Supplementary Material (ESI) for Chemical Communications

Isolation and characterization of the first circular single-stranded polymetallic lanthanide-containing helicate.

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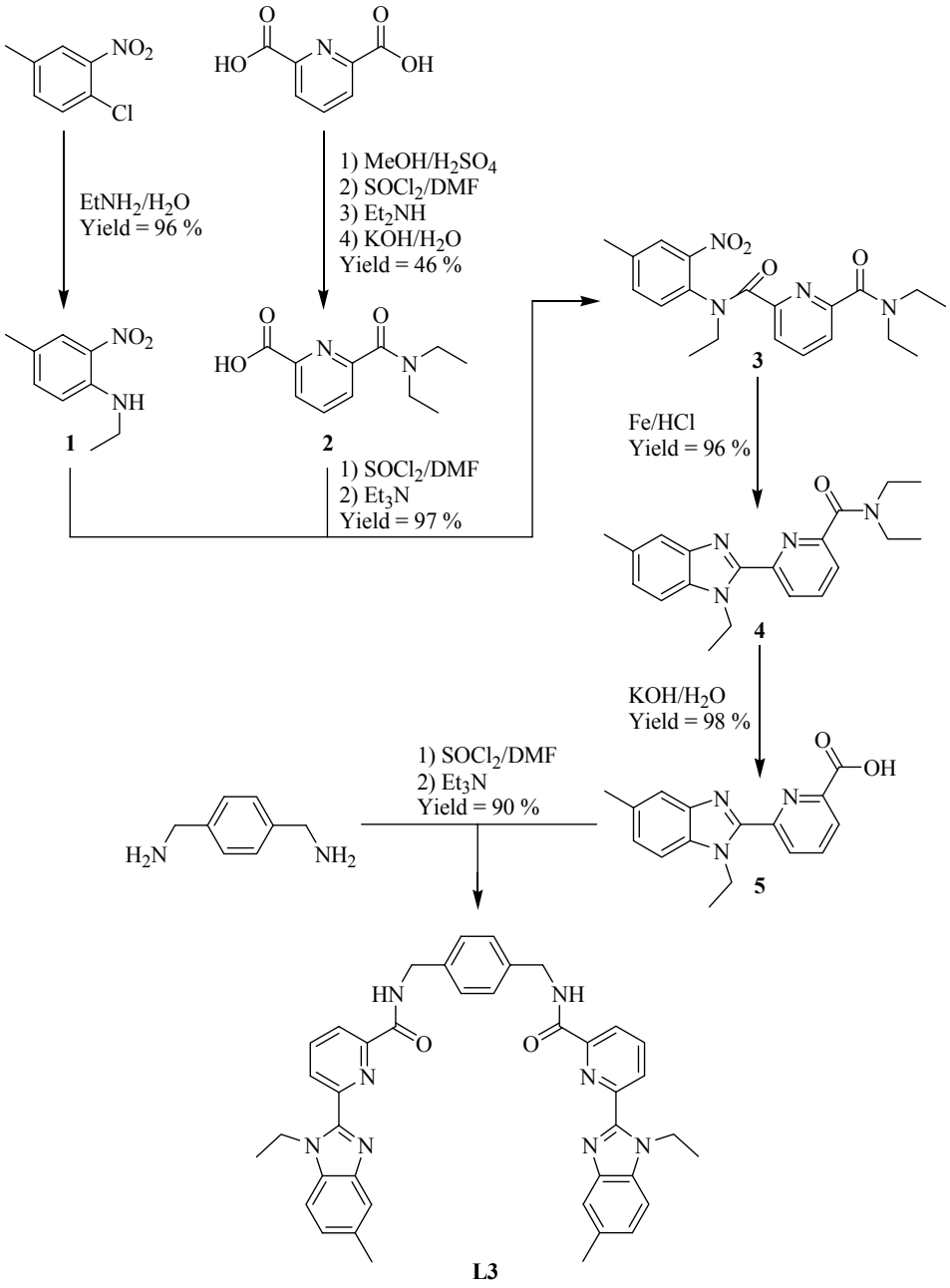
Supporting Information

(15 pages)

Experimental Section

Solvents and Starting Materials. Chemicals were purchased from Fluka AG and Aldrich, and used without further purification unless otherwise stated. The triflate salt $Eu(CF_3SO_3)_3 \cdot 5H_2O$ was prepared from the corresponding oxides (Rhodia, 99.99 %) and dried according to a published procedure.[1] The Ln content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.[2] Thionyl chloride was distilled from elemental sulfur, acetonitrile, dichloromethane, *N,N*-dimethyformamide and triethylamine were distilled from CaH_2. Silicagel (Fluka, 0.040-0.063 mm) was used for preparative column chromatography. 6-Diethylcarbamoyl-pyridine-2-carboxylic acid (**2**) was prepared according to a literature procedure.[3]



Scheme S1 Synthesis of ligand **L3**.

