How does the ligand affect the sensitivity of luminescent thermometers based on Tb-Eu complexes

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LIR and Sr simulation

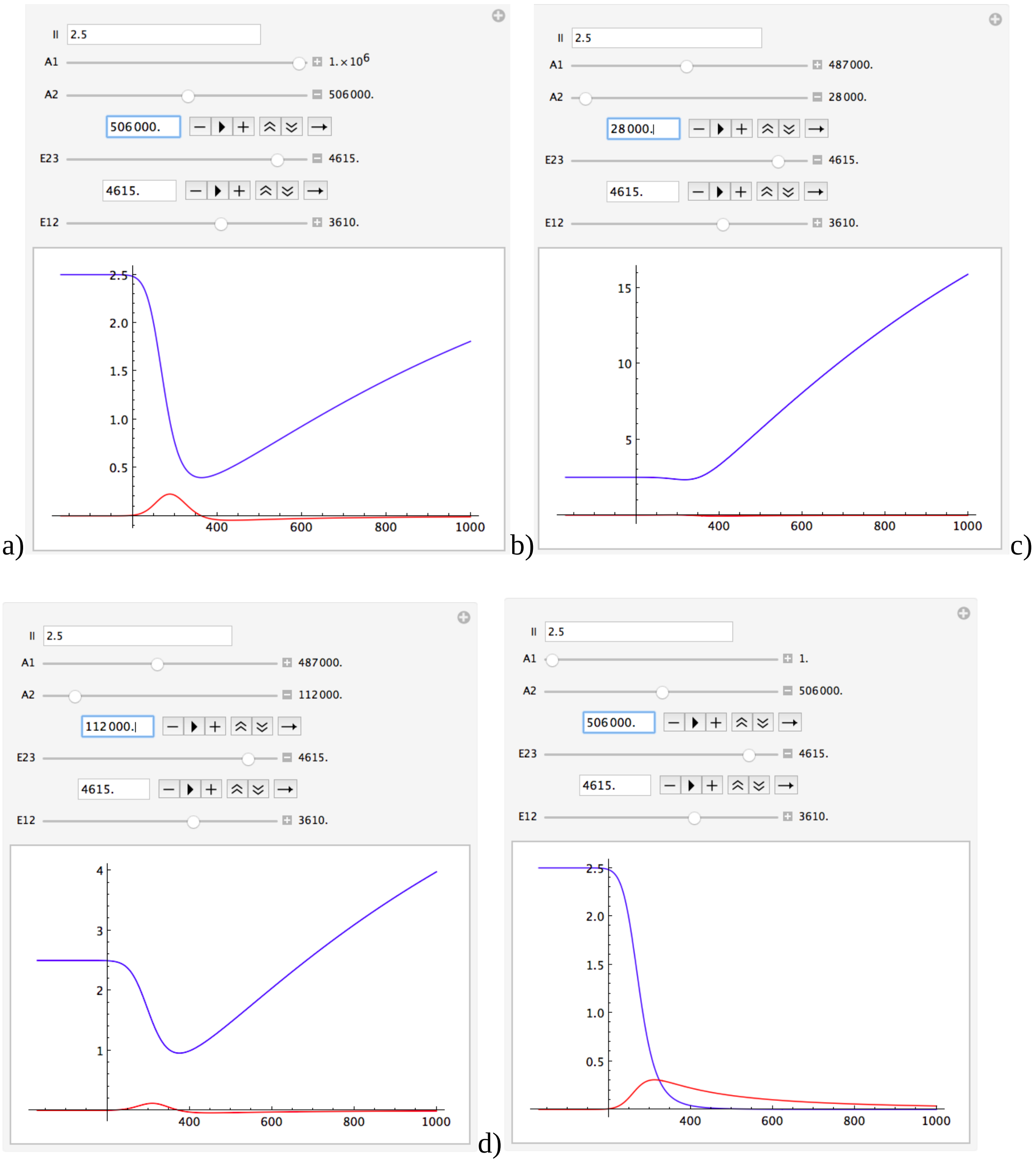

Fig. S1 The possible LIR and Sr dependencies on T. Illustrations are given for $E_{12} = 3601, E_{23} = 4615$: a) $A_1 = 10^6, A_2 = 506000$, b) $A_1 = 487000, A_2 = 28000$, c) $A_1 = 487000, A_2 = 112000$, d) $A_1 = 1, A_2 = 506000$.

