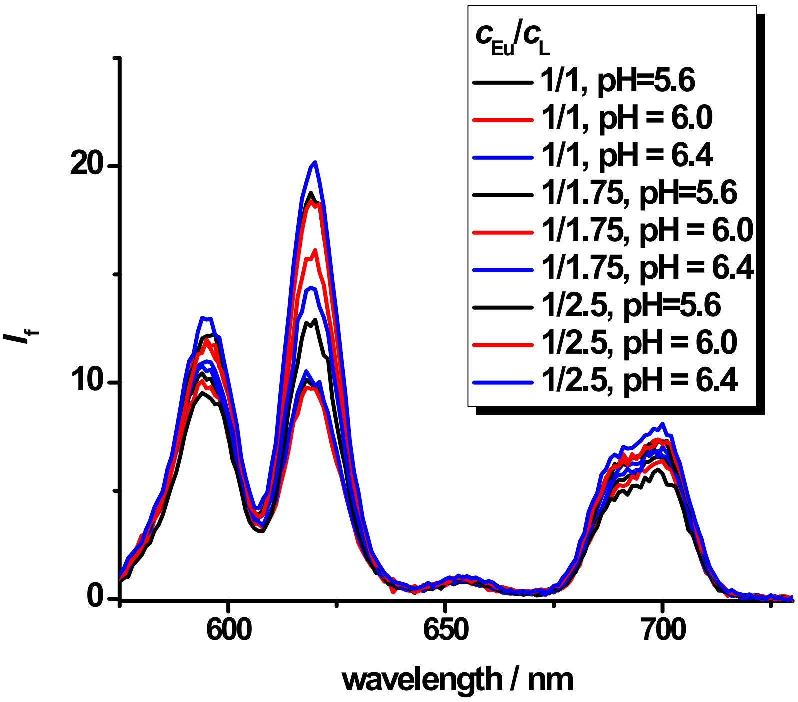

Fig. S1: The examples of emission spectra of $[Eu(do2a)]^+$ complex measured for various c_L / c_{Eu} ratios and pH = 5.6-6.4 (λ_{exc} = 394 nm, c_{Eu} = 1 mM, I = 0.1 M (KCl)).

Table S3: The calculated stability constants of $[Eu(do2a)]^+$ complex. The experimental conditions are the same as in Fig. S1.

pH **log β_{EuL}**	**Ratio c_L / c_{Eu}**		
	1	**1.75**	**2.5**
5.6	**12.65**	**12.52**	**13.19**
6.0	**11.78**	**12.11**	**12.31**
Average value	**$12.4_3 \pm 0.4_9$**		

