Building large supramolecular nanocapsules with europium cations

Josef Hamacek,*[a] Daniele Poggiali,[a] Soumaila Zebret,[a] Badr El Aroussi,[a] Markus W. Schneider[b] and Michael Mastalerz[b]

[a] *Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E. Ansermet, 1211 Geneva 4, Switzerland. Fax: +41-22-379-6830; Tel+41-22-379-6413; E-mail: Josef.Hamacek@unige.ch*
[b] *Ulm University, Institute of Organic Chemistry II and Advanced Materials, Albert-Einstein-Allee 11, D-89081 Ulm, Germany. Tel: +49-731-50-22855*

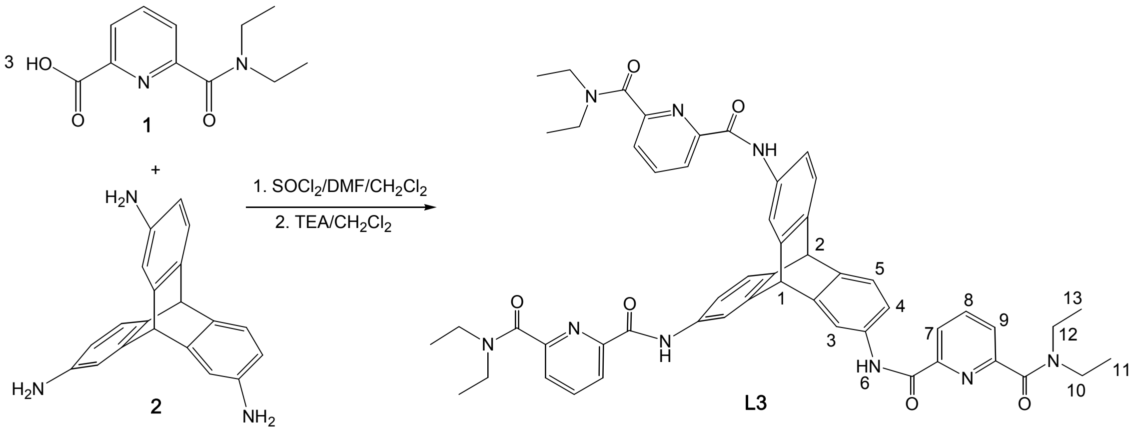
Electronic Supplementary Information

Experimental :

Solvents and starting materials.

Chemicals were purchased from Acros Organics, Fluka AG and Aldrich and used without further purification unless otherwise stated. Acetonitrile and dichloromethane were distilled over CaH_2. The europium perchlorate salt was prepared from the corresponding oxide (Rhodia and Aldrich, 99.99%) and dried according to published procedures. Eu(III) content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.

Scheme of the L3 synthesis (**L3** = $N^2,N^{2'},N^{2''}$-(9,10-dihydro-9,10-[1,2]benzenoanthracene-2,7,14-triyl)tris(N^6, N^6-diethylpyridine-2,6-dicarboxamide).



Synthesis of L3: 2-carboxy-6-diethylcarboxamidepyridine[1] (59.4 mg, 0.27 mmol) was activated with $SOCl_2$ (10 eq) in CH_2Cl_2 at reflux for 1.5 hours. The excess of $SOCl_2$ was evaporated and the residue was dried under vacuum. After dissolving in CH_2Cl_2, the mixture of triamine **2**[2] and triethylamine (20 mg, 0.07 mmol) was added dropwise to this solution. The reaction was stopped after 16 hours of mixing at r.t. The organic solvent was evaporated. The solid residue was purified by column chromatography (SiO_2, $MeOH/CH_2Cl_2$, 0.5-1.5% (v/v)). Finally, the isolated **L3** was dried under vacuum (77 % yield).

L3: ^1H NMR (CD_3CN) : δ= 1.24 (s, 6H, CH_3), 3.29 (s, 2H, CH_2), 3.54 (s, 2H, CH_2), 5.50 (s, 1H, CH), 5.58 (s, 1H, CH), 7.37 (q, 2H, CH), 7.67 (d, 1H, CH), 7.94 (s, 1H, CH), 8.03 (t, 1H, CH), 8.24 (d, 1H, CH), 9.79 (s, 1H, NH) ppm. ESI-MS (CH_3CN/CH_2Cl_2): *m*/*z* 912.8 ([**L3**+H^+]$^+$).

---

[1] N. Dalla-Favera, L. Guenée, G. Bernardinelli and C. Piguet, *Dalton Trans.*, 2009, 7625.
[2] C. Zhang and C.-F. Chen, J. Org. Chem., 2006, **71**, 6626.

