

SUPPORTING INFORMATION

Title: Tetrahedral Assembly with Lanthanides: Toward Discrete Polynuclear Complexes

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1. Synthesis and characterisation of L

Solvents and starting materials. These were purchased from Acros Organics, Fluka AG and Aldrich and used without further purification unless otherwise stated. N,N-dimethylformamide (DMF), acetonitrile and dichloromethane were distilled over CaH₂. 1,1,1-(Trisaminomethyl)ethane (TAME) was purchased from Fluka AG or synthesised according to published procedures.¹ The perchlorate salts were prepared from the corresponding oxides (Rhodia and Aldrich, 99.99 %) and dried according to published procedures. Ln(III) content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange. 6-(N,N-diethylcarbamoyl)pyridine-2-carboxylic acid was prepared according to published procedures.² *Caution! Perchlorate salts are potentially explosive and should be handled carefully in small quantities.*³

Preparation of 1,1,1-tris[carbamoyl-6-(N,N-diethylcarbamoylpyridine-2)methyl]ethane (L). 2,6-Pyridinedicarboxylic-N,N-diethylamide (1.521 g, 6.82 mmol) was refluxed with thionylchloride (5.25 ml, 0.0171 mol) and DMF (40 µl) in 50 ml CH₂Cl₂ for 1 hour. Excess of thionylchloride was evaporated and the dried solid residue was dissolved in dichloromethane (30 ml) at 0°C. 1,1,1-(Trisaminomethyl)ethane (TAME) was dissolved in dichloromethane (30 ml) containing triethylamine (0.3 ml). This solution is added dropwise (during 20 minutes) under an inert N₂ atmosphere to the solution of acylchloride. The resulting solution was stirred for 24 hours at room temperature and evaporated. The yellow-brown residue was partitioned between dichloromethane and half-saturated aq. NaHCO₃. The organic phase was further washed with half-saturated aq. NaHCO₃ (2 × 25 ml) and water (25 ml), dried (Na₂SO₄) and evaporated to dryness. The resulting crude compound was purified by column chromatography (silica gel, CH₂Cl₂-MeOH 98:2) and recrystallised from acetonitrile to afford L as white-beige solid (75-80 % yields).

¹ (a) R. J. Geue, G. H Searle, *Aust. J. Chem.* **1983**, *36*, 927. (b) K. N. Brown, C. R. Hockless, A. M. Sargeson, *Dalton Trans.* **1999**, 2171.

² C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681.

³ K. N. Raymond, *Chem. Eng. News* **1983**, *61*, 4.

2. Isolation and characterisation of the lanthanide complexes

Preparation and isolation of the complexes $[\text{Ln}_4\text{L}_4](\text{ClO}_4)_{12}\cdot x\text{H}_2\text{O}$. A solution of $\text{Ln}(\text{ClO}_4)_3\cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Gd}$; 0.041 mmol) in propionitrile (400 μl) was added to a solution of **L** (0.041 mmol) in propionitrile (400 μl) under stirring. The complex precipitates at room temperature. The resulting white microcrystalline powders are collected by filtration, washed with butyronitrile and dried under vacuum for 5 hours to give 92-95% of $\text{Ln}_4\text{L}_4(\text{ClO}_4)_{12}\cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, x = 5.2$; $\text{Tb}, x = 8.8$; $\text{Gd}, x = 7.6$; $\text{Lu}, x = 11.6$; Table S1).

Table S1. Elemental Analyses for $\text{Ln}_4\text{L}_4(\text{ClO}_4)_{12}\cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, x = 5.2$; $\text{Tb}, x = 8.8$; $\text{Gd}, x = 7.6$; $\text{Lu}, x = 11.6$).

Calculated Values are Given between Parentheses.

Compd	%C	%N	%H
Eu	37.94 (37.92)	10.48 (10.47)	4.60 (4.49)
Gd	37.46 (37.44)	10.31 (10.34)	4.57 (4.53)
Tb	37.24 (37.22)	10.25 (10.28)	4.63 (4.55)
Lu	36.37 (36.36)	9.98 (10.04)	4.54 (4.56)

Table S2. ^1H NMR Shifts for **L** and Its $\text{Ln}(\text{III})$ Complexes in CD_3CN at 298 K.