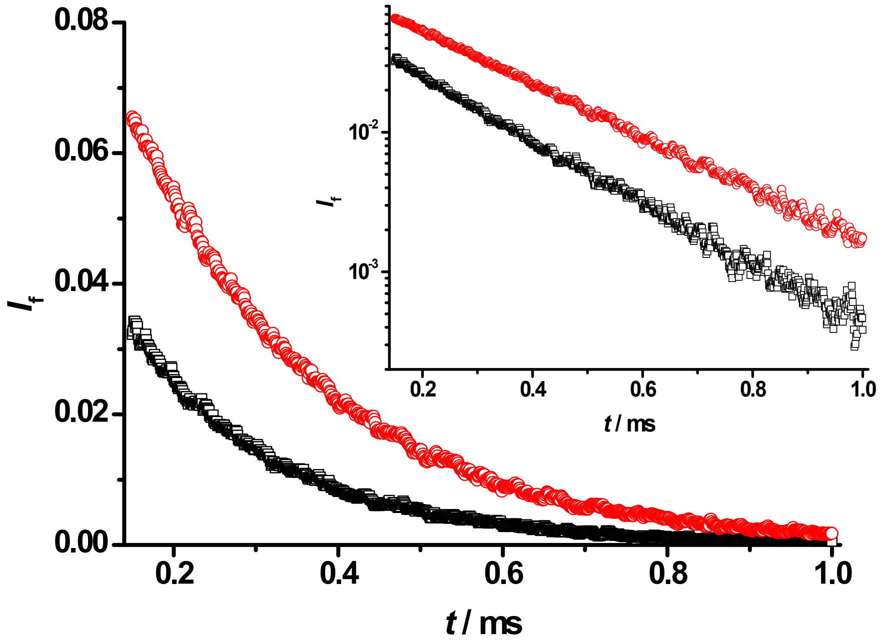

Fig. S2: The examples of luminescence-decay traces of the Eu(III)-H_2do2a system measured for the c_L / c_{Eu} = 1, pH = 5.6 (black) and c_L / c_{Eu} = 2.5, pH = 6.0 (red). (λ_{exc} = 394 nm, (λ_{em} = 618 nm c_{Eu} = 1 mM, I = 0.1 M (KCl)).

Table S4: The calculated stability constants of $[Eu(do2a)]^+$ complex[a].
The experimental conditions are the same as in Fig. S2.

pH / *q* [a] (log β_{EuL}[b])	**Ratio c_L / c_{Eu}**		
	1	**1.75**	**2.5**
5.6	4.72 (**13.24**)	4.35 (**12.85**)	4.11 (**12.72**)
6.0	4.60 (**12.51**)	4.31 (**12.06**)	3.83 (**12.07**)
Average value	**$12.5_7 \pm 0.4_6$**		

a) calculated as $q = 1.02\times10^{-3}\, k_{obs} - 0.17$ [see T. Kimura and Y. Kato, *J. Alloys Comp.*, **1998**, 278, 92-97)

b) assuming the equilibrium $[Eu(H_2O)_9]^{3+} + L \leftrightarrow [EuL(H_2O)_3]^+ + 6\ H_2O$

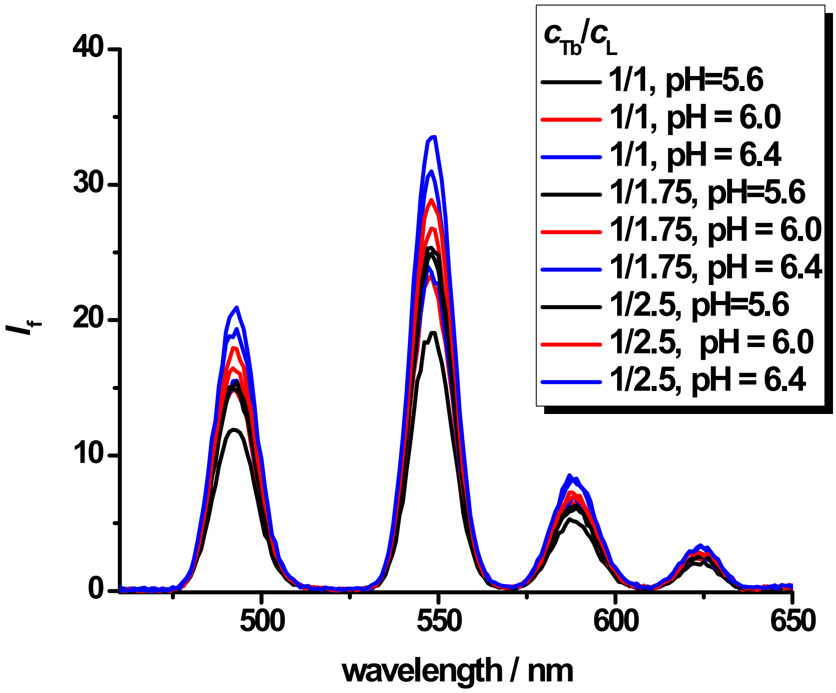

Fig. S3: The examples of emission spectra of $[Tb(do2a)]^+$ complex measured for various c_L / c_{Tb} ratios and pH = 5.6-6.4 (λ_{exc} = 355 nm, c_{Tb} = 1 mM, I = 0.1 M (KCl)).