Characterisation of the Eu(III) complexes with L3:

$[\mathbf{Eu_4L3_4}](\mathbf{ClO_4})_{12}$: ^{1}H NMR (CD_3CN) : δ= 1.03 (t, 3H, CH_3), 3.04 (m, 1H, CH_2), 3.38 (m, 1H, CH_2), 4.07 (s, 3H, CH_3), 4.16 (d, 1H, CH), 4.43 (s, 1H, CH), 5.30 (m, 1H, CH_2), 5.42 (s, 1H, NH), 5.42 (m, 1H, CH_2), 5.64 (d, 1H, CH), 5.83 (t, 1H, CH), 6.03 (s, 1H, CH), 7.34 (d, 1H, CH), 12.89 (s, 1H, CH), 13.77 (s, 1H, CH) ppm. ESMS (CD_3CN):): *m*/*z* 808.8 ($[\mathrm{Eu_4}\mathbf{L3}_4(\mathrm{ClO_4})_6]^{6+}$), 990.6 ($[\mathrm{Eu_4}\mathbf{L3}_4(\mathrm{ClO_4})_7]^{5+}$). Elemental analysis: Found: C, 43.93; H, 4.04; N, 8.71. Calc. for $[Eu_4(C_{53}H_{53}N_9O_6)_4](ClO4)_{12}\cdot 18.9$ H2O: C, 43.98; H, 4.34; N 8.71 %.

$[\mathbf{Eu_3L3_2}]^{9+}$: ^{1}H NMR (CD_3CN) (only identified peaks according to Figure S3): δ= 2.46 (t, 3H, CH_3), 2.5 (t, 3H, CH_3), 3.22 (d, 1H, CH), 4.05 (m, 1H, CH_2), 4.74 (s, 1H, CH), 5.21 (d, 1H, CH), 5.23 (m, 1H, CH_2), 5.73 (m, 1H, CH_2), 6.19 (t, 1H, CH), 6.37 (m, 1H, CH_2), 6.58 (d, 1H, CH), 6.68 (d, 1H, CH) ppm. ESMS (CD_3CN):): *m*/*z* 958.8 ($[\mathrm{Eu_3}\mathbf{L3}_2(\mathrm{ClO_4})_6]^{3+}$), 1487.7 ($[\mathrm{Eu_3}\mathbf{L3}_2(\mathrm{ClO_4})_7]^{2+}$).

$[\mathbf{Eu_4L3_4}](\mathbf{CF_3SO_3})_{12}$: ^{1}H NMR (CD_3CN) : δ= 1.05 (t, 3H, CH_3), 2.99 (m, 1H, CH_2), 3.35 (m, 1H, CH_2), 3.79 (s, 3H, CH_3), 4.28 (d, 1H, CH), 4.38 (s, 1H, CH), 5.14 (m, 1H, CH_2), 5.51 (s, 1H, CH), 5.53 (m, 1H, CH_2), 5.74 (t, 1H, CH), 5.84 (s, 1H, NH), 5.92 (s, 1H, CH) 7.26 (d, 1H, CH), 13.16 (s, 1H, CH), 14.05 (s, 1H, CH) ppm.

Spectroscopic measurements.

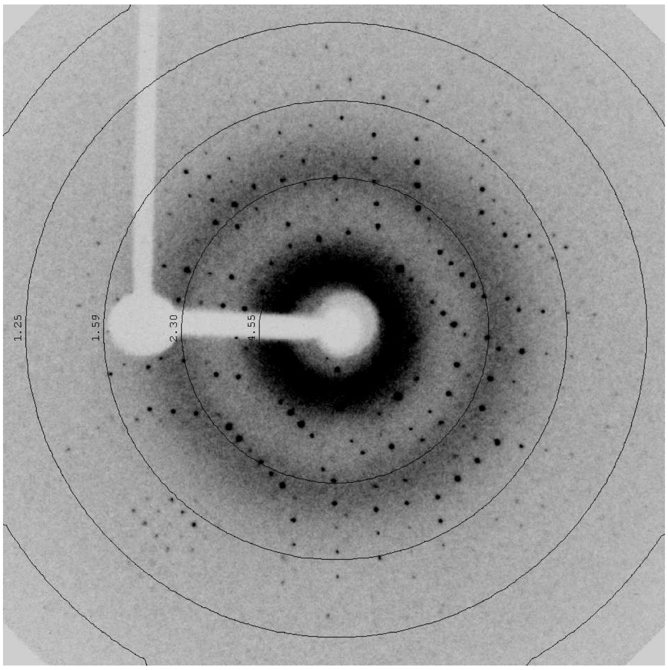
Electrospray mass spectra (ESMS) of Eu(III) complexes were recorded on a Finnigan SSQ7000 instrument with the optimised ionisation temperature (120 °C) from acetonitrile solutions. ^{1}H, ^{13}C and ^{35}Cl spectra were measured on a high-field NMR spectrometer (400 MHz, Bruker). Excitation and emission spectra as well as lifetime measurements were recorded on a Perkin-Elmer LS-50B spectrometer. The quantum yield in acetonitrile has been calculated with the equation $\Phi_x/\Phi_r = (A_r(\tilde{\nu})I_r(\tilde{\nu})n_x^2D_x)/(A_x(\tilde{\nu})I_x(\tilde{\nu})n_r^2D_r)$, where x refers to the sample and r to the reference (a solution of $[Eu(terpy)_3]^{3+}$ in acetonitrile); A is the absorbance, $\tilde{\nu}$ the excitation wavenumber used, I the intensity of the excitation light at this energy, n the refractive index, and D the integrated emitted intensity.[3] The crystallographic data were collected at 150 K on a Stoe IPDS diffractometer with graphite monochromatic Mo[Kα] radiation (λ = 0.7107 Å).