	H1	H2	H2'	H3	H4	H5	H6
L	0.94	3.30	3.23	9.01	8.17	8.06	7.67
$[\text{Eu}_4(\text{L})_4]^{12+}$	12.93	5.13	3.26	3.82	4.62	5.92	5.13
$[\text{Lu}_4(\text{L})_4]^{12+}$	0.41	3.30	2.87	8.31	8.12	8.73	8.36
	H7	H7'	H8	H9	H9'	H10	
L	3.70		1.27	3.58		1.18	
$[\text{Eu}_4(\text{L})_4]^{12+}$	5.58	4.37	2.75	3.45	2.87	1.22	
$[\text{Lu}_4(\text{L})_4]^{12+}$	3.21	3.05	0.76	3.95	3.80	1.48	

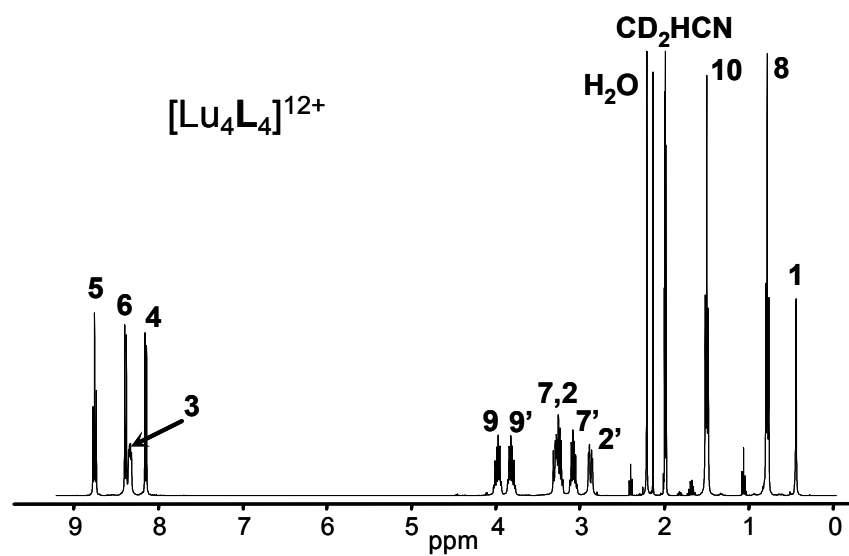


Figure S1. ^1H NMR spectrum of the tetrahedral complex $[\text{Lu}_4\text{L}_4]^{12+}$ in CD_3CN (298 K).

Diffusion NMR measurements (DOSY). Assuming that (i) Einstein-Smoluchowski-Stokes auto-diffusion theory holds and (ii) the molecules in solution can be roughly modelled by spheres, the auto-diffusion coefficient D_m is proportional to $(\bar{v}_m MM_m)^{-1/3}$, whereby \bar{v}_m stands for the specific volume and MM_m for the molecular mass of the molecule. The molecular mass of an unknown compound can be deduced with eq S1, when a reference compound, e.g., $[\text{Ru}(\text{bipy})_3]^{2+}$, is measured under the same conditions.

$$\frac{D_x}{D_r} = \sqrt[3]{\frac{\bar{v}_r \cdot MM_r}{\bar{v}_x \cdot MM_x}} \quad (\text{S1})$$