Table S5: The calculated stability constants of $[Tb(do2a)]^+$ complex. The experimental conditions are the same as in Fig. S3.

pH **log β_{EuL}**	**Ratio c_L / c_{Eu}**		
	1	**1.75**	**2.5**
5.6	**12.79**	**12.88**	**12.64**
6.0	**12.45**	**12.10**	**12.12**
Average value	**$12.5_0 \pm 0.3_3$**		

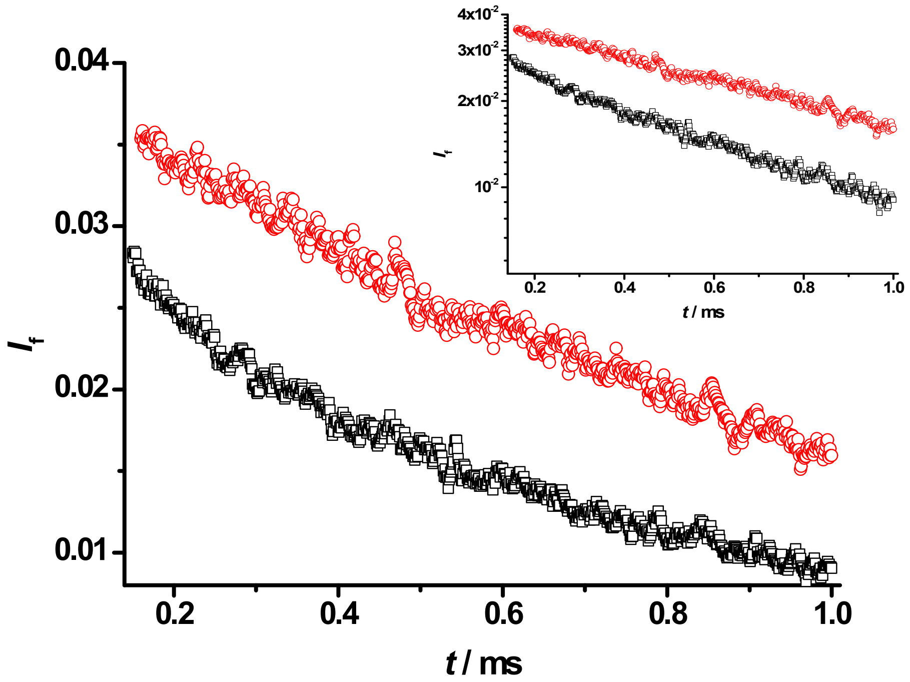

Fig. S4: The examples of luminescence-decay traces of the Tb(III)-H_2do2a system measured for the c_L / c_{Tb} = 1, pH = 5.6 (black) and c_L / c_{Tb} = 2.5, pH = 6.0 (red). (λ_{exc} = 355 nm, λ_{em} = 545 nm, c_{Tb} = 1 mM, I = 0.1 M (KCl)).

Table S6: The calculated stability constants of $[Tb(DO2A)]^+$ complex[a].
The experimental conditions are the same as in Fig. S4.

pH / *q* [a] (log β_{EuL} [b])	**Ratio c_L / c_{Eu}**		
	1	**1.75**	**2.5**
5.6	3.86 (**13.15**)	3.24 (**12.90**)	3.07 (**12.74**)
6.0	3.57 (**12.53**)	3.00 (**12.23**)	2.67 (**12.19**)
Avg value	**$12.6_2 \pm 0.3_8$**		

a) calculated as $q = 4.00\times10^{-3}\,k_{obs} - 0.93$ (see T. Kimura and Y. Kato, *J. Alloys Comp.*, **1998**, 278, 92-97).

b) assuming the equilibrium $[Tb(H_2O)_8]^{3+} + L \leftrightarrow [TbL(H_2O)_2]^+ + 6\,H_2O$