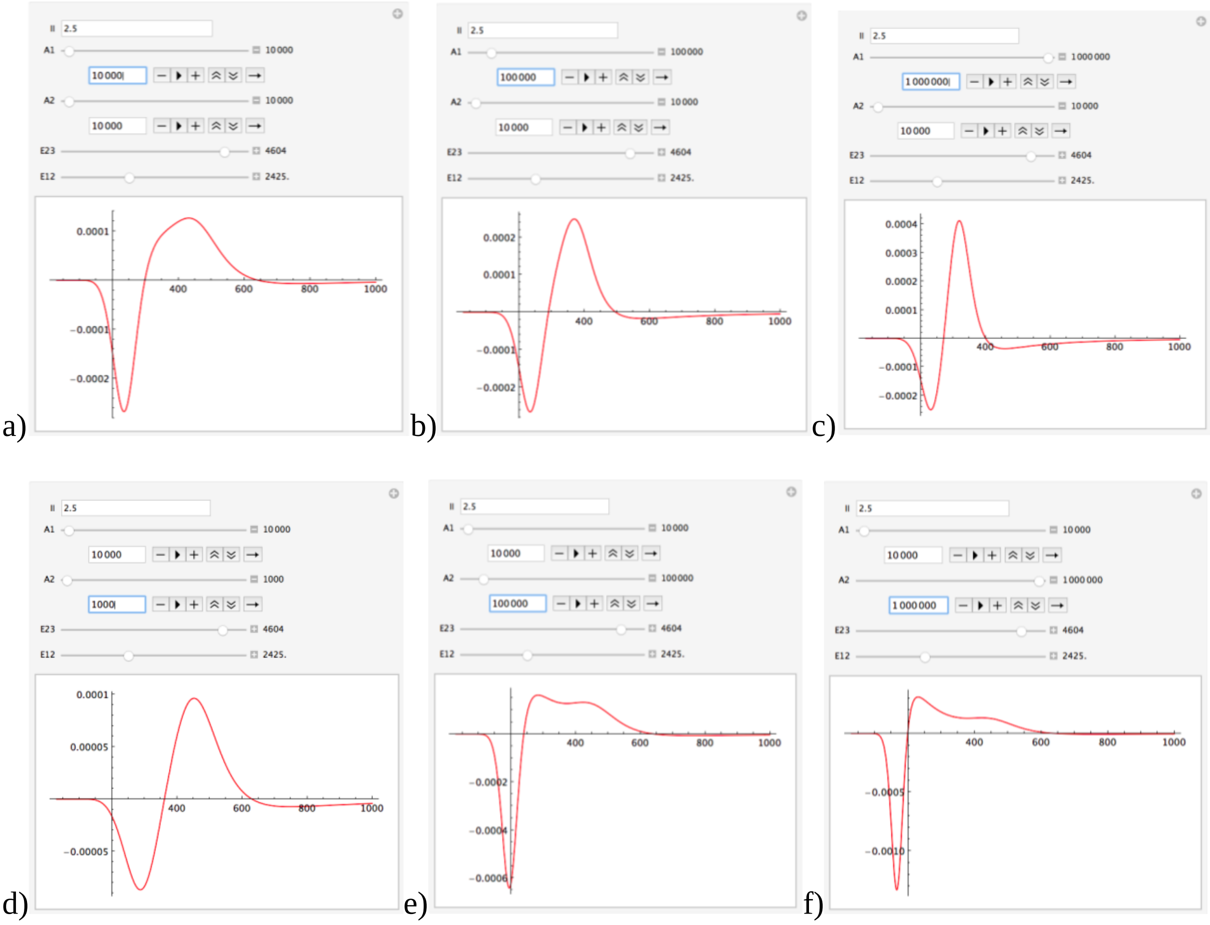

Fig. S2 T_{max} dependence on a-c) A1 value, a,d-f) A2 value

Fig. S3 T_{max} dependence on a-d) E23 value, d-h) E12 value

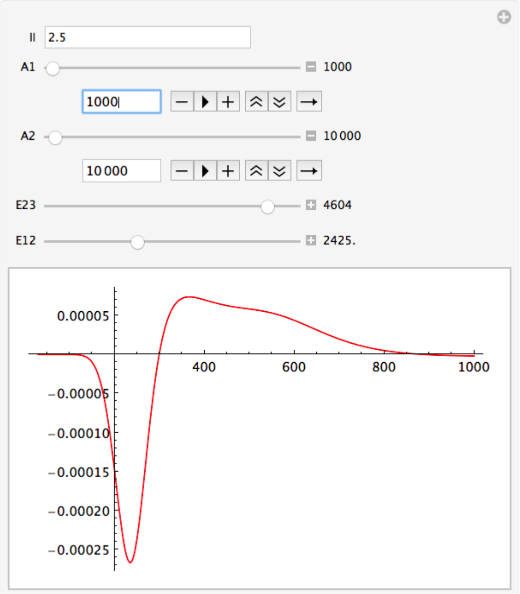

Fig. S1 Searching for the A2-E12 dependence to give T_{maz} = 312K at E_{23} fixed at 4604 K and a valuntarily selected A1=1000

Case study

Case (4,5)

$$\boldsymbol{S_{45}} = \frac{\boldsymbol{A_1(E_{23} - E_{12})}}{\left(\boldsymbol{A_1} + \mathbf{exp}\left(\boldsymbol{E_{12}}/\boldsymbol{T}\right)\right)\boldsymbol{T^2}} = \frac{\boldsymbol{A_1}}{\boldsymbol{A_1} + \mathbf{exp}\left(\boldsymbol{E_{12}}/\boldsymbol{T}\right)} \times \boldsymbol{S_{55}}$$

$$\mathbf{exp}\left(\boldsymbol{E_{12}}/\boldsymbol{T}\right) > \mathbf{0}$$

$$\boldsymbol{A_1} + \mathbf{exp}\left(\boldsymbol{E_{12}}/\boldsymbol{T}\right) > \boldsymbol{A_1}$$

$$\frac{\boldsymbol{A_1}}{\boldsymbol{A_1} + \mathbf{exp}\left(\boldsymbol{E_{12}}/\boldsymbol{T}\right)} < \mathbf{1}$$

$$\boldsymbol{S_{45}} < \boldsymbol{S_{55}}$$

Case (5,4)

$$\boldsymbol{S_{54}} = \frac{\boldsymbol{A_2(E_{23} - E_{12})}}{\left(\boldsymbol{A_2} + \mathbf{exp}\left(\boldsymbol{E_{23}}/\boldsymbol{T}\right)\right)\boldsymbol{T^2}} = \frac{\boldsymbol{A_2}}{\boldsymbol{A_2} + \mathbf{exp}\left(\boldsymbol{E_{23}}/\boldsymbol{T}\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (4,4)