Preparation of ethyl-(4-methyl-2-nitro-phenyl)-amine (1). A mixture of 4-chloro-3-nitrotoluene (17.2 g, 100 mmol) and ethylamine (100 mL, 70 % in water) was heated at 100 °C for 24 h in an autoclave and evaporated to dryness. The resulting red oil was dissolved in CH_2Cl_2/aqueous half-saturated NH_4Cl (200 mL/200 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with deionized water (50 mL), dried over $MgSO_4$, filtered and evaporated to dryness to afford ethyl-(4-methyl-2-nitro-phenyl)-amine **1** as an orange solid (17.30 g, 96 mmol, 96 %) which was pure enough to be used without further purification. ^{1}H NMR ($CDCl_3$): 1.36 (t, ^3J = 7.2 Hz, 3H), 2.26 (s, 3H), 3.33 (dq, ^3J = 7.2 Hz and ^3J = 5.0 Hz, 2H), 6.77 (d, ^3J = 8.7 Hz, 1H), 7.27 (dd, ^3J = 8.7 Hz and ^4J = 2.2 Hz, 1H), 7.87 (b, 1H), 7.97 (d, ^3J = 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): 14.5, 20.0, 37.8, 113.8, 124.7, 126.1, 131.3, 137.9, 143.9.

Preparation of pyridine-2,6-dicarboxylic acid 2-diethylamide 6-[ethyl-(4-methyl-2-nitro-phenyl)-amide] (3). A mixture of 6-diethylcarbamoyl-pyridine-2-carboxylic acid (**2**, 8.89 g, 40 mmol), CH_2Cl_2 (100 mL), thionyl chloride (30 mL, 400 mmol) and DMF (0.1 mL) was refluxed for 1.5 h under a nitrogen atmosphere and evaporated to dryness. The white residue was dried under vacuum for 30 min, dissolved in CH_2Cl_2 (75 mL) and cooled at 0 °C. A mixture of *N*-ethyl-(4-methyl-2-nitrophenyl)amine (**1**, 6.31 g, 35 mmol), triethylamine (25 mL) and CH_2Cl_2 (75 mL) was added dropwise over 10 min. The resulting solution was stirred for 10 min at 0 °C, refluxed for 2 h and evaporated to dryness. The brown residual oil was dissolved in CH_2Cl_2/aqueous half-saturated NH_4Cl (200 mL/300 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL). The combined organic phases were washed with deionized water (50 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The resulting crude compound was purified by column chromatography (silicagel, CH_2Cl_2/MeOH 100/0→98/2) to afford pyridine-2,6-dicarboxylic acid 2-diethylamide 6-[ethyl-(4-methyl-2-nitro-phenyl)-amide] **3** as a brown solide (13.02 g, 33.9 mmol, 97 %). ^{1}H NMR ($CDCl_3$): 0.88 (t, ^3J = 7.2 Hz, 3H), 1.18 (t, ^3J = 7.2 Hz, 3H), 1.21 (t, ^3J = 7.2 Hz, 3H), 2.33 (s, 3H), 2.97 (h, ^3J = 7.2 hz, 1H), 3.11 (h, ^3J = 7.2 Hz, 1H), 3.30 (h, ^3J

= 7.2 Hz, 1H), 3.54 (m, 2H), 4.29 (h, ^3J = 7.2 Hz, 1H), 7.00 (d, ^3J = 8.0 Hz, 1H), 7.22 (m, 1H), 7.31 (dd, ^3J = 7.5 Hz and ^4J = 1.3 Hz, 1H), 7.69 (d, ^3J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.77 (dd, ^3J = 7.5 Hz and ^4J = 1.3 Hz, 1H).^{13}C NMR ($CDCl_3$): 12.6, 12.9, 14.3, 21.1, 40.1, 42.9, 46.1, 123.7, 124.7, 126.0, 130.1, 131.9, 134.5, 137.9, 139.4, 146.1, 151.7, 153.2, 166.7, 167.5.