---

[3] S. Petoud, J.-C. G. Bünzli, C. Piguet, Q. Xiang and R. Thummel, *J. Luminesc.*, 1999, **82**, 69.

Crystal data refinement.

Despite numerous attempts of crystallization and data collection, the best data collected still show a rapid decrease of the intensity with the resolution. Beyond 1.25 Å resolution, no intensity was observed.



The structure was solved by the charge flipping method (Superflip).[4] The map output from Superflip clearly shows the coordination of the complex and the inclusion of perchlorate inside the complex cavity. All other calculations were performed with SHELXL97.[5]

The used strategy for the refinement of the $[Eu_4\mathbf{L3}_4]^{12+}$ structure with the best data collected:

(i) Only europium and the inner perchlorate atoms were refined anisotropically.

(ii) Fixed distance restraints (DFIX) were applied to all the 1-2 distances of the ligand and DANG for most of the 1-3 distances.

(iii) Of the twelve expected perchlorate counter-ions, only two are missing. These anions were also refined with fixe distance restraints (DFIX and DANG).

(iv) For the amidic hydrogen atoms, the 1-2 distances were fixed at 0.97(2)Å and the 1-3 distances at 1.98(4) Å. The coordinates of other hydrogen atoms were calculated.

(v) For most of the poorly resolved atoms the isotropic displacement parameters exceeded 0.2 Å^3 on free refinement. Constraints were thus applied to prevent the displacement parameters from exceeding this value.

(vi) All groups of atoms constituting aromatic rings were restrained to be coplanar (FLAT).

---

[4] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.

[5] G. M. Sheldrick, University of Göettingen, Germany., **1997**.

(vii) Scattering contributions from diffuse interstitial solvent were removed using the SQUEEZE routine in PLATON (Total Potential Solvent Accessible Void Vol = 2345.2 Å^3 and the Electron Count Cell = 389).

Despite all the restrains applied to the model, the disorder inherent to the structure prevented a good refinement of this one. As pointed out in the article, no detailed analysis of the structure is possible due to the low quality of the data.

Table S1. Crystal data and the structure refinement

Empirical formula	$C_{212} H_{212} Cl_{10} Eu_4 N_{36} O_{65}$	
Formula weight	5266.60	
Temperature	180 K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 27.320(5) Å	α= 90°.
	b = 27.320(5) Å	β= 90°.
	c = 22.754(3) Å	γ = 120°.
Volume	14708(4) Å^3	
Z	2	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	1.003 mm^{-1}	
Crystal size	0.1 x 0.1 x 0.01 mm^3	
Theta range for data collection	1.24 to 21.12°.	
Index ranges	-27<=h<=15, -27<=k<=22, -9<=l<=22	
Reflections collected	12374	
Independent reflections	5186 [R(int) = 0.0985]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5186 / 373 / 540	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.1333, wR2 = 0.3282	
R indices (all data)	R1 = 0.1798, wR2 = 0.3649	
Extinction coefficient	0.0013(3)	
Largest diff. peak and hole	0.746 and -0.555 e.Å^{-3}	

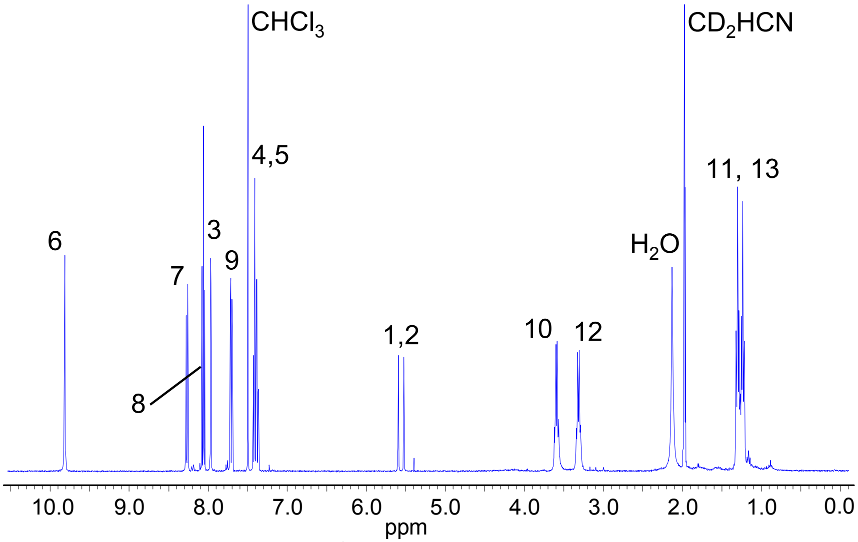


Figure S1. ^{1}H NMR spectrum of **L3**.