The measurements at 296 K give $D([\text{Ru}(\text{bipy})_3]^{2+}) = 13.5(2) \times 10^{-10} \text{ m}^2\text{s}^{-1}$, $D(\mathbf{L}) = 12.2(1) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ and $D([\text{Eu}_4\mathbf{L}_4]^{12+}) = 5.5(2) \times 10^{-10} \text{ m}^2\text{s}^{-1}$. The first value is similar to $D([\text{Ru}(\text{bipy})_3]^{2+}) = 13.6(4) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ determined previously by Canard and Piguet.⁴ If a spherical shape can be reasonably considered in solution for the reference compound $[\text{Ru}(\text{bipy})_3]^{2+}$, \mathbf{L} and the tetrametallic complex $[\text{Eu}_4(\mathbf{L})_4]^{12+}$, a quantitative estimation of $MM_{\text{Eu}_4\mathbf{L}_4}$ is obtained by application of eq S1 with the approximation $\bar{v}_{\text{Ru}(\text{bipy})_3} \sim \bar{v}_{\mathbf{L}} \sim \bar{v}_{\text{Eu}_4\mathbf{L}_4}$, which gives $MM_{\mathbf{L}} \approx 827(3) \text{ gmol}^{-1}$ and $MM_{\text{Eu}_4\mathbf{L}_4} \approx 5500(100) \text{ gmol}^{-1}$, which is about 1.13 and 1.56 times higher than the expected values 729 gmol^{-1} and 3525 gmol^{-1} , respectively. We can not expect much more precise values for \mathbf{L} and the complex taking into account the difference in specific volumes $\bar{v}_{\mathbf{L}} < \bar{v}_{\text{Eu}_4\mathbf{L}_4}$ neglected in the calculation. When the difference of 13 % is already observed for \mathbf{L} , we can reasonably attribute $MM_m = 5500 \text{ gmol}^{-1}$ to $[\text{Eu}_4\mathbf{L}_4]^{12+}$. We notice, that the MM_m determination for the large complex $[\text{RuLu}(\mathbf{L})_3]^{5+}$ ($D([\text{RuLu}(\mathbf{L})_3]^{4+}) = 8.0(1) \times 10^{-10} \text{ m}^2\text{s}^{-1}$, $MM_{\text{RuLnL}_3}^{\text{calc}} = 1907 \text{ gmol}^{-1}$) gives $MM_{\text{RuLnL}_3} = 2798 \text{ gmol}^{-1}$, which is about 47 % more than the calculated value.⁴

⁴ G. Canard, C. Piguet, *Inorg. Chem.* **2007**, *46*, 3511.