Preparation of 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid diethylamide (4). A mixture of pyridine-2,6-dicarboxylic acid 2-diethylamide 6-[ethyl-(4-methyl-2-nitro-phenyl)-amide] (**3**, 5.77 g, 15.0 mmol), ethanol (540 mL), water (150 mL), powdered iron (6.70 g, 120 mmol) and concentrated hydrochloric acid (37 %, 18 mL, 216 mmol) was refluxed for 18 h under nitrogen atmosphere, filtered and concentrated under vacuum. The residual aqueous layer was poured into a mixture of CH_2Cl_2 (200 mL), water (370 mL) and $Na_2H_2EDTA{\cdot}2\ H_2O$ (81 g, 217 mmol). The pH was adjusted to 7 with a 25 % aqueous ammonia solution, 30 % hydrogen peroxide solution (4.5 mL, 44.1 mmol) was slowly added and the mixture was stirred for 15 min. The pH was adjusted to 8.5 with a 25 % aqueous ammonia solution, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were washed with deionized water until neutral, dried over $MgSO_4$, filtered and evaporated to dryness. The resulting crude compound was purified by column chromatography (silicagel, CH_2Cl_2/MeOH 98/2) to afford 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid diethylamide **4** as a pale yellow solid (4.84 g, 14.4 mmol, 96 %). ^{1}H NMR ($CDCl_3$): 1.06 (t, ^3J = 7.1 Hz, 3H), 1.28 (t, ^3J = 7.1 Hz, 3H), 1.45 (t, ^3J = 7.1 Hz, 3H), 2.50 (s, 3H), 3.35 (q, ^3J = 7.1 Hz, 2H), 3.61 (q, ^3J = 7.1 Hz, 2H), 4.74 (q, ^3J = 7.1 Hz, 2H), 7.16 (d, ^3J = 8.3 Hz, 1H), 7.33 (d, ^3J = 8.3 Hz, 1H), 7.53 (d, ^3J = 7.7 Hz, 1H), 7.61 (s, 1H), 7.92 (t, ^3J = 7.9 Hz, 1H), 8.38 (d, ^3J = 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): 12.9, 14.3, 15.4, 21.6, 39.5, 40.5, 42.8, 109.7, 119.9, 122.4, 124.9, 125.1, 132.4, 134.4, 137.9, 143.1, 149.2, 149.5, 154.5, 168.5. IR (cm^{-1}): 1628, 1585, 1565. Mp = 129-131 °C.

Preparation of 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid (5). A mixture of 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid diethylamide (**4**, 3.36 g, 10.0 mmol), KOH (22.40 g, 400 mmol), EtOH (180 mL) and water (20 mL) was refluxed

for 24 h and concentrated under vacuum. The residual aqueous phase was diluted with water (100 mL) and the pH was adjusted to 2 with a 37 % aqueous hydrochloric acid solution. The white precipitate was filtered off, washed with water, dried under vacuum (2.74 g, 9.7 mmol, 98 %). It was pure enough to be used without further purification. ^{1}H NMR (DMSO): 1.44 (t, ^{3}J = 7.0 Hz, 3H), 2.46 (s, 3H), 4.89 (q, ^{3}J = 7.0 Hz, 2H), 7.26 (d, ^{3}J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.67 (d, ^{3}J = 8.4 Hz, 1H), 8.19 (m, 1H), 8.22 (t, ^{3}J = 7.7 Hz, 1H), 8.53 (dd, ^{3}J = 7.4 Hz and ^{4}J = 1.6 Hz, 1H). ^{13}C NMR (DMSO): 15.2, 21.1, 40.8, 111.0, 118.0, 125.4, 125.8, 127.2, 133.0, 133.5, 139.0, 139.7, 147.3, 148.0, 148.2, 165.8. IR (cm^{-1}): 3410, 1702, 1585, 1572. Mp = 243 °C.

Typical procedure for the synthesis of the ligands. Preparation of *N,N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-4,4'-methylenedianiline (L5). A mixture of 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid (**5**, 422 mg, 1.5 mmol), CH_2Cl_2 (30 mL), thionyl chloride (1.1 mL, 15.2 mmol) and DMF (0.01 mL) was refluxed for 1.5 h under a nitrogen atmosphere and evaporated to dryness. The white residue was dried under vacuum for 30 min, dissolved in CH_2Cl_2 (30 mL) and cooled at 0 °C. A mixture of 4,4'-méthylènedianiline (100 mg, 0.5 mmol), triethylamine (0.25 mL) and CH_2Cl_2 (30 mL) was added dropwise over 20 min. The resulting solution was stirred for 3 h at 25 °C, washed with 2 × 20 mL of aqueous half-saturated $NaHCO_3$, deionized water until neutral, dried over $MgSO_4$, filtered and evaporated to dryness. The resulting crude compound was triturated in 30 mL of acetonitrile, filtered, rinced with ligth petroleum ether and dried under vacuum. Recrystallisation from hot DMF afford *N,N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-4,4'-methylenedianiline **L5** as a white solid (350 mg, 0.48 mmol, 97 %). ^{1}H NMR ($CDCl_3$): 1.71 (t, ^{3}J = 7.2 Hz, 6H), 2.52 (s, 6H), 4.00 (s, 2H), 4.77 (q, ^{3}J = 7.2 Hz, 4H), 7.22 (dd, ^{3}J = 8.4 and ^{4}J = 1.4 Hz, 2H), 7.25 (d, ^{3}J = 8.5 Hz, 4H), 7.38 (d, ^{3}J = 8.3 Hz, 2H), 7.65 (s, 2H), 7.69 (d, ^{3}J = 8.5 Hz, 4H), 8.08 (t, ^{3}J = 7.8 Hz, 2H), 8.37 (dd, ^{3}J = 7.7 Hz and ^{4}J = 1.0 Hz, 2H), 8.56 (dd, ^{3}J = 7.7 Hz and ^{4}J = 1.0 Hz, 2H), 9.72 (s, 2H). ESI-MS (*m*/*z* (%)): 236.1 (70), 363.9 (85) $[L+2H]^{2+}$, 727.3 (90) $[L+H]^{+}$. Mp = 310 °C (dec).