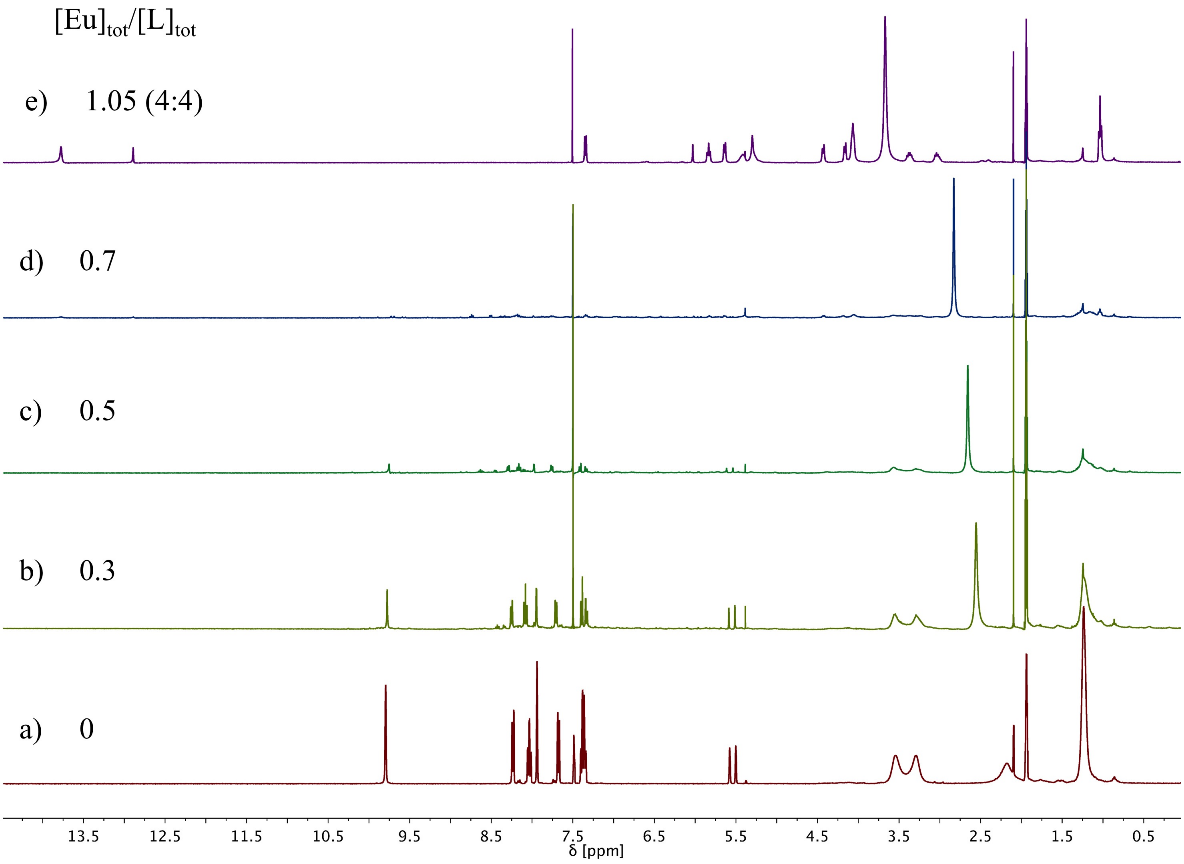


Figure S2. ^{1}H NMR titration of **L3** with Eu(III) from 0 to 1 equivalent ($CD_3CN/CDCl_3$). 0 eq (a), 0.3 eq (b), 0.5 eq (c), 0.7 eq (d), and 1.05 eq (e).

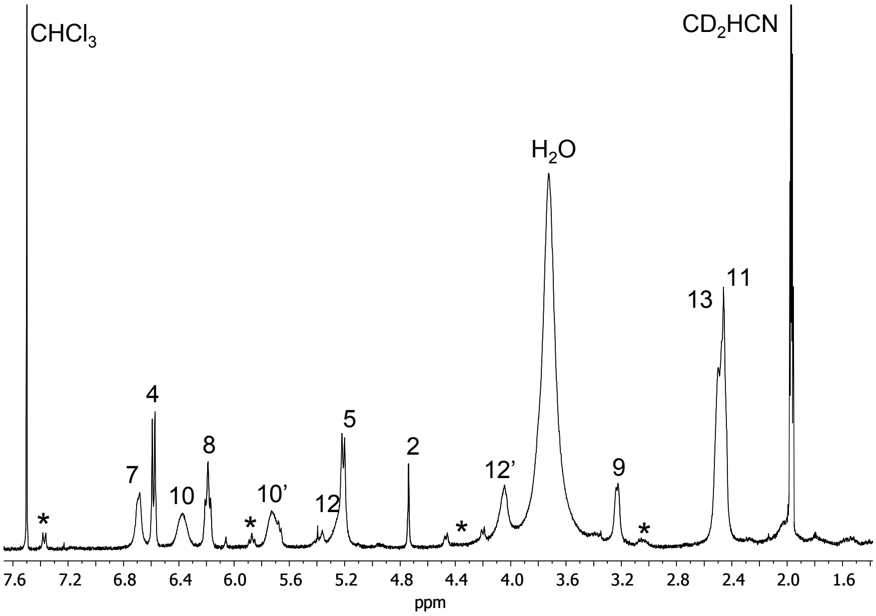


Figure S3. ^{1}H NMR spectrum of $[Eu_3\mathbf{L3}_2]^{9+}$ for the ratio [Eu]/[**L3**] ~ 1.7. The attribution is given for unambiguously identified peaks. The symbol * indicates the peaks of the tetranuclear complex $[Eu_4\mathbf{L3}_4]^{12+}$.