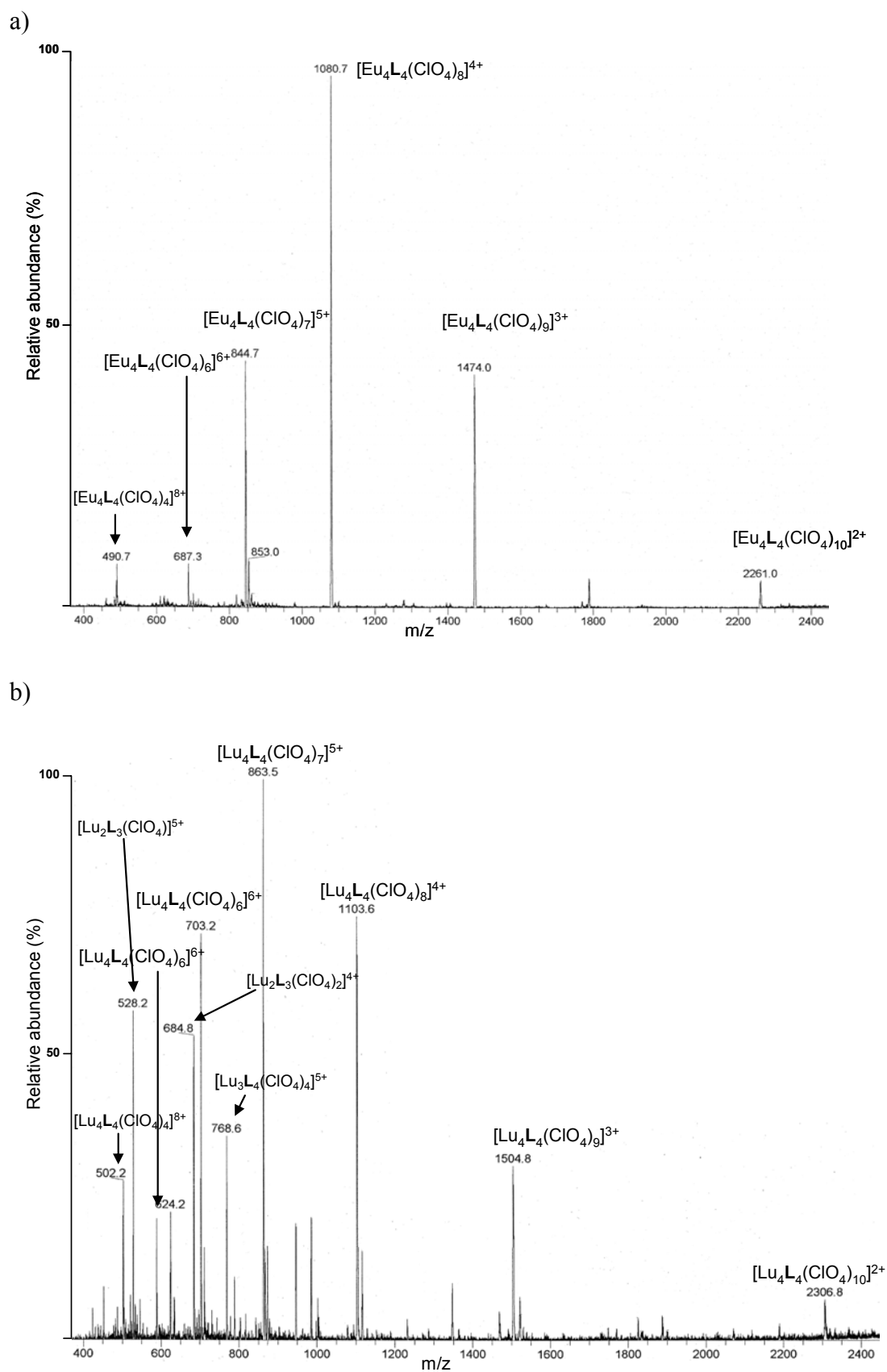
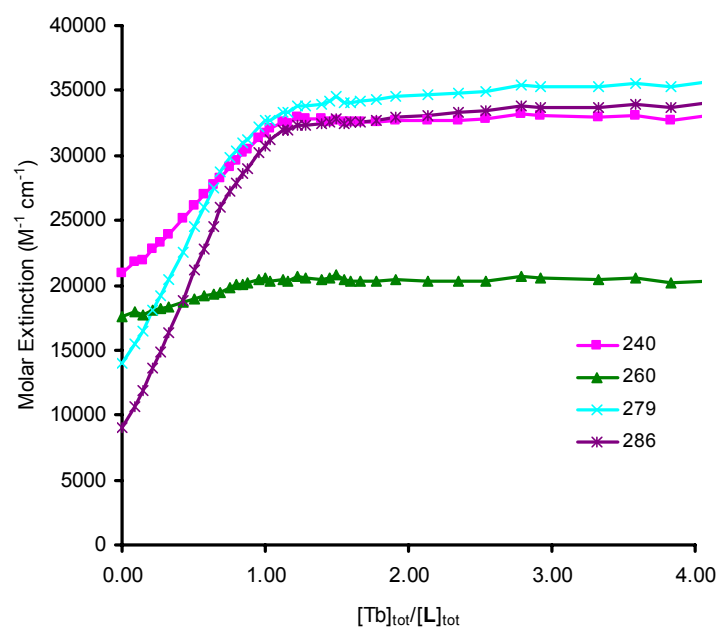


Figure S2. ESI-MS spectra of a) $[\text{Eu}_4\text{L}_4]^{12+}$ and b) $[\text{Lu}_4\text{L}_4]^{12+}$ (ionisation temperature 150 °C, $[\text{Ln}]_{\text{tot}}/[\text{L}]_{\text{tot}} = 1$, CH_3CN).

a)



b)