Preparation of *N,N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,4-di(aminomethyl)-benzene (L3). The ligand was prepared using the typical procedure described for **L5** starting from α,α'-amino-*p*-xylene (68 mg, 0.5 mmol) and 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid (**5**, 422 mg, 1.5 mmol), it was purified

by column chromatography (silicagel, CH_2Cl_2/MeOH 97/3) to afford *N*,*N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,4-di(aminomethyl)-benzene **L3** as a white solid (300 mg, 0.45 mmol, 90 %). ^{1}H NMR ($CDCl_3$): 1.37 (t, ^3J = 7.3 Hz, 6H), 2.52 (s, 6H), 4.61 (q, ^3J = 7.1 Hz, 4H), 4.73 (d, ^3J = 6.8 Hz, 4H), 7.18 (dd, ^3J = 8.3 Hz and ^4J = 1.0 Hz, 2H), 7.28 (d, ^3J = 8.3 Hz, 2H), 7.41 (s, 4H), 7.63 (s, 2H), 8.06 (t, ^3J = 7.8 Hz, 2H), 8.09 (bs, 2H), 8.33 (dd, ^3J = 7.5 Hz and ^4J = 1.0 Hz, 2H), 8.55 (dd, ^3J = 7.8 Hz and ^4J = 1.0 Hz, 2H). ESI-MS (CH_2Cl_2 + 0.01 % TFA): 236.1 (85), 281.1 (55), 333.0 (100) $[L+2H]^{2+}$, 383.3 (75), 664.8 (95) $[L+H]^+$. Mp = 262 °C.

Preparation of *N,N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,3-di(aminomethyl)-benzene (L4). The ligand was prepared using the typical procedure described for **L5** starting from α,α'-amino-*m*-xylene (68 mg, 0.5 mmol) and 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid (**5**, 422 mg, 1.5 mmol) to afford *N*,*N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,3-di(aminomethyl)-benzene **L4** as a white solid (300 mg, 0.45 mmol, 91 %). ^{1}H NMR ($CDCl_3$): 1.30 (t, ^3J = 7.2 Hz, 6H), 2.50 (s, 6H), 4.00 (s, 2H), 4.51 (q, ^3J = 7.2 Hz, 4H), 4.73 (d, ^3J = 5.9 Hz, 4H), 7.15 (dd, ^3J = 8.4 Hz and ^4J = 1.4 Hz, 2H), 7.22 (d, ^3J = 8.5 Hz, 4H), 7.37 (m, 4H), 7.59 (s, 2H), 7.95 (t, ^3J = 7.8 Hz, 2H), 8.14 (t, ^3J = 5.9 Hz, 2H), 8.23 (dd, ^3J = 7.7 Hz and ^4J = 1.0 Hz, 2H), 8.46 (dd, ^3J = 7.7 Hz and ^4J = 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 15.3, 21.6, 40.3, 43.6, 109.4, 120.0, 122.4, 125.4, 127.2, 127.4, 129.4, 132.6, 134.2, 138.4, 138.8, 142.9, 148.4, 148.9, 149.2, 164.0. ESI-MS (*m*/*z* (%)): 236.1 (52), 281.1 (38), 333.1 (100) $[L+2H]^{2+}$, 383.3 (95), 665.0 (97) $[L+H]^+$. Mp = 184 °C.

Preparation of *N,N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,6-diamino-hexane (L6). The ligand was prepared using the typical procedure described for **L5** starting from 1,6-diaminohexane (58 mg, 0.5 mmol) and 6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridine-2-carboxylic acid (**5**, 422 mg, 1.5 mmol), it was purified by column chromatography (silicagel, CH_2Cl_2/MeOH 97/3) to afford *N*,*N*'-di-([6-(1-ethyl-5-methyl-1H-benzoimidazol-2-yl)-pyridin-2-yl]-oxomethyl)-1,6-diamino-hexane **L6** as a white solid (300 mg, 0.47 mmol, 93 %). ^{1}H NMR ($CDCl_3$): 1.52 (b, 4H), 1.61 (t, ^3J = 7.1 Hz, 6H), 2.54 (s, 6H), 1.71 (b, 4H), 3.55 (q, ^3J = 7.1 Hz, 4H), 4.73 (q, ^3J = 7.1 Hz, 4H), 7.22 (dd, ^3J = 8.3 Hz and ^4J = 1.0 Hz, 2H), 7.37 (d, ^3J = 8.3 Hz, 2H), 7.67 (s, 2H), 7.85 (b, 2H), 8.04 (t, ^3J = 7.8 Hz, 2H), 8.28 (dd, ^3J = 7.8 Hz

and ^4J = 1.0 Hz, 2H), 8.51 (dd, ^3J = 7.8 Hz and ^4J = 1.0 Hz, 2H). ESI-MS (*m/z* (%)): 643.7 (39) $[L+H]^+$, 665.7 (100) $[L+Na]^+$. *Mp* = 200 °C.