$$\boldsymbol{S_{44}} = \frac{A_1\, A_2 (E_{23} - E_{12})}{\left(A_2 + \exp\left(E_{23}/T\right)\right)\left(A_1 + \exp\left(E_{12}/T\right)\right)T^2} = \frac{A_1\, A_2}{\left(A_2 + \exp\left(E_{23}/T\right)\right)\left(A_1 + \exp\left(E_{12}/T\right)\right)} \times \boldsymbol{S_{55}}$$

$$< \boldsymbol{S_{55}}$$

Case (3,5)

$$S_{34} = \frac{A_1(E_{23} - E_{12})}{\exp\left(E_{12}/T\right)T^2} = \frac{A_1}{\exp\left(E_{12}/T\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (5,3)

$$S_{43} = \frac{A_2(E_{23} - E_{12})}{\exp\left(E_{23}/T\right)T^2} = \frac{A_2}{\exp\left(E_{23}/T\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (3,4)

$$S_{34} = \frac{A_1\,A_2(E_{23}-E_{12})}{(A_2+\exp\left({}^{E_{23}}/_{T}\right))\exp\left({}^{E_{12}}/_{T}\right)T^2} = \frac{A_1\,A_2}{(A_2+\exp\left({}^{E_{23}}/_{T}\right))\exp\left({}^{E_{12}}/_{T}\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (4,3)

$$S_{43} = \frac{A_1\,A_2(E_{23}-E_{12})}{(A_1+\exp\left({}^{E_{12}}/_{T}\right))\exp\left({}^{E_{23}}/_{T}\right)T^2} = \frac{A_1\,A_2}{(A_1+\exp\left({}^{E_{12}}/_{T}\right))\exp\left({}^{E_{23}}/_{T}\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (5,2)

$$S_{25} = \frac{A_2E_{23} - E_{12}(\exp\left(-{}^{E_{23}}/_{T}\right) + A_2)}{\exp\left({}^{E_{23}}/_{T}\right)T^2}$$

$$\mathbf{1})\ \boldsymbol{E_{23} \geq E_{12}}$$

1a) $\frac{A_2E_{23} - E_{12}(\exp\left(-{}^{E_{23}}/_{T}\right) + A_2)}{\exp\left({}^{E_{23}}/_{T}\right)T^2} > 0$

$$\frac{A_2E_{23} - E_{12}(\exp\left(-{}^{E_{23}}/_{T}\right) + A_2)}{\exp\left({}^{E_{23}}/_{T}\right)T^2} > \frac{(E_{23}-E_{12})}{T^2}$$

$$A_2E_{23} - E_{12}(\exp\left(-{}^{E_{23}}/_{T}\right) + A_2) > E_{23}\exp\left({}^{E_{23}}/_{T}\right) - E_{12}\exp\left({}^{E_{23}}/_{T}\right)$$

$$A_2(E_{23}-E_{12}) > E_{23}\exp\left({}^{E_{23}}/_{T}\right)$$

$$(E_{23}-E_{12})/E_{23} > \exp\left({}^{E_{23}}/_{T}\right)/A_2$$

$$1 - E_{12}/E_{23} > \exp\left({}^{E_{23}}/_{T}\right)/A_2$$

Since A_1>>exp(E_{12}/T) and A_2~exp(-E_{23}/T)<<exp(E_{23})/T

$$\exp\left({E_{23}}/{T}\right)/A_2 \sim 0$$

Thus $S_{25} > S_{55}$ requires

$$\begin{cases} E_{12} \approx E_{23} \\ \exp\left(-{E_{23}}/{T}\right) \approx 0 \end{cases}$$

1b) $\frac{A_2E_{23}-E_{12}\left(\exp\left(-{E_{23}}/{T}\right)+A_2\right)}{\exp\left({E_{23}}/{T}\right)T^2} < 0$

$$\frac{E_{12}\left(\exp\left(-{E_{23}}/{T}\right)+A_2\right)-A_2E_{23}}{\exp\left({E_{23}}/{T}\right)T^2} > \frac{(E_{23}-E_{12})}{T^2}$$

$$E_{12}\left(\exp\left(-{E_{23}}/{T}\right)+A_2\right)-A_2E_{23} > \left(E_{23}\exp\left({E_{23}}/{T}\right)-E_{12}\exp\left({E_{23}}/{T}\right)\right)$$

$$E_{12}\exp\left(-{E_{23}}/{T}\right) > \left(E_{23}-E_{12}\right)\left(\exp\left({E_{23}}/{T}\right)-A_2\right) \approx (E_{23}-E_{12})\exp\left({E_{23}}/{T}\right)$$

$$\exp\left(-{2E_{23}}/{T}\right) > \frac{E_{23}}{E_{12}} - 1$$

Thus $S_{25} > S_{55}$ requires $E_{12} \approx E_{23}$

$$\boldsymbol{E_{23} \leq E_{12}}$$

2a) $\frac{A_2E_{23}-E_{12}\left(\exp\left(-{E_{23}}/{T}\right)+A_2\right)}{\exp\left({E_{23}}/{T}\right)T^2} < 0$

$$A_2E_{23}-E_{12}\left(\exp\left(-{E_{23}}/{T}\right)+A_2\right) > (E_{23}-E_{12})\exp\left({E_{23}}/{T}\right)$$

$$A_2(E_{23}-E_{12})-E_{12}\exp\left(-{E_{23}}/{T}\right) > (E_{12}-E_{23})\exp\left({E_{23}}/{T}\right)$$

$$(E_{23}-E_{12})\left(A_2+\exp\left({E_{23}}/{T}\right)\right) > E_{12}\exp\left(-{E_{23}}/{T}\right)$$

$$(E_{23} - E_{12}) \exp\left({E_{23}}/{T}\right) > E_{12} \exp\left(-{E_{23}}/{T}\right)$$

$$\frac{E_{23}}{E_{12}} - 1 > \exp\left(-{2E_{23}}/{T}\right)$$

Thus $S_{25} > S_{55}$ requires

$$\begin{cases} E_{12} \approx E_{23} \\ \exp\left(-{E_{23}}/{T}\right) \approx 0 \end{cases}$$