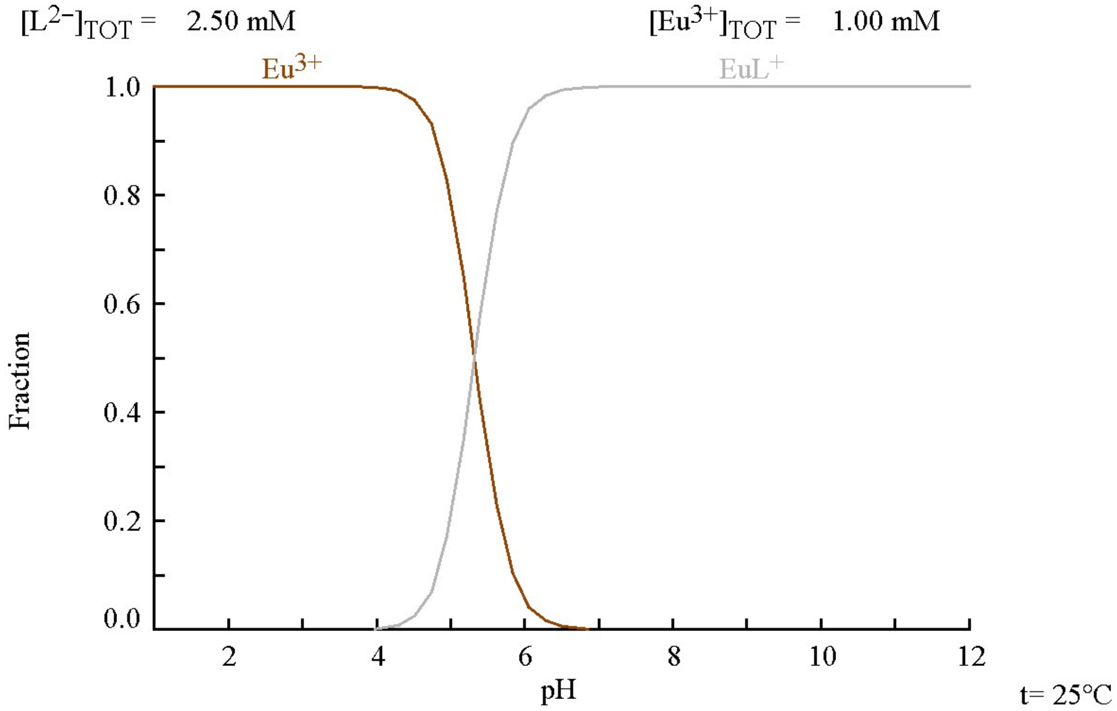

Fig. S5: The distribution diagram of Eu(III)-H_2do2a system (equilibrium speciation diagram).

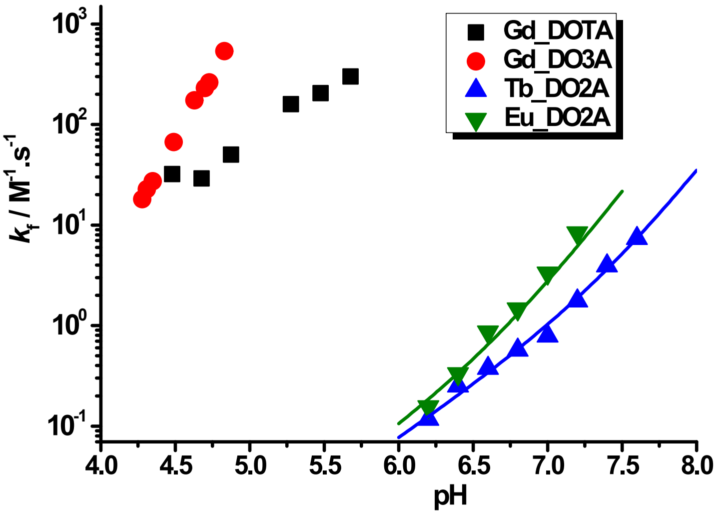

Fig. S6: The formation of Eu(III) and Tb(III) complexes with H_2do2a ligand and Gd(III) complexes with H_3do3a and H_4dota ligands (the experimental data were taken and recalculated from [Refs. 1 and 2].

[Ref. 1] X. Wang, T. Jin, V. Comblin, A. Lopez-Mut, E. Merciny and J.F. Desreux, *Inorg. Chem.,* **1992**, 31, 1095-1099.