Synthesis of the complex $[Eu_3(L3)_3(CF_3SO_3)_9](H_2O)_4$. **L3** (20 mg, 0.029 mmol) dissolved in dichloromethane (2 mL) was added to $Eu(CF_3SO_3)_3{\cdot}5H_2O$ (20 mg, 0.029 mmol) in acetonitrile (2 mL). After stirring at RT for 1 h, diethylether was slowly diffused for 24 h. Filtration of the resulting mixture gave $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_9](H_2O)_4$ as white microcrystals (31.5 mg, 0.024 mmol, 84 %). Anal Calcd for $Eu_3C_{129}H_{122}N_{24}O_{37}S_9F_{27}$: C, 39.89; H, 3.17; N, 8.63. Found: C, 39.80; H, 3.25; N, 8.52. Very fragile X-ray quality prisms of $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_5(CH_3CN)_9(H_2O)_2$ (**1**) could be obtained by slow diffusion of diisopropylether into a concentrated acetonitrile solution of $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_9](H_2O)_4$.

Single Crystal Structure Determinations. Summary of crystal data, intensity measurements and structure refinements for $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_5(CH_3CN)_9(H_2O)_2$ (**1**) are collected in Table S1. The crystal was mounted on quartz fibers with protection oil. Cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer with graphite-monochromated Mo[Kα] radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects and for absorption. The structure were solved by direct methods (SIR97),[4] all other calculation were performed with XTAL[5] system and ORTEP[6] programs. The atomic positions of the hydrogen atoms were calculated except for those of the solvent molecules, which were refined with restraints on bond lengths and bond angles, and blocked during the last cycle of the refinement process. The water molecules O5w and O6w (without hydrogen atoms) were refined with population parameters *PP* = 0.5. The disordered triflates g and k were each refined on two different sites with population parameters of 0.25/0.75 and 0.3/0.7 respectively. All non-hydrogen atoms were refined with anisostropic displacement parameters. CCDC 261626 contains the supplementary crystallographic data. These data can be obtained free of charge via

www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

References

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Table S1 Summary of crystal data, intensity measurement and structure refinement for $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_5(CH_3CN)_9(H_2O)_2$ (**1**).

Formula	$Eu_3C_{151}H_{157}N_{35}O_{38}S_9F_{27}$
fw	4327.0
Color	colorless
Crystal system	triclinique
Space group	$P\bar{1}$
a, Å	14.7345(11)
b, Å	21.8136(12)
c, Å	31.790(2)
α, deg.	100.262(7)
β, deg.	100.850(8)
γ, deg.	103.813(8)
V, Å^3	9475(1)
Z	2
d_{calc}, g·cm^{-3}	1.517
$\mu_{Mo\text{-}K\alpha}$, mm^{-1}	1.185
T_{min}/T_{max}	0.7125 / 0.7985
Crystal size, mm	0.25 x 0.30 x 0.32
2θ max (deg)	4.1° < 2θ < 51.9°
No. of reflns collected	100'621
No. of independent reflns	34'501
R_{int}	0.060
No. of obsd [a] (used[b]) reflns	18'853 (19896)
No. of variables	2228
Weighting scheme, ω	$1/(\sigma^2(F_0)+0.00015(F_0)^2)$
Max. et Min. Δρ, eÅ^{-3}	3.91 / -2.39
GOF (*F*) [c] (all data)	1.93(1)
R [d], ωR [e]	0.063 / 0.065

[a] $|Fo| > 4\sigma(Fo)$. [b] Used in the refinements (including reflns with $|Fo| \leq 4\sigma(Fo)$ if $|Fc| > |Fo|$). [c] $S = [\Sigma \{((F_o\text{-}F_c) / \sigma(F_o))^2\} / (N_{ref} - N_{var})]^{1/2}$. [d] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [e] $\omega R = [\Sigma (\omega|Fo|-|Fc|)^2 / \Sigma \omega|Fo|^2]^{1/2}$

Table S2 Selected bond distances (Å) in $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_5(CH_3CN)_9(H_2O)_2$ (**1**).