2b) $\frac{A_2E_{23} - E_{12}(\exp\left(-{E_{23}}/{T}\right) + A_2)}{\exp\left({E_{23}}/{T}\right)T^2} < 0$

$$E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right) - A_2E_{23} > (E_{23} - E_{12}) \exp\left({E_{23}}/{T}\right)$$

$$A_2(E_{12} - E_{23}) > -E_{23} \exp\left(-{E_{23}}/{T}\right)$$

$$A_2(E_{23} - E_{12}) < \exp\left(-{E_{23}}/{T}\right)$$

$$1 - \frac{E_{12}}{E_{23}} < \exp\left(-{E_{23}}/{T}\right)/A_2$$

Thus $S_{25} > S_{55}$ requires $E_{12} \approx E_{23}$

$$\boldsymbol{E_{23} \leq E_{12}}$$

Thus $S_{25} > S_{55}$ only if $E_{12} = E_{23}$. Let's consider this case.

In this case $S_{55} = 0$ and

$$\max(S_{25}) = \max\left(\frac{E_{23}\left(\exp\left(-{E_{12}}/_{T}\right) + A_1\right) - A_1 E_{12}}{\exp\left({E_{12}}/_{T}\right) T^2}\right) = \max\left(\frac{E_{12}\left(\exp\left(-{E_{12}}/_{T}\right) + A_1\right) - A_1 E_{12}}{\exp\left({E_{12}}/_{T}\right) T^2}\right)$$

$$= \max\left(\frac{E_{12}\exp\left(-{E_{12}}/_{T}\right)}{\exp\left({E_{12}}/_{T}\right) T^2}\right) = \max\left(\frac{E_{12}\exp\left(-{2E_{12}}/_{T}\right)}{T^2}\right)$$

$$\exp\left(-{2E_{12}}/_{T}\right) < 1 \Rightarrow$$

$$\max(S_{25}) < \frac{E_{12}}{T^2} = S_{55}(at\ E_{23} = 0)$$

So looking for the highest S_r we should not consider this either.

Case (2,5)

Similarily,

$$\max(S_{25}) < \max(S_{55})$$

unless $E_{12} = E_{23}$, which does not lead to the high sensitivity.

Case (3,3)

$$S_{33} = \frac{A_1\, A_2(E_{23} - E_{12})}{\exp\left({(E_{12} + E_{23})}/_{T}\right) T^2} = \frac{A_1\, A_2}{\exp\left({(E_{12} + E_{23})}/_{T}\right)} \times \boldsymbol{S_{55}} < \boldsymbol{S_{55}}$$

Case (2,4)

$$S_{24} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/_{T}\right) + A_1\right) - A_1 A_2 E_{12}}{\left(A_2 + \exp\left({E_{23}}/_{T}\right)\right)\exp\left({E_{12}}/_{T}\right) T^2}$$

Let’s consider if it is possible that $S_{24} > S_{55}$.

1) Both are positive. For that

$$\begin{cases} E_{12} < E_{23} \\ E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right)) > A_1 E_{12} \end{cases}$$

$$\begin{cases} E_{23} > E_{12} \\ E_{23} > \dfrac{A_1}{(\exp\left(-{E_{12}}/{T}\right) + A_1))} E_{12} \end{cases}$$

Thus the latter is authomatically true if the former is, and the only condition is $E_{23} > E_{12}$.

$$S_{24} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 A_2 E_{12}}{(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) T^2} > \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

$$A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) \boldsymbol{E_{23}} + (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) \boldsymbol{E_{12}}$$

$$> A_1 A_2 \boldsymbol{E_{12}} + (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) \boldsymbol{E_{23}}$$

$$\boldsymbol{E_{23}}(A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right))$$

$$> \boldsymbol{E_{12}}(A_1 A_2 - (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right))$$

As $A_2 \sim \left(A_2 + \exp\left({E_{23}}/{T}\right)\right)$ and $\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) \ll \exp\left({E_{12}}/{T}\right)$,

$$A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) \approx -(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right)$$

And as $(A_2 + \exp\left({E_{23}}/{T}\right)) \sim A_2$ and $\exp\left({E_{12}}/{T}\right) \gg A_1$

$$A_1 A_2 - \left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right) \approx -\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right)$$

From that

$$\boldsymbol{E_{23}}(A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right))$$

$$> \boldsymbol{E_{12}}(A_1 A_2 - (A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right))$$

is equal to

$$\boldsymbol{E_{23}}(-(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right)) > \boldsymbol{E_{12}}(-(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right))$$

$$\boldsymbol{E_{23}}(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) < \boldsymbol{E_{12}}(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right)$$

Meaning that $\boldsymbol{S_{24}} > \boldsymbol{S_{55}} \Leftrightarrow \boldsymbol{E_{12}} > \boldsymbol{E_{23}}$**, which contradicts the condition.**