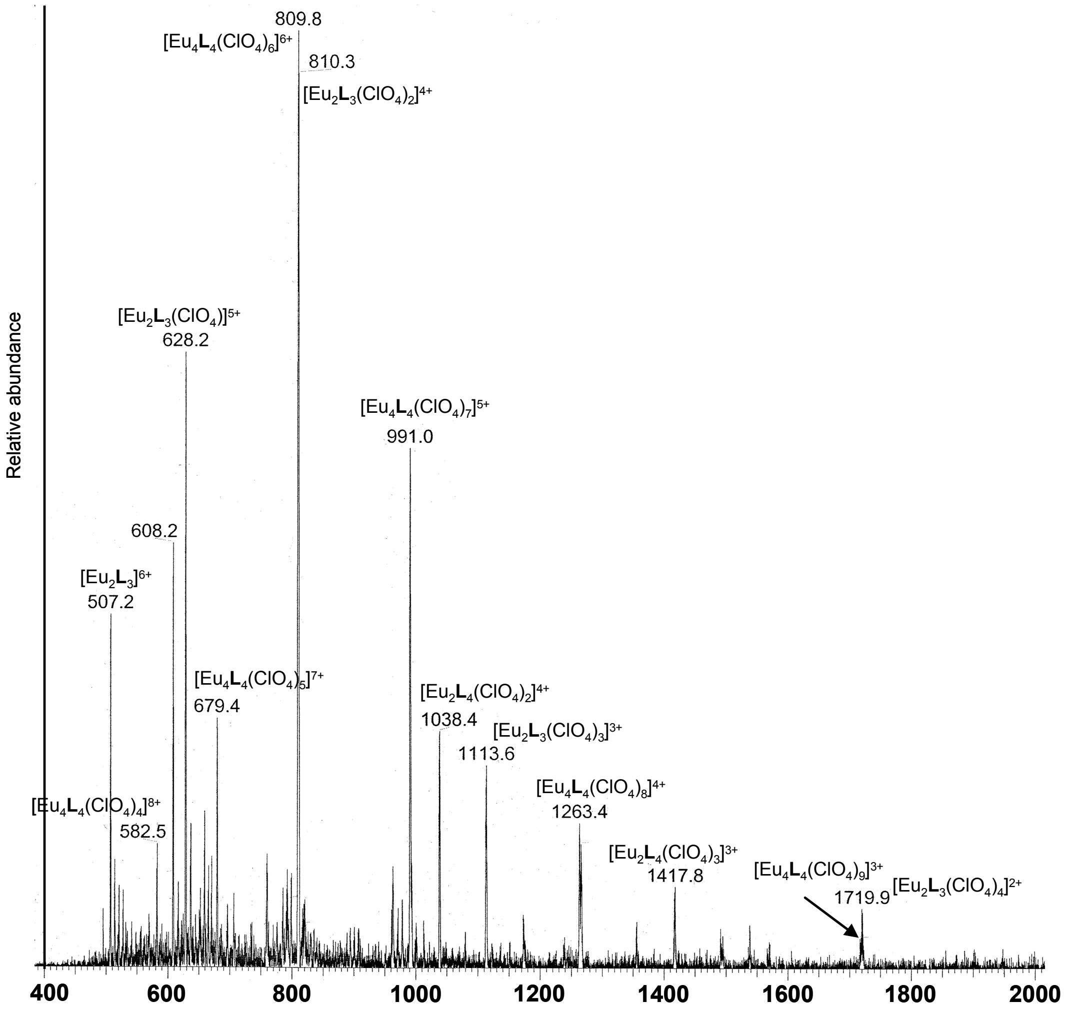


Figure S4. ESMS spectra of the isolated complex $[Eu_4\mathbf{L3}_4]^{12+}$ dissolved in acetonitrile ($T_{ionization}$ = 120°C).