[Ref. 2] K. Kumar and M.F. Tweddle, *Inorg. Chem.*, **1993**, 37, 4193-4199.

The formation of $[Eu(do2a)]^+$ complex - reaction mechanism

The formation of Eu(III) complex can be described by two-step reaction mechanism (the charges of species are omitted for the sake of clarity):

$$\begin{aligned} &\mathrm{Eu} + \mathrm{H}_x\mathrm{L} \xleftrightarrow{K^*} [\mathrm{Eu}(\mathrm{H}_y\mathrm{L})]^* + (x-y)\mathrm{H}^+ \\ &[\mathrm{Eu}(\mathrm{H}_y\mathrm{L})]^* \xrightarrow{k^*} [\mathrm{EuL}] + y\mathrm{H}^+ \end{aligned} \qquad \text{(Eq\_C)}$$

Generally, the rate of formation of Eu(III) complex can be described as

$$v = k_{2,\mathrm{f}} \times [\mathrm{Eu}]_{\mathrm{tot}} \times [\mathrm{L}]_{\mathrm{tot}} \qquad \text{(S18)}$$

For reaction mechanism mentioned above, the rate of formation of Eu(III) complex is

$$v = k^* \times [\mathrm{EuL}^*] \qquad \text{(S19)}$$

knowing the equilibrium constant K^*

$$K^* = \frac{[\mathrm{EuL}^*]}{[\mathrm{Eu}] \times [\mathrm{H}_x\mathrm{L}]} \qquad \text{(S20)}$$

In metal excess ($c_{\mathrm{Eu}} >> c_{\mathrm{L}}$), the previous equations can be modified as

$$v = k^* \times \frac{K^* \times [\mathrm{Eu}]_{\mathrm{tot}}}{1 + K^* \times [\mathrm{Eu}]_{\mathrm{tot}}} \times [\mathrm{L}]_{\mathrm{tot}} \Rightarrow k_{\mathrm{f,obs}} = k^* \times \frac{K^* \times [\mathrm{Eu}]_{\mathrm{tot}}}{1 + K^* \times [\mathrm{Eu}]_{\mathrm{tot}}} \qquad \text{(S21)}$$

and analogously in ligand excess ($c_{\mathrm{Eu}} << c_{\mathrm{L}}$)

$$v = k^* \times \frac{K^* \times [\mathrm{L}]_{\mathrm{tot}}}{1 + K^* \times [\mathrm{L}]_{\mathrm{tot}}} \times [\mathrm{Eu}]_{\mathrm{tot}} \Rightarrow k_{\mathrm{f,obs}} = k^* \times \frac{K^* \times [\mathrm{L}]_{\mathrm{tot}}}{1 + K^* \times [\mathrm{L}]_{\mathrm{tot}}} \qquad \text{(S22)}$$

It is evident $k_{2,\mathrm{f}} = k^* \times K^*$ [Refs 1, 2]. Also in case when nominator ≈ 1, then

$$k_{\mathrm{f,obs}} = k^* \times K^* \times [\mathrm{Eu}]_{\mathrm{tot}} = k_{2,\mathrm{f}} \times [\mathrm{Eu}]_{\mathrm{tot}} \quad (c_{\mathrm{Eu}} >> c_{\mathrm{L}}) \qquad \text{(S23A)}$$

$$k_{\mathrm{f,obs}} = k^* \times K^* \times [\mathrm{L}]_{\mathrm{tot}} == k_{2,\mathrm{f}} \times [\mathrm{L}]_{\mathrm{tot}} \quad (c_{\mathrm{Eu}} << c_{\mathrm{L}}) \qquad \text{(S23B)}$$

1. X. Wang, T. Jin, V. Comblin, A. Lopez-Mut, E. Merciny and J.F. Desreux, *Inorg. Chem.*, 1992, **31**, 1095-1099.
2. M.P.C. Campello, S. Lacerda, I.C. Santos, G.A. Pereiera, G.F.G.C. Geraldes, J. Kotek, P. Hermann, J. Vaněk, P. Lubal, V. Kubíček, E. Tóth and I. Santos, *Chem. Eur. J.*, 2010, **16**, 8446-8465.