2) **Both are negtive: For that $\boldsymbol{E_{23}} < \boldsymbol{E_{12}} \frac{A_1}{(\exp\left(-{E_{12}}/{T}\right)+A_1))}$ (and authomatically <$\boldsymbol{E_{12}}$)**

$$S_{24} = \frac{A_1 A_2 E_{12} - A_2 E_{23}\,(\exp\left(-{E_{12}}/{T}\right) + A_1)}{(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right) T^2} > \frac{(E_{12} - E_{23})}{T^2} = S_{55}$$

$$A_1 A_2 \boldsymbol{E_{12}} + \boldsymbol{E_{23}}\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right)$$
$$> A_2 \boldsymbol{E_{23}}\,(\exp\left(-{E_{12}}/{T}\right) + A_1) + \boldsymbol{E_{12}}(A_2 + \exp\left({E_{23}}/{T}\right)) \exp\left({E_{12}}/{T}\right)$$

$$\boldsymbol{E_{12}}\left(A_1 A_2 - \left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right)\right)$$
$$> \boldsymbol{E_{23}}(A_2\,(\exp\left(-{E_{12}}/{T}\right) + A_1) - \left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right))$$

Again, this is equal to

$$\boldsymbol{E_{12}}\left(-\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right)\right) > \boldsymbol{E_{23}}(-\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right))$$

$$\boldsymbol{E_{12}}\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right) < \boldsymbol{E_{23}}\left(A_2 + \exp\left({E_{23}}/{T}\right)\right) \exp\left({E_{12}}/{T}\right)$$

$$\boldsymbol{E_{12}} < \boldsymbol{E_{23}}$$

which contradicts to the conditions.

3) $\boldsymbol{S_{55}} < \boldsymbol{0} < \boldsymbol{S_{24}}$**. For that**

$$\boldsymbol{E_{12}} > \boldsymbol{E_{23}} > \boldsymbol{E_{12}} \frac{A_1}{\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right)}$$

The conditions of $\boldsymbol{S_{24}} < \boldsymbol{S_{55}}$ **is**

$$S_{24} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 A_2 E_{12}}{\left(A_2 + \exp\left({E_{23}}/{T}\right)\right)\exp\left({E_{12}}/{T}\right) T^2} > \frac{(E_{12} - E_{23})}{T^2} = S_{55}$$

$$\boldsymbol{E_{23}}\left(A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) + \left(A_2 + \exp\left({E_{23}}/{T}\right)\right)\exp\left({E_{12}}/{T}\right)\right)$$
$$> \left(\left(A_2 + \exp\left({E_{23}}/{T}\right)\right)\exp\left({E_{12}}/{T}\right) + A_1 A_2\right)\boldsymbol{E_{12}}$$

Similarily equal to

$$\boldsymbol{E_{23}}\left(A_2 + \exp\left({E_{23}}/{T}\right)\right)\exp\left({E_{12}}/{T}\right) > \left(A_2 + \exp\left({E_{23}}/{T}\right)\right)\exp\left({E_{12}}/{T}\right)\boldsymbol{E_{12}}$$

$$\boldsymbol{E_{23}} > \boldsymbol{E_{12}}$$

which contradicts to the conditions.

Case (4,2)

Similarily, always

$$S_{42} = \frac{A_1 A_2 E_{23} - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\exp\left({E_{23}}/{T}\right)\left(A_1 + \exp\left({E_{12}}/{T}\right)\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (1,5)

$$S_{15} - S_{55} = \frac{E_{23}\exp\left(-{E_{12}}/{T}\right) - A_1 E_{12}}{\exp\left({E_{12}}/{T}\right) T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\exp\left({E_{12}}/{T}\right) T^2}\left(\boldsymbol{E_{23}}\left(\exp\left(-{E_{12}}/{T}\right) - \exp\left({E_{12}}/{T}\right)\right) - \boldsymbol{E_{12}}\left(A_1 - \exp\left({E_{12}}/{T}\right)\right)\right)$$

$$\approx \frac{1}{\exp\left({E_{12}}/{T}\right) T^2}\left(-\boldsymbol{E_{23}}\left(\exp\left({E_{12}}/{T}\right)\right) + \boldsymbol{E_{12}}\left(\exp\left({E_{12}}/{T}\right)\right)\right) = \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55}$$

$$< 0$$

Thus again it is always that

$$S_{15} = \frac{E_{23}\exp\left(-{E_{12}}/{T}\right) - A_1 E_{12}}{\exp\left({E_{12}}/{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (5,1)

Similarily,

$$S_{51} = \frac{A_2 E_{23} - E_{12}\exp\left(-{E_{23}}/{T}\right)}{\exp\left({E_{23}}/{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (1,4)

$$S_{14} - S_{55} = \frac{A_2 E_{23} \exp\left(-{}^{E_{12}}/_{T}\right) - A_1 A_2 E_{12}}{\left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right) T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right) T^2} \left(\boldsymbol{E_{23}}(A_2 \exp\left(-{}^{E_{12}}/_{T}\right)\right.$$

$$\left. - \left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right)) - \boldsymbol{E_{12}}(A_1 A_2 - \left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right))\right)$$

$$\approx \frac{1}{\left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right) T^2} \left(-\boldsymbol{E_{23}} \left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right)\right.$$

$$\left. + \boldsymbol{E_{12}} \left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right)\right) = \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55} < 0$$

Thus again it is always that

$$S_{14} = \frac{A_2 E_{23} \exp\left(-{}^{E_{12}}/_{T}\right) - A_1 A_2 E_{12}}{\left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (4,1)

