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>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>log$K_{HL}$</td>
<td>11.45</td>
<td>11.38</td>
<td>10.91</td>
<td>10.94</td>
<td>10.91;10.94</td>
</tr>
<tr>
<td>log$K_{H2L}$</td>
<td>9.54</td>
<td>9.62</td>
<td>9.45</td>
<td>9.55</td>
<td>9.45; 9.54</td>
</tr>
<tr>
<td>log$K_{H3L}$</td>
<td>4.00</td>
<td>3.95</td>
<td>4.09</td>
<td>3.85</td>
<td>4.09; 3.85</td>
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<tr>
<td>log$K_{H4L}$</td>
<td>2.36</td>
<td>2.62</td>
<td>3.18</td>
<td>2.55</td>
<td>3.18; 2.55</td>
</tr>
<tr>
<td>log$K_{H5L}$</td>
<td>&lt;2.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{H6L}$</td>
<td>&lt;2.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

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 |
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>log$K_{LaL}$</td>
<td>---</td>
<td>16.6</td>
<td>10.94</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{CeL}$</td>
<td>---</td>
<td>---</td>
<td>11.31</td>
<td>11.3</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{EuL}$</td>
<td>---</td>
<td>---</td>
<td>12.99</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{GdL}$</td>
<td>---</td>
<td>19.4; 19.1</td>
<td>13.06</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{TbL}$</td>
<td>---</td>
<td>---</td>
<td>12.93</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{YbL}$</td>
<td>---</td>
<td>20.6</td>
<td>13.26</td>
<td>13.4</td>
<td>---</td>
</tr>
<tr>
<td>log$K_{CaL}$</td>
<td>---</td>
<td>7.8</td>
<td>7.16</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$ Potentiometry, $^b$ Capillary zone electrophoresis, $^c$ Spectrophotometry

References:

Table S2. Overview of molecular structures of ternary \([\text{Ln(do2a)(dpa)}]^+\) and binary \([\text{Eu(do2a)}]^+\) complexes.

\[
\begin{array}{ll}
| \text{Complex} | \text{Bond Lengths} | \\
|----------------|------------------|
| \([\text{Eu(do2a)(dpa)}]^+\) complex | \([\text{Ref. 1]}\) | \\
| \text{Eu-N1\textsuperscript{macro}} | 2.67 Å | \\
| \text{Eu-N2\textsuperscript{macro}} | 2.59 Å | \\
| \text{Eu-N3\textsuperscript{macro}} | 2.67 Å | \\
| \text{Eu-N4\textsuperscript{macro}} | 2.58 Å | \\
| \text{Eu-O1\textsuperscript{macro}} | 2.38 Å | \\
| \text{Eu-O2\textsuperscript{macro}} | 2.37 Å | \\
| \text{Eu-O1\textsuperscript{DPA}} | 2.40 Å | \\
| \text{Eu-O2\textsuperscript{DPA}} | 2.41 Å | \\
| \text{Eu-N\textsuperscript{DPA}} | 2.51 Å | \\
| \text{[Tb(do2a)(dpa)]}^+ complex} | \([\text{Ref. 2]}\) | \\
| \text{Tb-N1\textsuperscript{macro}} | 2.64 Å | \\
| \text{Tb-N2\textsuperscript{macro}} | 2.57 Å | \\
| \text{Tb-N3\textsuperscript{macro}} | 2.66 Å | \\
| \text{Tb-N4\textsuperscript{macro}} | 2.56 Å | \\
| \text{Tb-O1\textsuperscript{macro}} | 2.36 Å | \\
| \text{Tb-O2\textsuperscript{macro}} | 2.35 Å | \\
| \text{Tb-O1\textsuperscript{DPA}} | 2.39 Å | \\
| \text{Tb-O2\textsuperscript{DPA}} | 2.40 Å | \\
| \text{Tb-N\textsuperscript{DPA}} | 2.49 Å | \\
| \text{[Eu(do2a)]}^+ complex} | \([\text{Ref. 3]}\) | \\
| \text{Eu-N1\textsuperscript{macro}} | 2.70 Å \textsuperscript{LC}; 2.71 Å \textsuperscript{SC} | \\
| \text{Eu-N2\textsuperscript{macro}} | 2.61 Å \textsuperscript{LC}; 2.62 Å \textsuperscript{SC} | \\
| \text{Eu-N3\textsuperscript{macro}} | 2.72 Å \textsuperscript{LC}; 2.73 Å \textsuperscript{SC} | \\
| \text{Eu-N4\textsuperscript{macro}} | 2.61 Å \textsuperscript{LC}; 2.62 Å \textsuperscript{SC} | \\
| \text{Eu-O1\textsuperscript{macro}} | 2.35 Å \textsuperscript{LC}; 2.34 Å \textsuperscript{SC} | \\
| \text{Eu-O2\textsuperscript{macro}} | 2.30 Å \textsuperscript{LC}; 2.29 Å \textsuperscript{SC} | \\
\end{array}
\]
\[
\begin{align*}
\text{Eu-O}_1^\text{water} & : 2.70 \, \text{Å}^{\text{LC}}; 2.63 \, \text{Å}^{\text{SC}} \\
\text{Eu-O}_2^\text{water} & : 2.63 \, \text{Å}^{\text{LC}}; 2.72 \, \text{Å}^{\text{SC}} \\
\text{Eu-O}_3^\text{water} & : 2.59 \, \text{Å}^{\text{LC}}; 2.59 \, \text{Å}^{\text{SC}}
\end{align*}
\]