Eu1···Eu2	11.9977(7)				
Eu1···Eu3	12.3217(8)				
Eu2···Eu3	11.7933(8)				
Eu1-O1a	2.384(6)	Eu2-O2a	2.392(5)	Eu3-O2b	2.385(7)
Eu1-N2a	2.601(9)	Eu2-N6a	2.577(7)	Eu3-N6b	2.595(8)
Eu1-N3a	2.553(7)	Eu2-N7a	2.586(7)	Eu3-N7b	2.556(6)
Eu1-O2c	2.411(7)	Eu2-O1b	2.422(7)	Eu3-O1c	2.383(7)
Eu1-N6c	2.621(8)	Eu2-N2b	2.594(7)	Eu3-N2c	2.595(7)
Eu1-N7c	2.577(8)	Eu2-N3b	2.564(9)	Eu3-N3c	2.532(7)
Eu1-O1d	2.461(9)	Eu2-O1e	2.416(8)	Eu3-O1f	2.401(8)
Eu1-O1w	2.405(8)	Eu2-N1m	2.537(8)	Eu3-O1g	2.46(1)
Eu1-O2w	2.415(6)	Eu2-O3w	2.409(6)	Eu3-N1n	2.60(1)

Table S3 Selected least-squares plane data for $[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_5(CH_3CN)_9(H_2O)_2$ (**1**).

F1 (Bz : N3a, N4a, C14a, C15a, C16a, C17a, C18a, C19a, C20a)

F2 (Py : N2a, C9a, C10a, C11a, C12a, C13a)

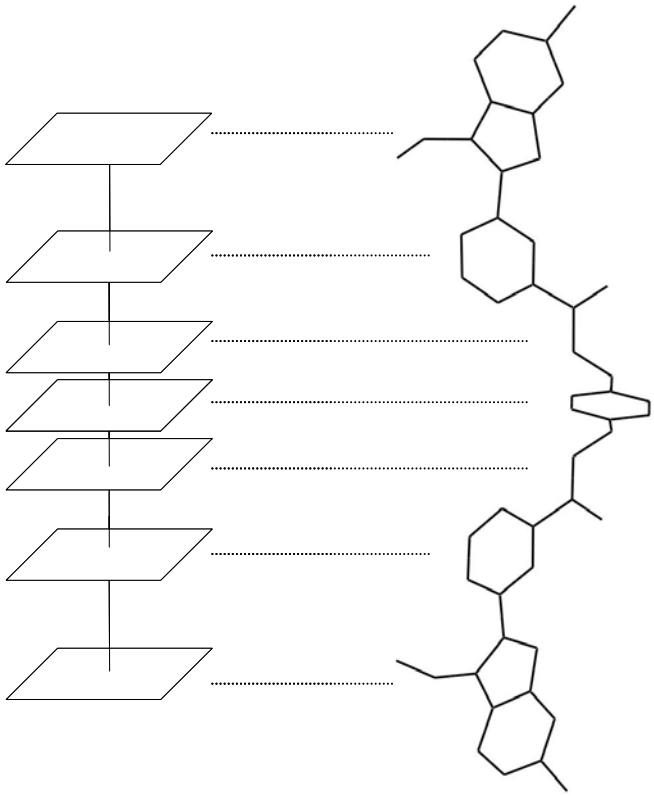
F3 (Am : N1a, C8a, C9a, O1a)

F4 (Bn : C1a, C2a, C3a, C4a, C5a, C6a)

F5 (Am : N5a, C22a, C23a, O2a)

F6 (Py : N6a, C23a, C24a, C25a, C26a, C27a)

F7 (Bz : N7a, N8a, C28a, C29a, C30a, C31a, C32a, C33a, C34a)



Abbreviation: Py: pyridine; Bz: benzimidazole; Bn: benzene; Am: amide

	Deviations, Å	
Least-squares planes description, strand a	max	atom
F1 (Bz: N3a, N4a, C14a, C15a, C16a, C17a, C18a, C19a, C20a)	0.017	C19a
F2 (Py: N2a, C9a, C10a, C11a, C12a, C13a)	0.014	C11a
F3 (Am: N1a, C8a, C9a, O1a)	0.014	C9a
F4 (Bn: C1a, C2a, C3a, C4a, C5a, C6a)	0.016	C3a
F5 (Am: N5a, C22a, C23a, O2a)	0.013	C23a
F6 (Py: N6a, C23a, C24a, C25a, C26a, C27a)	0.013	C26a
F7 (Bz: N7a, N8a, C28a, C29a, C30a, C31a, C32a, C33a, C34a)	0.016	C32a

Least-squares planes description, strand b	Deviations, Å max	atom
F1 (Bz : N3b, N4b, C14b, C15b, C16b, C17b, C18b, C19b, C20b)	0.018	C18b
F2 (Py : N2b, C9b, C10b, C11b, C12b, C13b)	0.017	C11b
F3 (Am : N1b, C8b, C9b, O1b)	0.016	C9b
F4 (Bn : C1b, C2b, C3b, C4b, C5b, C6b)	0.015	C2b
F5 (Am : N5b, C22b, C23b, O2b)	0.015	C23b
F6 (Py : N6b, C23b, C24b, C25b, C26b, C27b)	0.015	C25b
F7 (Bz : N7b, N8b, C28b, C29b, C30b, C31b, C32b, C33b, C34b)	0.019	C32b