Similarily,

$$S_{41} = \frac{A_2 E_{23} \exp\left(-{}^{E_{12}}/_{T}\right) - A_1 A_2 E_{12}}{\left(A_2 + \exp\left({}^{E_{23}}/_{T}\right)\right) \exp\left({}^{E_{12}}/_{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case(2,3)

$$S_{23} = \frac{A_2 E_{23} \left(\exp\left(-{}^{E_{12}}/_{T}\right) + A_1\right) - A_1 A_2 E_{12}}{\exp\left({}^{E_{12} + E_{23}}/_{T}\right) T^2}$$

$$S_{23} - S_{55} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 A_2 E_{12}}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2}\left(\boldsymbol{E_{23}}\left(A_2 \exp\left(-{E_{12}}/{T}\right) + A_1 A_2 - \exp\left({E_{12} + E_{23}}/{T}\right)\right)\right.$$

$$\left. - \boldsymbol{E_{12}}\left(A_1 A_2 - \exp\left({E_{12} + E_{23}}/{T}\right)\right)\right)$$

$$\approx \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2}\left(\boldsymbol{E_{23}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right) - \boldsymbol{E_{12}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right)\right)$$

$$= \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55} < 0$$

Thus always

$$S_{23} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 A_2 E_{12}}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (3,2)

Similarily,

$$S_{32} = \frac{A_1 A_2 E_{23} - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (1,3)

$$S_{13} = \frac{A_2 E_{23}\, exp\left(-{E_{12}}/{T}\right) - A_1 A_2 E_{12}}{\left(exp\left({E_{23} + E_{12}}/{T}\right)\right) T^2}$$

$$S_{13} - S_{55} = \frac{A_2 E_{23}\, exp\left(-{}^{E_{12}}/_{T}\right) - A_1 A_2 E_{12}}{\left(exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right) T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\left(exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right) T^2}\left(\boldsymbol{E_{23}}\left(A_2\, exp\left(-{}^{E_{12}}/_{T}\right) - exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right)\right.$$

$$\left. - \boldsymbol{E_{12}}\left(A_1 A_2 - exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right)\right)$$

$$\approx \frac{1}{\left(exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right) T^2}\left(\boldsymbol{E_{23}}\left(-\, exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right) - \boldsymbol{E_{12}}\left(-\, exp\left({}^{E_{23}+E_{12}}/_{T}\right)\right)\right)$$

$$= \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55} < 0$$

Thus

$$S_{13} = \frac{A_2 E_{23}\, exp\left(-{}^{E_{12}}/_{T}\right) - A_1 A_2 E_{12}}{(exp\left({}^{E_{23}+E_{12}}/_{T}\right))T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (3,1)

Similarily,

$$S_{31} = \frac{A_1 A_2 E_{23} - A_1 E_{12} \exp\left(-{}^{E_{23}}/_{T}\right)}{\exp\left({}^{E_{12}+E_{23}}/_{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (2,2)

$$S_{22} = \frac{A_2 E_{23}\,(\exp\left(-{}^{E_{12}}/_{T}\right) + A_1) - A_1 E_{12}(\exp\left(-{}^{E_{23}}/_{T}\right) + A_2)}{\exp\left({}^{E_{12}+E_{23}}/_{T}\right) T^2}$$

$$S_{22} - S_{55} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2}\Bigg(\boldsymbol{E_{23}}\left(A_2\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - \exp\left({E_{12} + E_{23}}/{T}\right)\right)$$

$$- \boldsymbol{E_{12}}\left(A_1\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right) - \exp\left({E_{12} + E_{23}}/{T}\right)\right)\Bigg)$$

$$\approx \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2}\left(\boldsymbol{E_{23}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right) - \boldsymbol{E_{12}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right)\right)$$

$$= \frac{\boldsymbol{E_{12}} - \boldsymbol{E_{23}}}{T^2} = -S_{55} < 0$$

Thus it is always that

$$S_{22} = \frac{A_2 E_{23}\left(\exp\left(-{E_{12}}/{T}\right) + A_1\right) - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\exp\left({E_{12} + E_{23}}/{T}\right) T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (1,2)

$$S_{12} = \frac{A_2 E_{23}\exp\left(-{E_{12}}/{T}\right) - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\left(\exp\left({E_{23} + E_{12}}/{T}\right)\right) T^2}$$

$$S_{12} - S_{55} = \frac{A_2 E_{23} \exp\left(-{E_{12}}/{T}\right) - A_1 E_{12}\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right)}{\left(\exp\left({E_{23} + E_{12}}/{T}\right)\right)T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right)T^2}\left(\boldsymbol{E_{23}}\left(A_2 \exp\left(-{E_{12}}/{T}\right) - \exp\left({E_{12} + E_{23}}/{T}\right)\right)\right.$$

$$\left. - \boldsymbol{E_{12}}\left(A_1\left(\exp\left(-{E_{23}}/{T}\right) + A_2\right) - \exp\left({E_{12} + E_{23}}/{T}\right)\right)\right)$$

$$\approx \frac{1}{\exp\left({E_{12} + E_{23}}/{T}\right)T^2}\left(\boldsymbol{E_{23}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right) - \boldsymbol{E_{12}}\left(-\exp\left({E_{12} + E_{23}}/{T}\right)\right)\right)$$

$$= \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55} < 0$$

Thus it is always that

$$S_{12} = \frac{A_2 E_{23} \exp\left(-{E_{12}}/{T}\right) - A_1 E_{12}(\exp\left(-{E_{23}}/{T}\right) + A_2)}{(\exp\left({E_{23} + E_{12}}/{T}\right))T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Case (2,1)

Similarily,

$$\mathrm{S}_{21} = \frac{\mathrm{A}_2\mathrm{E}_{23}\,(\exp\left(-{\mathrm{E}_{12}}/{\mathrm{T}}\right) + \mathrm{A}_1) - \mathrm{A}_1\mathrm{E}_{12}\exp\left(-{\mathrm{E}_{23}}/{\mathrm{T}}\right)}{\exp\left({\mathrm{E}_{12} + \mathrm{E}_{23}}/{\mathrm{T}}\right)\mathrm{T}^2} < \frac{(\mathrm{E}_{23} - \mathrm{E}_{12})}{\mathrm{T}^2} = \mathrm{S}_{55}$$