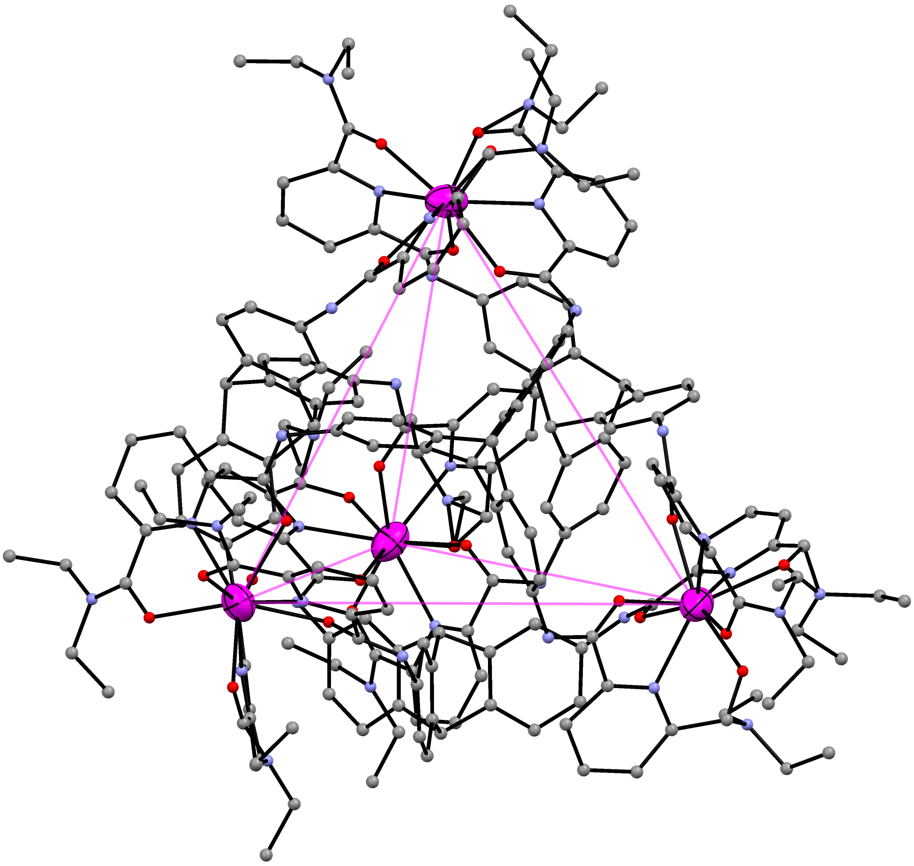
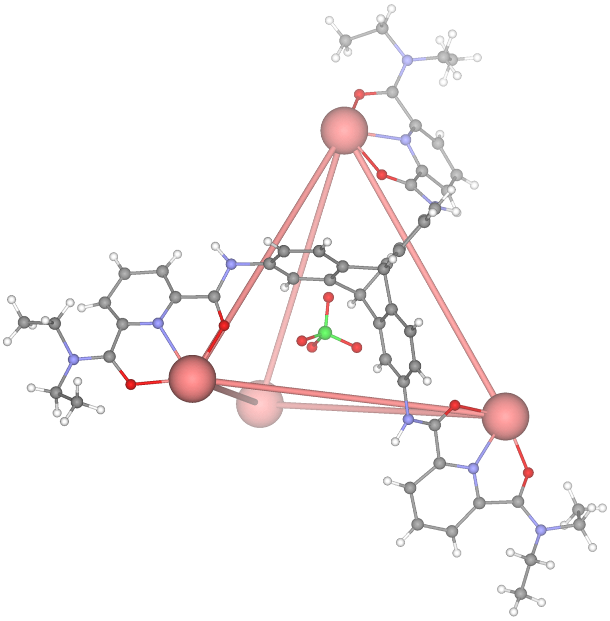
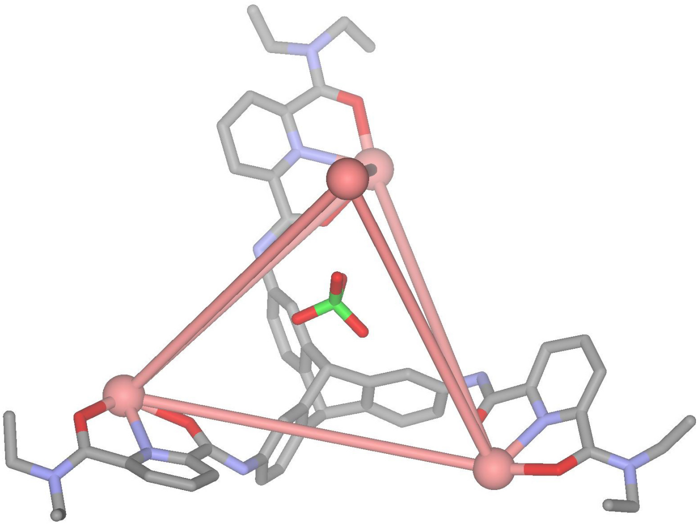


Figure S5. X-Ray crystal structure of $[Eu_4\mathbf{L3}_4]^{12+}$. The four Eu(III) in the vertexes of the tetrahedron are represented in ORTEP view (50% ellipsoid). The hydrogen atoms, solvent molecules and perchlorate anions are omitted for clarity.



a)



b)

Figure S6. Detailed view of the ligand orientation and the encapsulated perchlorate anion within the tetrahedron in $[Eu_4L3_4]^{12+}$.