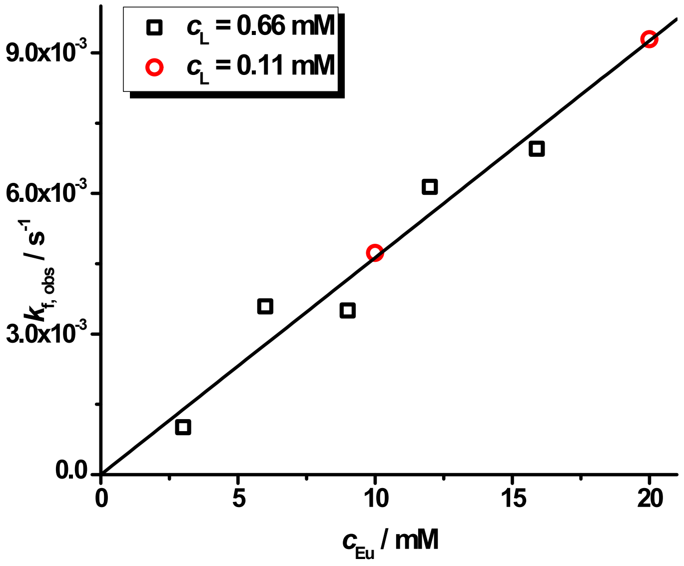

Fig. S7.: The plot of pseudo-first rate constants of Eu(III) complex formation as function of europium(III) concentration. The second-order rate constant 0.463 $M^{-1}s.^{-1}$ was obtained as slope linear dependence.

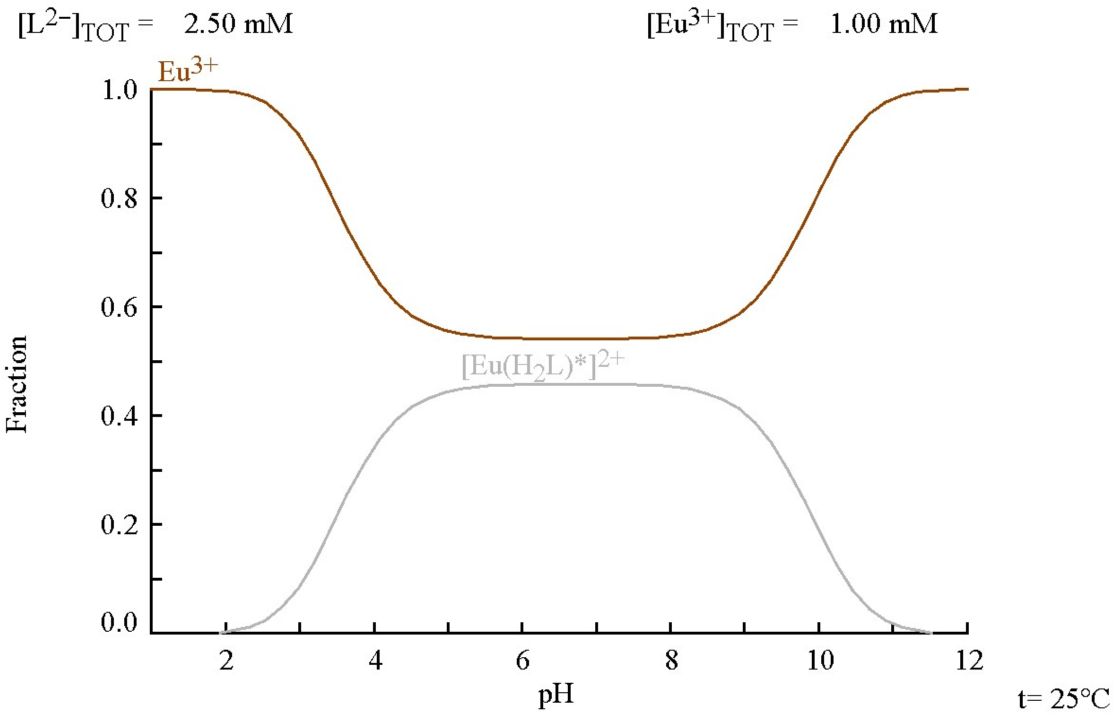

Fig. S8: The distribution diagram of Eu(III)-H_2do2a system (kinetic speciation diagram).