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


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

\[ q_{H_2O-EuL} = 1.05 \times k_{H_2O} - 0.70 \]  \hspace{1cm} (S1)

and/or other form was obtained after rearrangement

\[ K_{H_2O-EuL} = \frac{q_{H_2O-EuL} + 0.70}{1.05} \]  \hspace{1cm} (S2)

The equilibrium constant for the following reaction at given pH

\[ [\text{Eu(H}_2\text{O)}_9]^{3+} + L \xrightarrow{K_{\text{trns}}} [\text{EuL(H}_2\text{O)}_3]^{2+} + 6 \text{H}_2\text{O} \]  \hspace{1cm} (Eq_A)

is defined as

\[ K_{\text{eff,EuL}} = \frac{[\text{EuL}]}{[\text{Eu}] \times [L]} \]  \hspace{1cm} (S3)

and the mass-balance equations are valid

\[ c_{Eu} = [\text{EuL}] + [\text{Eu}] \]  \hspace{1cm} (S4A)

\[ c_{L} = [\text{EuL}] + [L] \]  \hspace{1cm} (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]

\[ k_{H_2O-Eu-L} = k_{H_2O-EuL} \times \delta_{EuL} + k_{H_2O-Eu} \times (1 - \delta_{EuL}) \]  \hspace{1cm} (S5)

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

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

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

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

\[ q_{H_2O-Eu-L} + 0.70 \times \frac{1.05}{1.05} = q_{H_2O-EuL} + 0.70 \times \frac{1.05}{1.05} \times \delta_{EuL} + q_{H_2O-Eu} \times 0.70 \times (1 - \delta_{EuL}) \]  \hspace{1cm} (S7)

and the new Equation is obtained after arrangement:

\[ q_{H_2O-Eu-L} = q_{H_2O-EuL} \times \delta_{EuL} + q_{H_2O-Eu} \times (1 - \delta_{EuL}) \]  \hspace{1cm} (S8)

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

\[ \delta_{EuL} = \frac{q_{H_2O-Eu} - q_{H_2O-EuL}}{q_{H_2O-Eu} - q_{H_2O-EuL}} \]  \hspace{1cm} (S9)

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

\[ \delta_{EuL} = \frac{q_{H_2O-EuL} - q_{H_2O-EuL}}{6} \]  \hspace{1cm} (S10)

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

\[ \log \beta_{EuL} = \log K_{\text{eff,EuL}} - \log \alpha_{L(H)} \]  \hspace{1cm} (S11)

where the term is calculated as

\[ \alpha_{L(H)} = 1 + K_{p1} \times [H^+] + K_{p2} \times [H^+]^2 + ... \]  \hspace{1cm} (S12)
Analogously, the equilibrium constant for the following reaction at given pH

\[[\text{Tb}(\text{H}_2\text{O})_8]^{3+} + \text{L} \rightleftharpoons [\text{TbL}(\text{H}_2\text{O})_2]^{2+} + 6 \text{H}_2\text{O}\]  