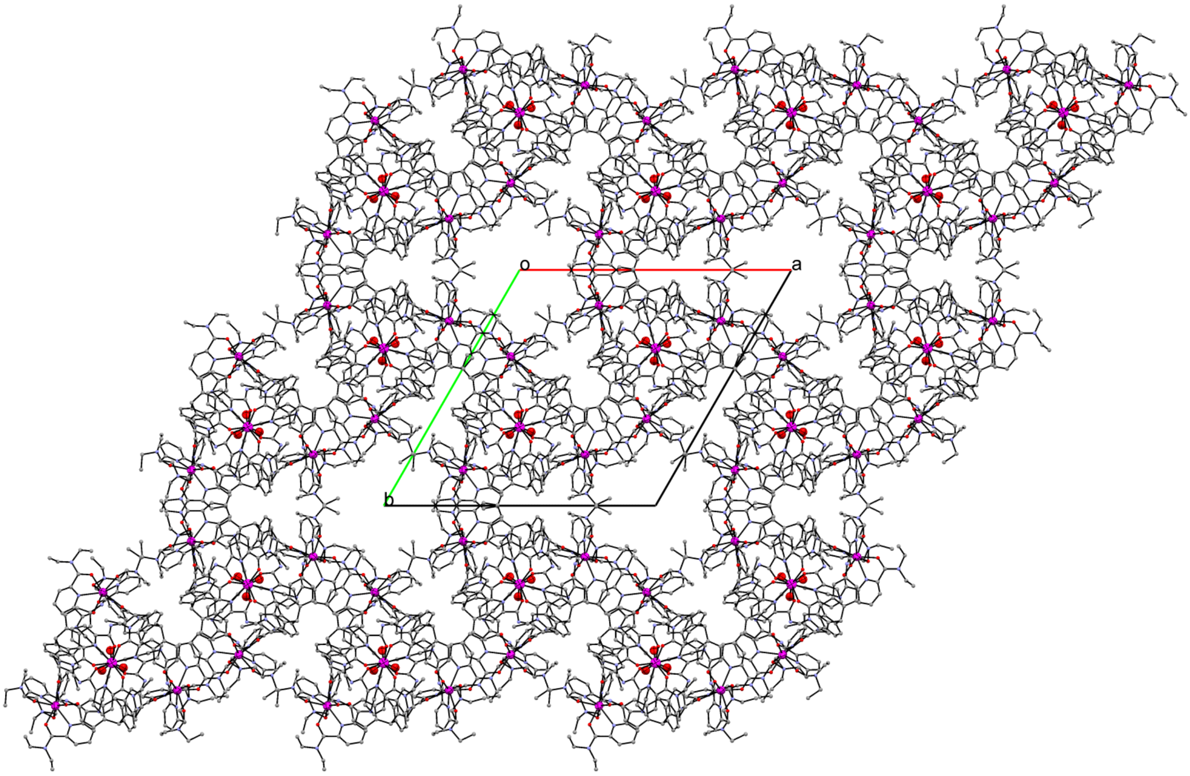


Figure S7. Crystal packing of $[Eu_4\mathbf{L3}_4]^{12+}$.: view along the *c* axis. The hydrogen atoms, the solvent molecules and the disordered non-encapsulated perchlorate anions are omitted for clarity.

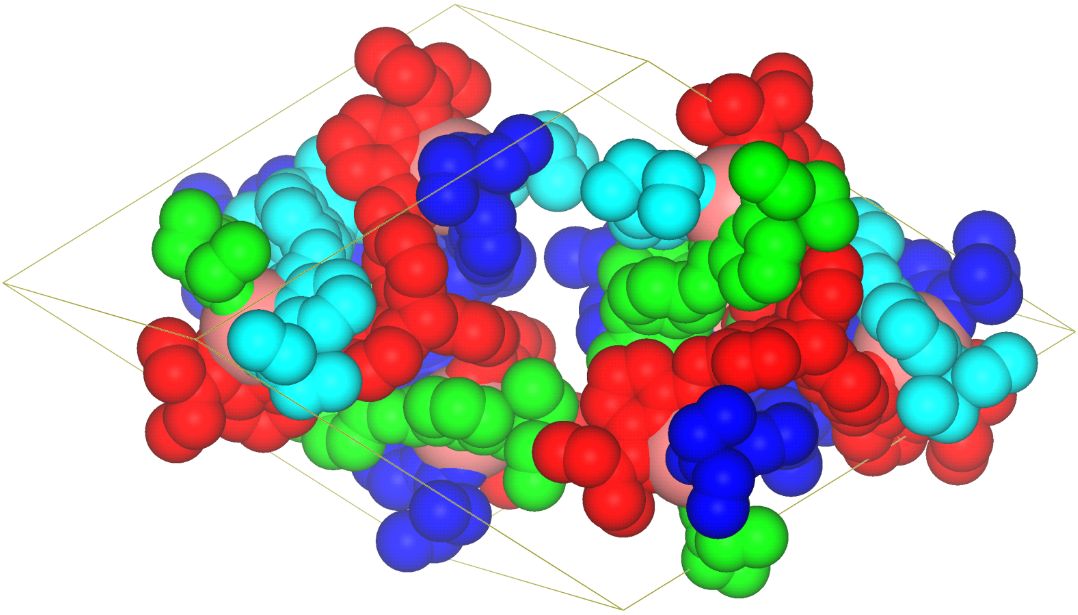


Figure S8. Space filled view of the two stereo isomer ΔΔΔΔ and ΛΛΛΛ in the cell unit ($[Eu_4\mathbf{L3}_4]^{12+}$).