Thermodynamics vs. kinetics of [Ln(do2a)]$^+$ complexes

The consistency of obtained kinetic parameters can be verified by calculation of stability constant of Ln(III) complexes. For the following chemical reaction

$$\mathrm{LnL^+ + H^+ \Leftrightarrow Ln^{3+} + HL^-} \qquad \text{(Eq\_D)}$$

the kinetic rate law ii defined as

$$v = k_\mathrm{H} \times [\mathrm{LnL}] \times [\mathrm{H^+}] = k_\mathrm{HL} \times [\mathrm{Ln}] \times [\mathrm{HL}] \qquad \text{(S24)}$$

which can be defined in enlarged form

$$v = k_\mathrm{H} \times \beta_\mathrm{LnL} \times [\mathrm{Ln}] \times [\mathrm{L}] \times [\mathrm{H^+}] = k_\mathrm{HL} \times [\mathrm{Ln}] \times K_\mathrm{HL} \times [\mathrm{H^+}] \times [\mathrm{L}] \qquad \text{(S25)}$$

where equilibrium constants are defined as

$$\beta_\mathrm{LnL} = \frac{[\mathrm{LnL}]}{[\mathrm{Ln}] \times [\mathrm{L}]} \text{ and } K_\mathrm{HL} = \frac{[\mathrm{HL}]}{[\mathrm{H^+}] \times [\mathrm{L}]} \qquad \text{(S26)}$$

Then after simplification

$$k_\mathrm{H} \times \beta_\mathrm{LnL} = k_\mathrm{HL} \times K_\mathrm{HL} \qquad \text{(S27)}$$

the final relationship is derived

$$\beta_\mathrm{LnL} = \frac{k_\mathrm{HL}}{k_\mathrm{H}} \times K_\mathrm{HL} \qquad \text{(S28A)}$$

or in logarithmic form as

$$\log \beta_\mathrm{LnL} = \log(\frac{k_\mathrm{HL}}{k_\mathrm{H}}) + \log K_\mathrm{HL} \qquad \text{(S28B)}$$

The meaning of rate constants k_HL and k_H defined for the formation and dissociation reaction of Ln(III) complexes is connected with parameters defined earlier. The overall rate constant for formation of Ln(III) complex

$$\mathrm{Ln^{3+} + HL^-} \xrightarrow{k_\mathrm{HL}} \mathrm{LnL + H^+} \qquad \text{(Eq\_E)}$$

The dissociation constant of Ln(III) complex was described by another reaction pathway as

$$\mathrm{LnL^+ + H^+} \xleftrightarrow{K_\mathrm{H,LnL}} \mathrm{Ln(HL)^{2+}} \qquad \text{(Eq\_F)}$$

$$\mathrm{Ln(HL)^{2+}} \xrightarrow{k_\mathrm{Ln(HL)}} \mathrm{Ln^{3+} + HL^-} \qquad \text{(Eq\_G)}$$

The pseudo-first order rate constant for Ln(III) complex dissociation is defined as

$$k_\mathrm{d,obs} = \frac{k_\mathrm{Ln(HL)} \times K_\mathrm{H,LnL} \times [\mathrm{H^+}]}{1 + K_\mathrm{H,LnL} \times [\mathrm{H^+}]} = \frac{k_\mathrm{H} \times [\mathrm{H^+}]}{1 + K_\mathrm{H,LnL} \times [\mathrm{H^+}]} \qquad \text{(S29)}$$

where

$$k_\mathrm{H} = k_\mathrm{Ln(HL)} \times K_\mathrm{H,LnL} \qquad \text{(S30)}$$