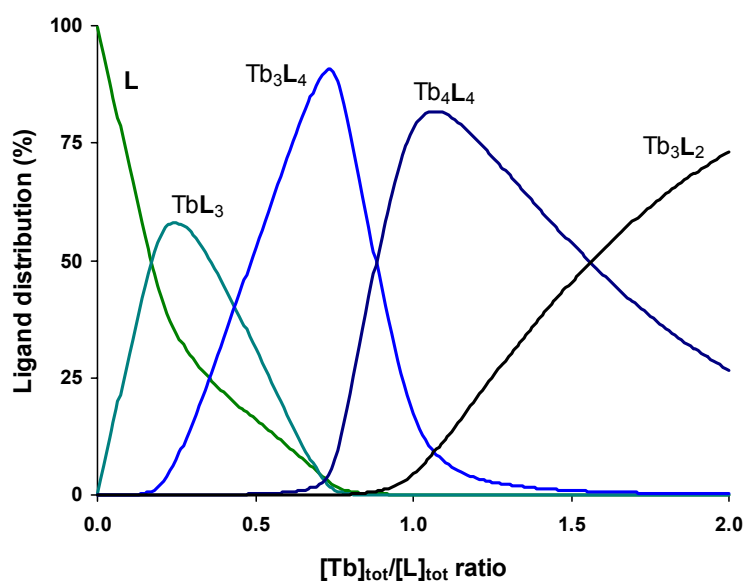


Figure S3. a) Variation of the observed molar extinctions at four different wavelengths during the spectrophotometric batch titration of **L** ($[\mathbf{L}]_{\text{tot}} = 3 \times 10^{-4}$ M) with $\text{Tb}(\text{ClO}_4)_3$ ($[\text{Tb}]_{\text{tot}}/[\mathbf{L}]_{\text{tot}} = 0-5$, 298 K, CH_3CN). b) Distribution curves calculated with the fitted stability constants (see text) for $[\mathbf{L}]_{\text{tot}} = 1 \times 10^{-3}$ M.

3. Crystallographic data

X-ray data for $[\text{Tb}_4(\text{C}_{38}\text{H}_{51}\text{N}_9\text{O}_6)_4] \cdot 11(\text{ClO}_4) \cdot (\text{B}(\text{C}_6\text{H}_5)_4) \cdot 3(\text{CH}_3\text{CN}) \cdot 5(\text{CH}_3\text{OH}) \cdot 2(\text{H}_2\text{O})$ were deposited to the Cambridge Crystallographic Data Centre in cif format (CCDC-679893). Many attempts have been undertaken to obtain crystals of sufficient quality for X-ray diffraction. From these trials it appears that adequate crystals could be obtained only by slow diffusion of *t*-butylmethylether into a solution of $[\text{Tb}_4\text{L}_4](\text{ClO}_4)_{12}$ in methanol/acetonitrile with addition of 1 eq of tetrabutyl-ammonium tetraphenylborate. In addition to the crystal structure reported therein (α -form: space group $P2_1/c$, $a = 27.0222(12)$, $b = 22.4891(20)$, $c = 42.3331(20)$ Å, $\beta = 102.388(5)^\circ$, $V = 25127(2)\text{Å}^3$, $Z = 4$, the number of independent formulae units per asymmetric unit $Z' = 1$), two other unit cells have been identified for this complex:

β -form: Monoclinic, $P2_1/n$, $a = 42.5163(15)$, $b = 22.3862(7)$, $c = 53.9704(18)$ Å, $\beta = 102.530(4)^\circ$, $V = 50144(3)\text{Å}^3$, $Z = 8$ (the number of independent formulae units per asymmetric unit $Z' = 2$), $\lambda = 0.71073$ Å, $T = 150$ K, 172619 reflections collected, 52570 independent ($R_{int} = 0.139$) and 17299 (i.e. about 33%) observed reflections ($F_o > 4\sigma(F_o)$). The molecular structure of the two independent $[\text{Tb}_4(\text{L})_4]$ complexes in the asymmetric unit is similar to those one reported here but the poor data to parameter ratio does not allow to obtain better result.

γ -form: Monoclinic, $P2_1/c$, $a = 61.1572(3)$, $b = 22.2743(2)$, $c = 74.4548(4)$ Å, $\beta = 104.5150(10)^\circ$, $V = 98187.6(11)\text{Å}^3$, $Z = 16$ (the number of independent formulae units per asymmetric unit $Z' = 4$), $\lambda = 0.80000$ Å (synchrotron radiation), $T = 100$ K, 173512 reflections collected, 94459 independent ($R_{int} = 0.077$) and 79597 (i.e. about 84%) observed reflections ($F_o > 4\sigma(F_o)$).