Least-squares planes description, strand c	Deviations, Å max	atom
F1 (Bz : N3c, N4c, C14c, C15c, C16c, C17c, C18c, C19c, C20c)	0.018	C19c
F2 (Py : N2c, C9c, C10c, C11c, C12c, C13c)	0.016	C11c
F3 (Am : N1c, C8c, C9c, O1c)	0.014	C9c
F4 (Bn : C1c, C2c, C3c, C4c, C5c, C6c)	0.016	C3c
F5 (Am : N5c, C22c, C23c, O2c)	0.015	C23c
F6 (Py : N6c, C23c, C24c, C25c, C26c, C27c)	0.016	C24c
F7 (Bz : N7c, N8c, C28c, C29c, C30c, C31c, C32c, C33c, C34c)	0.015	C32c

Interplanar angles, strand a

	F2	F3	F4	F5	F6	F7
F1	1	2	90	57	61	38
F2		2	90	59	62	39
F3			89	59	62	39
F4				86	88	83
F5					7	23
F6						24

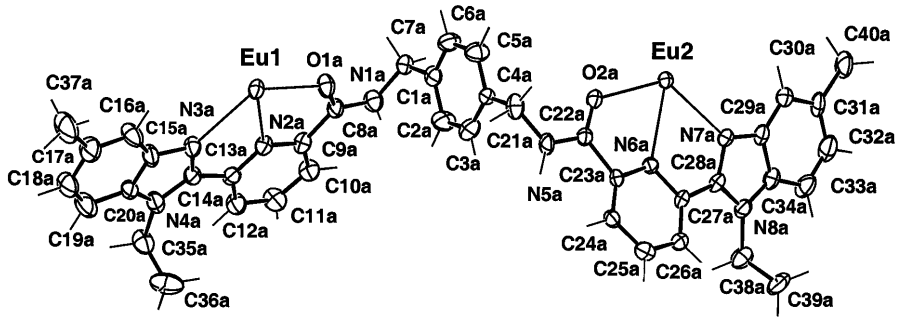
Interplanar angles, strand b

	F2	F3	F4	F5	F6	F7
F1	10	18	87	68	71	59
F2		9	90	59	61	49
F3			83	52	56	45
F4				87	87	84
F5					6	13
F6						13

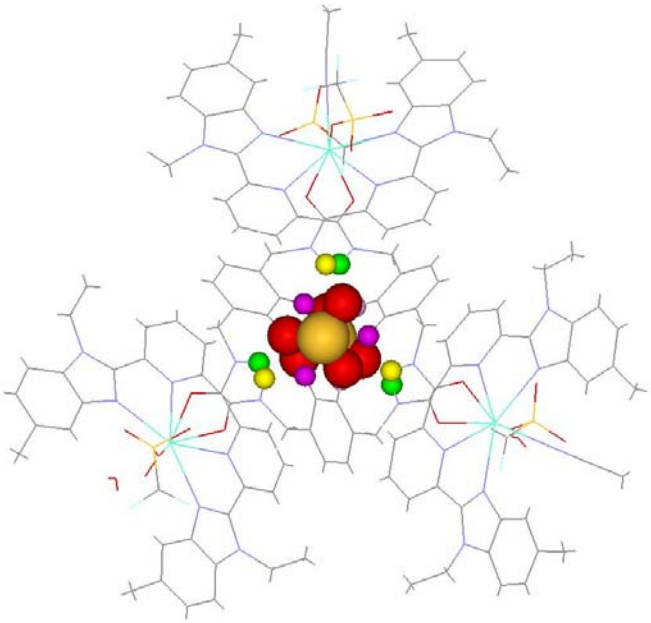
Interplanar angles, strand c

	F2	F3	F4	F5	F6	F7
F1	2	11	89	54	55	51
F2		11	90	55	57	52
F3			81	48	52	47
F4				76	88	90
F5					16	14
F6						5

a)



b)



c)

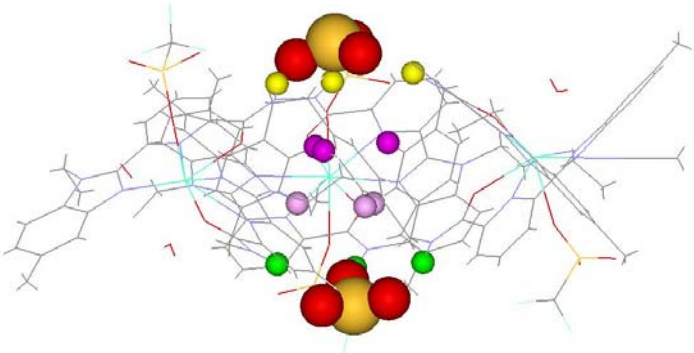


Fig S1 a) Complete numbering scheme used for the ligand strand a in the crystal structure of **1** (atomic numbering for strands b and c follows the same scheme)**.** Views of the $\{[Eu_3(\mathbf{L3})_3(CF_3SO_3)_4(CH_3CN)_2(H_2O)_3](CF_3SO_3)_2\}^{3+}$ cationic aggregate respectively b) along and c) perpendicular to the pseudo-threefold axis highlighting the ionic triflates *j* and *l* capping the two half bowl-shaped cavities. The surface of the bottom cavity is defined by H3a,b,c (pale pink spheres) and H05a,b,c (green spheres). The surface of the top cavity is defined by H2a,b,c (dark pink spheres) and H05a,b,c (yellow spheres).