(Eq_B)

is defined as

\[K_{\text{eff, TbL}} = \frac{[\text{TbL}]}{[\text{Tb}][\text{L}]}\]  

(S13)

as well as

\[q_{\text{H}_2\text{O,TbL-Tb}} = q_{\text{H}_2\text{O,TbL}} \times \delta_{\text{TbL}} + q_{\text{H}_2\text{O,Tb}} \times (1 - \delta_{\text{TbL}})\]  

(S14)

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

\[\delta_{\text{TbL}} = \frac{q_{\text{H}_2\text{O,Tb}} - q_{\text{H}_2\text{O,TbL-Tb}}}{q_{\text{H}_2\text{O,Tb}} - q_{\text{H}_2\text{O,TbL}}}\]  

(S15)

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

\[\delta_{\text{TbL}} = \frac{8 - q_{\text{H}_2\text{O,TbL-Tb}}}{6}\]  

(S16)

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

To get stability constant independent on pH:

\[\log \beta_{\text{EuL}} = \log K_{\text{eff,EuL}} - \log \alpha_{\text{L(H)}}\]  

(S17)

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 ($\lambda_{exc} = 394$ 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.

<table>
<thead>
<tr>
<th>pH</th>
<th>log $\beta_{EuL}$</th>
<th>Ratio $c_L / c_{Eu}$</th>
<th>1</th>
<th>1.75</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>12.65</td>
<td>12.52</td>
<td>12.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>11.78</td>
<td>12.11</td>
<td>12.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average value</td>
<td>12.4 ± 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Fig. S2:** The examples of luminescence-decay traces of the Eu(III)-H₂do2a system measured for the $c_L / c_{Eu} = 1$, pH = 5.6 (black) and $c_L / c_{Eu} = 2.5$, pH = 6.0 (red). ($\lambda_{exc} = 394$ nm, $\lambda_{em} = 618$ nm $c_{Eu} = 1$ mM, I = 0.1 M (KCl)).

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

<table>
<thead>
<tr>
<th>pH / q</th>
<th></th>
<th>Ratio $c_L / c_{Eu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(log $\beta_{EuL}^{a,b}$)</td>
<td>1</td>
<td>1.75</td>
</tr>
<tr>
<td>5.6</td>
<td>4.72 (13.24)</td>
<td>4.35 (12.85)</td>
</tr>
<tr>
<td>6.0</td>
<td>4.60 (12.51)</td>
<td>4.31 (12.06)</td>
</tr>
<tr>
<td>Average value</td>
<td>12.57 ± 0.46</td>
<td></td>
</tr>
</tbody>
</table>

a) calculated as $q = 1.02 \times 10^{-3} k_{obs} - 0.17$ [see T. Kimura and Y. Kato, *J. Alloys Comp.*, 1998, 278, 92-97]

b) assuming the equilibrium $[Eu(H_2O)_6]^{3+} + L \leftrightarrow [EuL(H_2O)_3]^{+} + 6$ H₂O
**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 ($\lambda_{exc} = 355$ 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.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\log \beta_{EuL}$</th>
<th>Ratio $c_L / c_{Eu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>5.6</td>
<td>12.79</td>
<td>12.88</td>
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<td>6.0</td>
<td>12.45</td>
<td>12.10</td>
</tr>
<tr>
<td></td>
<td><strong>Average value</strong></td>
<td>12.5 $\pm$ 0.3 3</td>
</tr>
</tbody>
</table>
Fig. S4: The examples of luminescence-decay traces of the Tb(III)-H$_2$do2a system measured for the $c_L / c_{\text{Tb}} = 1$, pH = 5.6 (black) and $c_L / c_{\text{Tb}} = 2.5$, pH = 6.0 (red). ($\lambda_{\text{exc}}$ = 355 nm, $\lambda_{\text{em}}$ = 545 nm, $c_{\text{Tb}}$ = 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.

<table>
<thead>
<tr>
<th>pH / $q$ $^a$</th>
<th>(log $\beta_{\text{kal.}}$)</th>
<th>Ratio $c_L / c_{\text{Eu}}$</th>
<th>1</th>
<th>1.75</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>3.86 (13.15)</td>
<td>3.24 (12.90)</td>
<td>3.07 (12.74)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>3.57 (12.53)</td>
<td>3.00 (12.23)</td>
<td>2.67 (12.19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg value</td>
<td>12.62 ± 0.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ calculated as $q = 4.00 \times 10^{-3} k_{\text{obs}} - 0.93$ (see T. Kimura and Y. Kato, J. Alloys Comp., 1998, 278, 92-97).