The unit cell of the α -form can be transformed into the unit cell of the β -form by the transformation matrix

$\begin{pmatrix} 001 \\ 010 \\ 200 \end{pmatrix}$, while the unit cell of the β -form can be transformed into the unit cell of the γ -form by the transformation

matrix $\begin{pmatrix} 101 \\ 010 \\ 10\bar{1} \end{pmatrix}$. The γ -form suggests the most complex structure with $Z' = 4$. Refinement of this structure using the

synchrotron diffraction data was complicated by an overlap of reflections. Reconstruction of the reciprocal space revealed for the γ -form a substructure with $c_{\text{substructure}} = 74.4548(4)/4 = 18.6137(1)$ Å and $Z' = 1$. Identification of the three related unit cells and the existence of a substructure for one of them suggest various ordering schemes for the $[\text{Tb}_4\text{L}_4]^{12+}$ complexes, involving weak interactions. This order, however, does not largely affect the individual complexes.

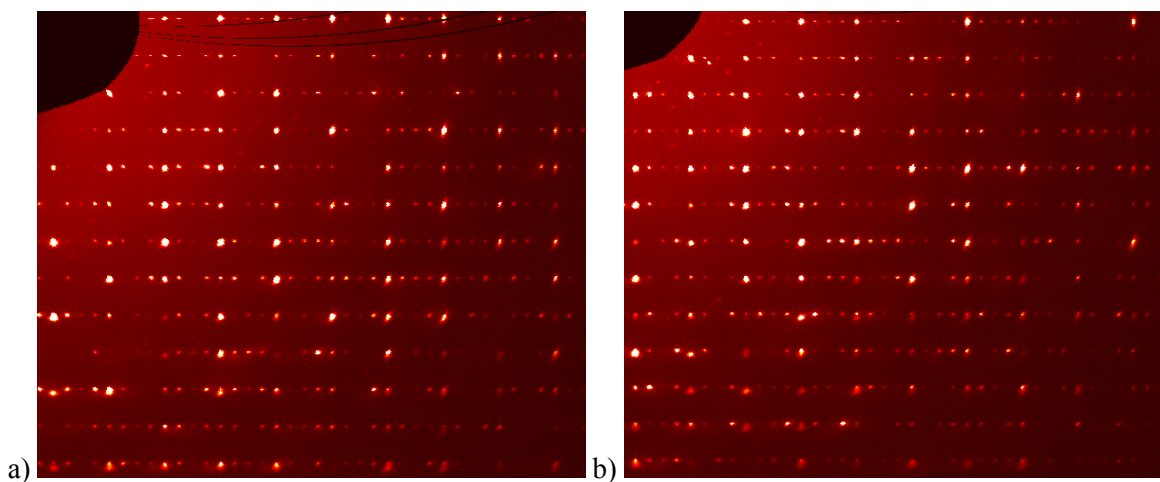


Figure S4. Reciprocal space sections a) $hk0$ and b) $hk1$, which illustrate a four times smaller substructure in the γ -form.