Case (1,1)

$$\mathrm{S}_{11} = \frac{A_2 E_{23} \exp\left(-{E_{12}}/{T}\right) - A_1 E_{12} \exp\left(-{E_{23}}/{T}\right)}{(\exp\left({E_{23} + E_{12}}/{T}\right))T^2}$$

$$S_{11} - S_{55} = \frac{A_2 E_{23} \exp\left(-{}^{E_{12}}/_{T}\right) - A_1 E_{12} \exp\left(-{}^{E_{23}}/_{T}\right)}{(\exp\left({}^{E_{23} + E_{12}}/_{T}\right))T^2} - \frac{(E_{23} - E_{12})}{T^2}$$

$$= \frac{1}{\exp\left({}^{E_{12} + E_{23}}/_{T}\right)T^2}\left(\boldsymbol{E_{23}}\left(A_2 \exp\left(-{}^{E_{12}}/_{T}\right) - \exp\left({}^{E_{12} + E_{23}}/_{T}\right)\right)\right.$$

$$\left. - \boldsymbol{E_{12}}\left(A_1 \exp\left(-{}^{E_{23}}/_{T}\right) - \exp\left({}^{E_{12} + E_{23}}/_{T}\right)\right)\right)$$

$$\approx \frac{1}{\exp\left({}^{E_{12} + E_{23}}/_{T}\right)T^2}\left(\boldsymbol{E_{23}}\left(-\exp\left({}^{E_{12} + E_{23}}/_{T}\right)\right) - \boldsymbol{E_{12}}\left(-\exp\left({}^{E_{12} + E_{23}}/_{T}\right)\right)\right)$$

$$= \frac{\boldsymbol{E_{12} - E_{23}}}{T^2} = -S_{55} < 0$$

Thus again always

$$\mathrm{S}_{11} = \frac{A_2 E_{23} \exp\left(-{}^{E_{12}}/_{T}\right) - A_1 E_{12} \exp\left(-{}^{E_{23}}/_{T}\right)}{(\exp\left({}^{E_{23} + E_{12}}/_{T}\right))T^2} < \frac{(E_{23} - E_{12})}{T^2} = S_{55}$$

Detailed study of literature $Eu_xTb_{1-x}L$ systems

Table S1 Relative thermometer sensitivity of some $Eu_xTb_{1-x}L$ systems and triplet state energy of L ligands.

№	link	$Eu_xTb_{1-x}L$	$E(T_1)$, cm^{-1}	T, K	**S_r, %K^{-1}**			$Exp(E_{23}/T)$	A_2	$Exp(E_{12}/T)$	A_1	**Case**
					exp	$\frac{E_{12}}{T^2}$	$\frac{E_{23}-E_{12}}{T^2}$					
1	[28]	pdms-eddpo(1%)-[$Tb_{0,90}Eu_{0,10}(bzac)_3$](0,25%)	23058	203	**11,05**	**11,17232**	**1,89315**	1,52E8	8,85E8	7,07E9	4,13E10	**5,5**
2	[28]	pdms-eddpo(1%)-[$Tb_{0,95}Eu_{0,05}(bzac)_3$](0,25%)		188	**9,22**	**13,02626**	**2,2073**	6,81E8	2,84E9	4,32E10	1,80E11	**5,5**
3	[28]	pdms-eddpo(1%)-[$Tb_{0,99}Eu_{0,01}(bzac)_3$](0,25%)		203	**7,87**	**11,17232**	**1,89315**	1,52E8	6,30E8	7,07E9	2,94E10	**4,5**
4	[28]	pdms-eddpo(1%)-[$Tb_{0,995}Eu_{0,005}(bzac)_3$](0,25%)		203	**7,72**	**11,17232**	**1,89315**	1,52E8	6,18E8	7,07E9	2,88E10	**4,5**
5	[29]	$Eu_{0,088}Tb_{0,2287}$(phen)(btc)(dmf)·dmf	22075 (phen)	393	**2,37**	**2,98092**	**1,42085** **(0,37284)**	2,82E4	1,80E5	1,22E5	7,78E5	**3,4**

6	29	$Eu_{0,174}Tb_{0,2188}$(phen)(btc)(dmf)·dmf	23200 (btc)		**2,71**	**2,98092**	**1,42085** **(0,37284)**	2,82E4	2,05E5	1,22E5	8,89E5	**3,4**
7	30	$[Eu_{0,53}Tb_{0,47}(tfac)_8]_2^-Na_2^+$	22800	353	**2,70**	**3,69476**	**0,92398**	1,77E4	5,17E4	4,62E5	1,35E6	**4,5**
8	30	$[Eu_{0,41}Tb_{0,59}(tfac)_8]_2^-Na_2^+$	22800	315	**1,33**	**4,63996**	**1,16035**	5,76E4	6,59E4	2,22E6	2,55E6	**4,4**
9	31	$Tb_{0.9}Eu_{0.1}$PIA	25866	300	**3,53**	5,12	**3,62**	7,95E2	2,65E4	2.46E11	8,2E12	**5,5**
10	32	$Eu_{0.0069}Tb_{0.9931}$-DMBDC	23306	200	**1,15**	11,51	**1,06**	9,95E5	8,5E7	2.04E6	9&65E9	**5,5**
11	19	d-U(600)-$Eu_{0,25}Tb_{0,75}(btfa)_3$(bpeta)	21793	300	**3,0**	**5,11556**	**2,88915**	7,95E2	8,26E2	4,62E6	4,80E6	**4,4**
12	33	$Eu_{0,25}Tb_{0,75}(btfa)_3$(4,4’-bpy)(EtOH)	22212	225	**4,00**	**9,09432**	**3,94543**	1,07E5	1,09E5	7,70E8	7,81E8	**4,4**
13	27	$[(CH_3)_2NH_2]Eu_{0,036}Tb_{0,964}$bptc	29070	310	**9,42**	**4,79084**	**8,1893**	2,99E1 7	3,44E17	2,82E6	3,24E6	**4,4**
14	18	$[Eu_{0,37}Tb_{0,63}(btc)H_2O](H_2O)$(DMF)	23200 (26504)[1]	313	**0,68**	**4,69945**	**0,58778** **(4,26457)**	1,53E1 2	2,44E11	2,44E6	3,90E5	**3,3**
15	34	$[Tb_2(bpydc)_3(H_2O)_3](dmf)_2$@3%Eu(tfac)$_3$·$2H_2O$	21505 (bpydc)	225	**2,59**	**9,09432**	**5,95478** **(2,27429)**	4,62E6	5,25E6	7,70E8	8,77E8	**4,4**