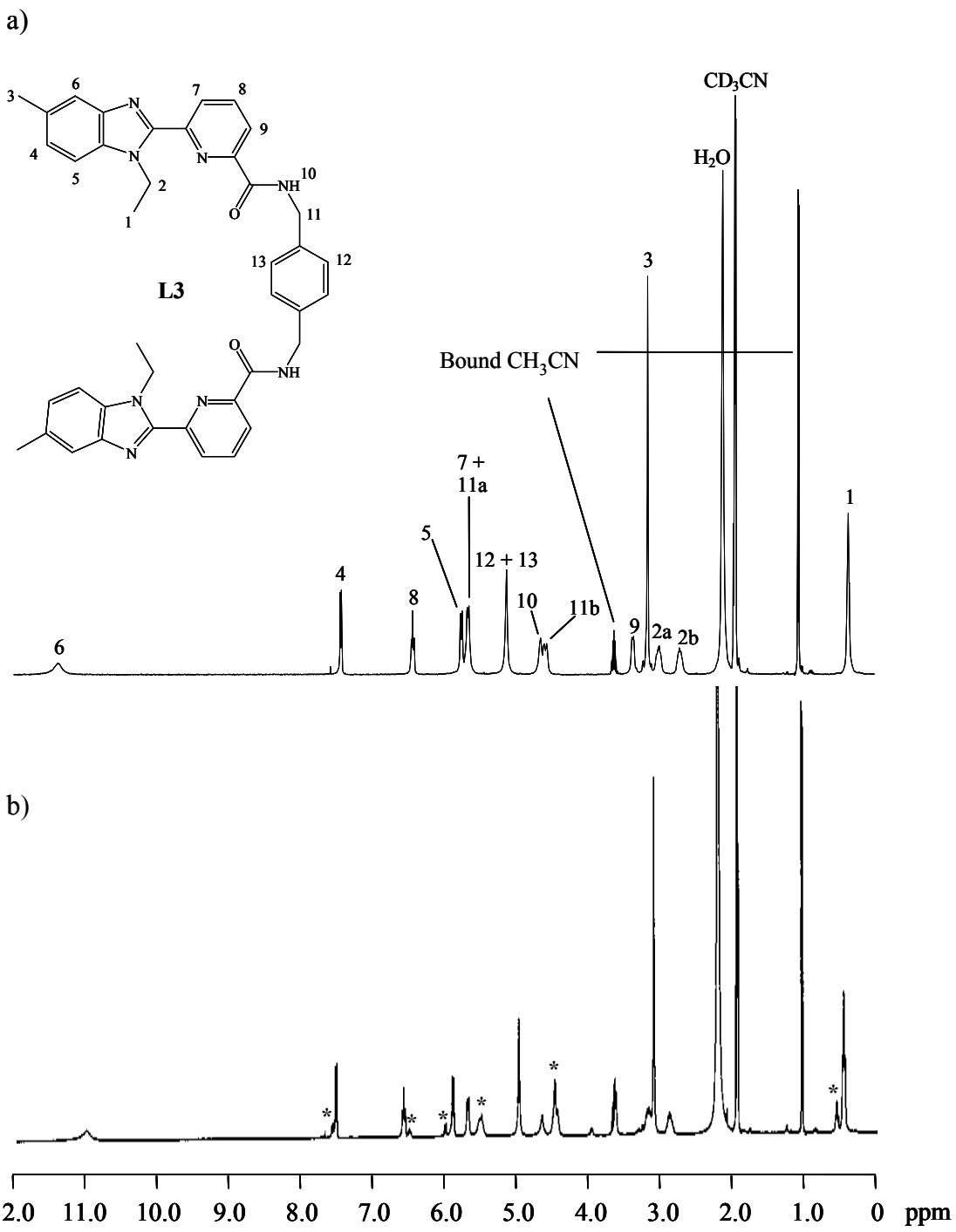


Fig. S2 Numbering scheme for the protons of the ligand **L3** and ^{1}H NMR spectra of $[Eu_3(\mathbf{L3})_3]^{9+}$ in CD_3CN (298 K), a) immediately after dissolution of crystals of **1**, and b) after one day. The * highlight the new species which is slowly formed upon re-equilibration.