$^b$ assuming the equilibrium $[\text{Tb(H}_2\text{O)}_8]^{3+} + L \leftrightarrow [\text{TbL(H}_2\text{O)}_2]^{3+} + 6 \text{H}_2\text{O}$
**Fig. S5:** The distribution diagram of Eu(III)-H$_2$do2a system (equilibrium speciation diagram).
Fig. S6: The formation of Eu(III) and Tb(III) complexes with H$_2$do2a ligand and Gd(III) complexes with H$_3$do3a and H$_4$dota ligands (the experimental data were taken and recalculated from [Refs. 1 and 2].


The formation of \([\text{Eu(do2a)}]^+\) 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):

\[
\text{Eu} + H_y L \xleftarrow{K^*} [\text{Eu}(H_y L)]^* + (x - y)H^+ \\
[\text{Eu}(H_y L)]^* \xrightarrow{k^*} [\text{EuL}] + yH^+ 
\]  
(Eq. C)

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

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

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

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

knowing the equilibrium constant \(K^*\)

\[ K^* = \frac{[\text{EuL}]^*}{[\text{Eu}] \times [H_y L]} \]  
(S20)

In metal excess \((c_{\text{Eu}} \gg c_L)\), the previous equations can be modified as

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

and analogously in ligand excess \((c_{\text{Eu}} \ll c_L)\)

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

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

\[ k_{\text{obs}} = k \times K^* [\text{Eu}]_{\text{tot}} = k_{2,f} \times [\text{Eu}]_{\text{tot}} \]  
(c_{\text{Eu}} \gg c_L)  
(S23A)

\[ k_{\text{obs}} = k \times K^* [L]_{\text{tot}} = k_{2,f} \times [L]_{\text{tot}} \]  
(c_{\text{Eu}} \ll c_L)  
(S23B)

**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$_2$do2a 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

\[
\text{LnL}^+ + H^+ \Leftrightarrow \text{Ln}^{3+} + \text{HL}^-
\]  
(Eq_D)

the kinetic rate law ii defined as

\[
v = k_H \times [\text{LnL}] \times [H^+] = k_{HL} \times [\text{Ln}] \times [\text{HL}]
\]

which can be defined in enlarged form

\[
v = k_H \times \beta_{\text{LnL}} \times [\text{Ln}] \times [L] \times [H^+] = k_{HL} \times [\text{Ln}] \times K_{HL} \times [H^+] \times [L]
\]

(S25)

where equilibrium constants are defined as

\[
\beta_{\text{LnL}} = \frac{[\text{LnL}]}{[\text{Ln}] \times [L]} \quad \text{and} \quad K_{HL} = \frac{[\text{HL}]}{[H^+] \times [L]}
\]

(S26)

Then after simplification

\[
k_H \times \beta_{\text{LnL}} = k_{HL} \times K_{HL}
\]

(S27)

the final relationship is derived

\[
\beta_{\text{LnL}} = \frac{k_{HL}}{k_H} \times K_{HL}
\]

(S28A)

or in logarithmic form as

\[
\log \beta_{\text{LnL}} = \log \left( \frac{k_{HL}}{k_H} \right) + \log K_{HL}
\]

(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

\[
\text{Ln}^{3+} + \text{HL}^- \xrightarrow{k_{\text{form}}} \text{LnL} + H^+
\]

(Eq_E)

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

\[
\text{LnL}^+ + H^+ \xleftarrow{k_{\text{diss}}} \text{Ln}^{3+} + \text{HL}^-
\]

(Eq_F)

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

\[
k_{d,\text{obs}} = \frac{k_{\text{LnL}} \times K_{H,\text{LnL}} \times [H^+]}{1 + K_{H,\text{LnL}} \times [H^+]} = \frac{k_H \times [H^+]}{1 + K_{H,\text{LnL}} \times [H^+]}
\]

(S29)

where

\[
k_H = k_{\text{Ln(L)H}} \times K_{H,\text{LnL}}
\]

(S30)