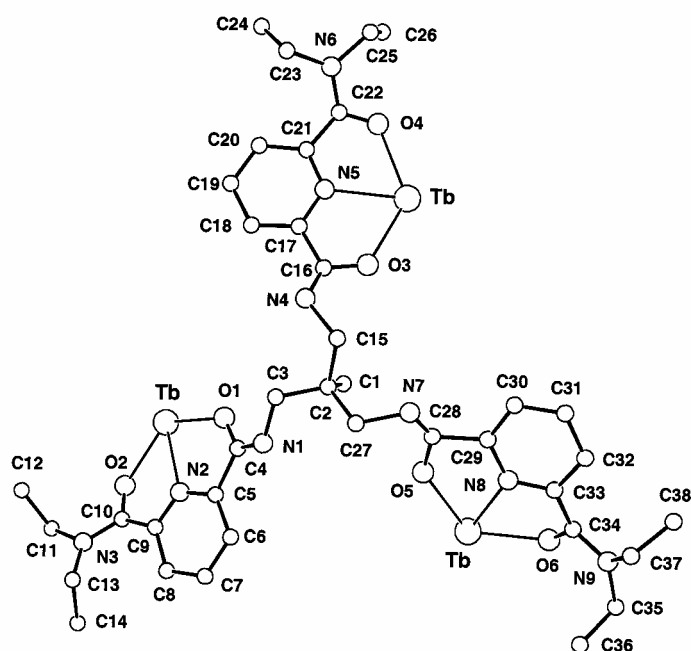


Figure S5. Atom numbering scheme for the ligands *a*, *b*, *c* and *d* of the $[\text{Tb}_4(\text{C}_{38}\text{H}_{51}\text{N}_9\text{O}_6)_4]$ cation.

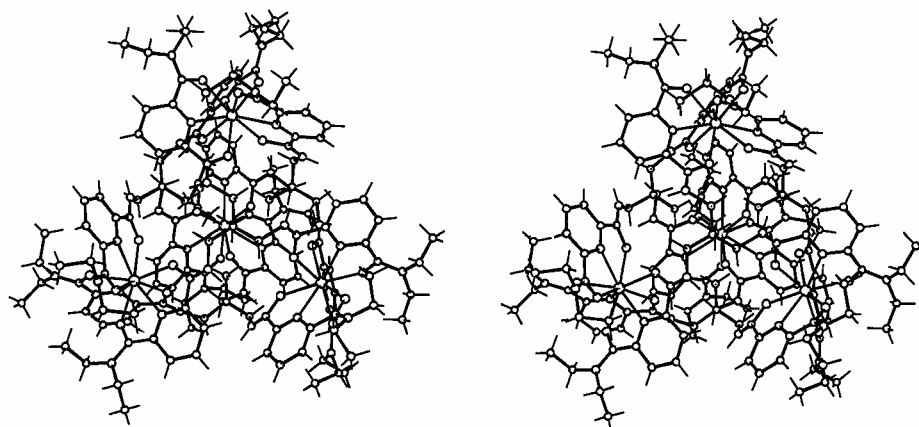


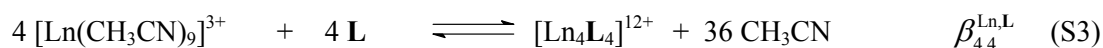
Figure S6. Stereo view of the crystal structure of the $[\text{Tb}_4(\text{C}_{38}\text{H}_{51}\text{N}_9\text{O}_6)_4]$ cation.

4. Thermodynamic extended site-binding model for $[\text{Ln}_4\text{L}_4]^{12+}$

The macroscopic stability constants of the supramolecular assembly $[\text{Ln}_4\text{L}_4]^{12+}$ can be modelled with four microscopic parameters according to the following general equation:⁵

$$\beta_{m,n}^{\text{M,L}} = (\omega_{m,n}^{\text{M,L}} \omega_{m,n}^{\text{chir}}) \cdot \prod_{i=1}^{\text{tot}} (f_i^{\text{M,L}}) \cdot \prod_{i=1}^{\text{intra}} (c_i^{\text{eff}}) \cdot \prod_{i<j} (u_{ij}^{\text{MM}}) \cdot \prod_{k<l} (u_{kl}^{\text{LL}}) \quad (\text{S2})$$

Where m , n correspond to the stoichiometric coefficients in the molecule, tot is the total number of connections between the ligands and metal ions ($\text{tot} = n \cdot p$, whereby p is the number of available binding sites of L) and intra describe the number of intramolecular connections ($\text{intra} = n \cdot p - m - n + 1$) within the assembly. The lanthanide ions are considered as trivalent and the principle of maximum occupancy holds for the saturated complexes $[\text{Ln}_4\text{L}_4]^{12+}$. In order to correctly calculate the symmetry numbers,⁶ the solvent molecules must be considered for the complexation equilibrium:



The stability constant of $[\text{Ln}_4(\text{L})_4]^{12+}$ is then predicted as:

$$\beta_{4,4}^{\text{Ln,L}} = (\omega_{4,4}^{\text{Ln,L}} \cdot \omega_{4,4}^{\text{chir}}) \cdot (f^{\text{Ln,L}})^{12} \cdot (u^{\text{LL}})^{12} \cdot (u^{\text{LnLn}})^6 \cdot (c^{\text{eff}})^5 \quad (\text{S4})$$

whereby $\omega^{\text{Ln,L}}$ is the symmetry number of an assembly, ω^{chir} is the chirality factor, $f^{\text{Ln,L}}$ is the binding affinity related to the connection between one coordination site and one metal ion, u^{LL} and u^{LnLn} hold for interligand and intermetallic interactions, c^{eff} is the effective concentration. It has been recently shown, that the intramolecular reactions in monometallic tripodal complexes are energetically disfavoured.^{6b} The self-assembly of $[\text{Ln}_4\text{L}_4]^{12+}$ consists of 5 intramolecular and 7 intermolecular reactions (the ratio $\text{intra}/\text{tot} = 0.42$). Comparing to the monometallic tripods with 2 intramolecular and 1 intermolecular reactions ($\text{intra}/\text{tot} = 0.67$), the tetrametallic complexes exhibit a lower intra/tot ratio and their formation is thermodynamically favored over the monometallic ones.

⁵ a) J. Hamacek, M. Borkovec, C. Piguet, *Chem. Eur. J.* **2005**, *11*, 5217. b) J. Hamacek, M. Borkovec, C. Piguet, *Chem. Eur. J.* **2005**, *11*, 5227.

⁶ a) G. Ercolani, C. Piguet, M. Borkovec, J. Hamacek, *J. Phys. Chem. B* **2007**, *111*(42), 12195. b) G. Canard, S. Koeller, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2007**, *130* (3), 1025.

5. Phosphorescence spectra

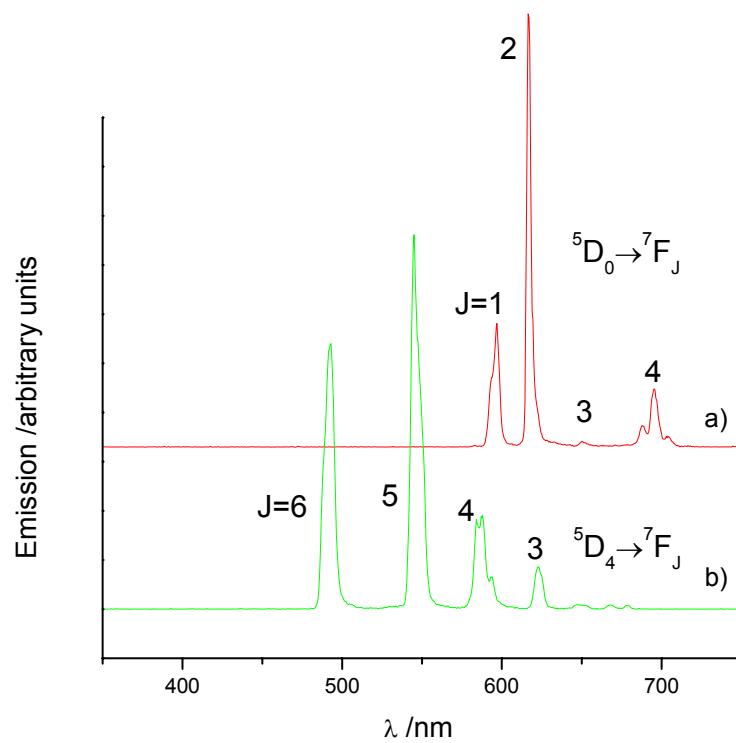


Figure S7. Time-resolved phosphorescence spectra of a) $\text{Eu}_4\text{L}_4(\text{ClO}_4)_{12}$ and b) $\text{Tb}_4\text{L}_4(\text{ClO}_4)_{12}$ in solid state at 77 K (delay 50 μs , $\lambda_{\text{exc}} = 279$ nm).