16	[34]	$[Tb_2(bpydc)_3(H_2O)_3](dmf)_2@7,3\%Eu(tfac)_3\cdot 2H_2O$	22800 (tfac)	325	**1,33**	**4,35882**	**2,85406** **(1,09004)**	4,10E4	5,01E4	1,42E6	1,73E6	**4,4**
17	[35]	$Tb_{0,995}Eu_{0,005}@Al(OH)(bpydc)$	21505	333	**3,00**	**4,1519**	**2,71858**	1,18E2	1,30E2	1,01E6	1,11E6	**4,4**
18	[23]	$Eu_{0,01}Tb_{0,99}(btc)$	23200 (26504)[1]	300	**0,42**	**5,11556**	**0,63982** **(4,64217)**	5,17E12	4,67E11	4,62E6	4,18E5	**3,3**
19	[36]	$[Tb_{0,98}Eu_{0,02}(oa)_{0,5}(dstp)]\cdot 3H_2O$[1]	24570	275	**2,4**	**6,08793**	**1,84505**	8,55E-4	2,37E-4	1,86E7	5,17E6	**4,4**
21	[37]	$Tb_{0,99}Eu_{0,01}(bdc)_{1,5}\cdot(H_2O)_2$	26211	318	**0,31**	**4,55283**	**3,71463**	2,62E21	2,18E10	1,94E6	1,62E5	**3,3**
22	[38]	$[Tb_{0,99}Eu_{0,01}(hfa)_3(dpbp)]_2$	22000 (hfa)	200	**0,52**	**11,51**	**5,756**	9,95E5	8,99E4	9,94E9	8,98E8	**3,3**
23	[39]	$Tb_{0,95}Eu_{0,05}HY$	26600	4	**31**	**28775**	**26975,5**	∞	∞	∞	∞	**--**
24	[40]	cycEu-phTb	20501	298	**0,85**	**5,18445**	**5,02135**	1,62	2,75E-1	5,12E6	8,68E5	**4,3**
25	[41]	cycTb-phEu		200	**1,86**	**11,51**	**11,1479**	2,06	3,44E-1	9,94E9	1,66E9	**4,3**

[1] Two triplets of two metals were listed – 24570 (oa)19050 (dstp). The latter is involved (otherwise Sr = **8,657)**

26		$Tb_{0,95}Eu_{0,05}$(btb)	23426	14	**2,85**	**2348,97959**	**127,89347**	∞	∞	6,62	1,48	**4,3**
27	42	$Tb_{0,95}Eu_{0,05}$(pdc)	23809	333	**1,37**	**4,1519**	**0,27089**	2,49E6	1,26E7	1,01E6	5,11E6	**3,4**
28	43	$Eu_{0,088}Tb_{0,912}(ad)_{0,5}(phth)(H_2O)_2$	20833 (phth)	303	**0,42**	**5,01476**	**4,3367**	7,80	7,56E-1	3,97176E6	3,85E5	**3,3**
29	44	$Ln(ad)_{0,5}(phth)(H_2O)_2$; Ln = 3$Eu^{III}$:10$Tb^{III}$		303	**0,59**	**5,01476**	**4,3367**	7,80	1,06	3,97E6	5,40E5	**3,3**
30	44	$Eu_{0,01}Tb_{0,99}$(bdc-F_4)	27465	50	**0,75**	**184,16**	**222,42568**	1,95E88	6,56E85	9,77E39	3,29E37	**3,3**
31	45	$Eu_{0,5}Tb_{0,5}(L)_1$@PMMA	22420	77	**0,46**	**77,65222**	**28,64065**	2,45E16	3,94E14	9,278E25	1,49E24	**3,3**
32	46	$Tb_{0,005}Eu_{0,995}$@UiO-67-bpydc	21505	180	**3,01**	**14,20988**	**9,30434**	6,84E3	2,21E3	1,28E11	4,15E10	**4,4**
33	24	$\{[Tb_{0,9064}Eu_{0,0936}(dcptp)(NO_3)]\cdot(H_2O)\}_2$	25445 (25217)[1]	300	**21,5**	**5,11556**	**2,94918 (2,58469)**	1,08E10	8,96E10	4,62E6	3,84E7	**3,5**
34[&]	26	$Tb_{0,897}Eu_{0,103}$(tcptpy)	22321	340	**8,41**	**3,9827**	**1,59217**	3,39E3	1,79E4	7,60E5	4,01E6	**5,5**

[&] Re-plotted LIR with re-calculated Sr, which only reached 5.55%/K and is similar to the value (5.12%/K), predicted by the theory.