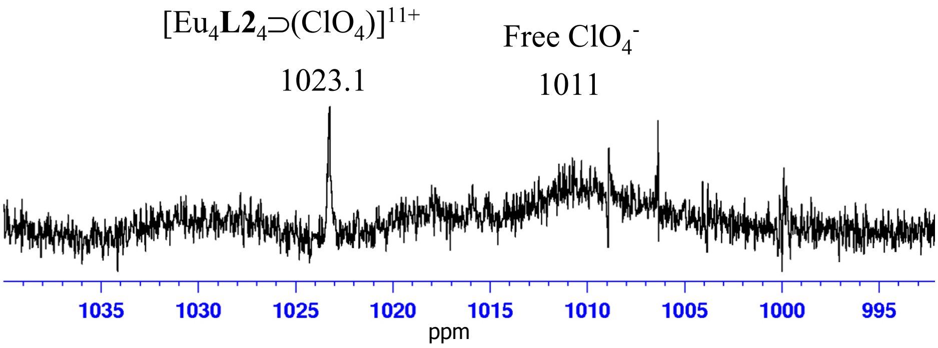


Figure S9. ^{35}Cl NMR spectrum of $\{[Eu_4\mathbf{L3}_4]\supset(ClO_4)\}^{11+}$ in deuterated acetonitrile.

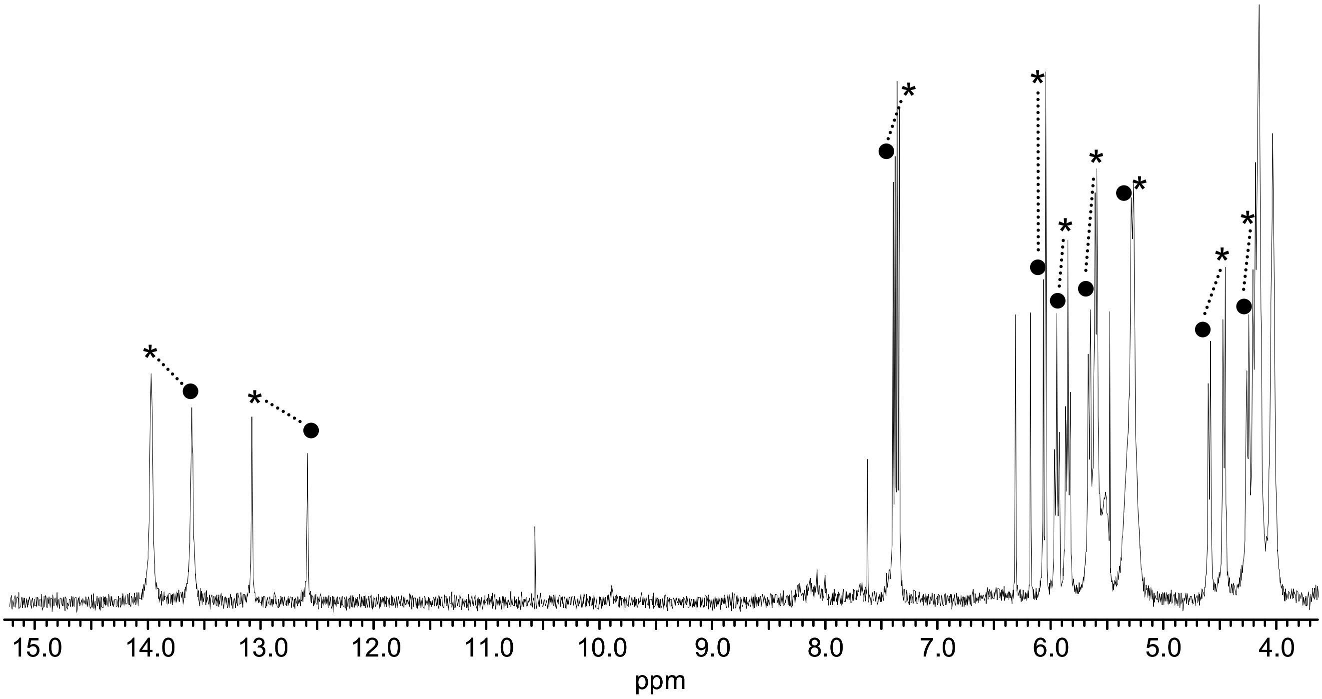


Figure S10. ^{1}H NMR spectrum of the CD$_3$CN solution of [Eu$_4$**L3**$_4$](ClO$_4$)$_{12}$ upon addition of 32 eq of N(*n*-Bu)$_4$CF$_3$SO$_3$ (with respect to the tetranuclear complex). * = {[Eu$_4$**L3**$_4$]⊃(ClO$_4$)}$^{11+}$, • = {[Eu$_4$**L3**$_4$]⊃(BF$_4$)}$^{11+}$. The dotted line indicates the signals related to the same proton (H1-H9) in the above cage complexes.