# Self-assembly formation of mechanically interlocked [2]- and [3]catenanes using lanthanide ion [Eu(III)] templation and ring closing metathesis reactions

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# **Electronic Supplementary Information**

**ESI.1:** Molecular models of the complex L1<sub>3</sub>.Eu and the catenane resulting from a triple RCM, obtained from calculation in the MM2 force field with Chem3D.



**ESI.2:** MM2 molecular models of the different isomers resulting from a triple RCM, depending on the number of inter- and intra-ligands RCM.



**ESI.3:** Synthesis in 5 steps from the triethylenhglycol of the precursor 2 and synthesis protocols of compound 1-5, L1, L1<sub>3</sub>.Eu and Cat• L2<sub>3</sub>.Eu.



#### 2,6-Pyridinedicarboxylic acid chloride (1):

2,6-Pyridinedicarboxylic acid (5 g, 29.9 mmol) was refluxed overnight in thionylchloride (50 ml). The mixture was reduced to dryness under reduced pressure, before compound **1** was obtained as a white powder in 99% yield (5.97 g). Calculated for C<sub>7</sub>H<sub>3</sub>NO<sub>2</sub>Cl<sub>2</sub>:  $[M+H]^+$  *m/z* = 202.9542; Found: 202.9563;  $\delta_{\rm H}$  (400 MHz, MeOD-D<sub>4</sub>, 298.2 K) 8.39 (2H, d, *J* = 7.56 Hz, Ar-H4), 8.22 (1H, t, *J* = 7.56 Hz, Ar-H2); Selected IR bands (cm<sup>-1</sup>): 1751s (v<sub>CO</sub>).

#### 2-(2-(allyloxy)ethoxy)ethoxy)ethanol (3):

To a solution of triethylene glycol (30g, 200 mmol) in toluene (20 mL) at room temperature, allyl chloride (18.04 mL, 219.7 mmol) and NaOH (16 g, 400 mmol) were added. The resulting mixture was refluxed for 3 days. Upon filtration of a white residue and evaporation of the solvent under reduced pressure, the brown oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with brine (50 mL) and distilled water (50 mL). The resulting orange oil was further purified by silica column chromatography using hexane-EtOAc from 7:3 to 1:1 gradient, yielding a colourless oil (10.38 g, 54.6 mmol, 27.3% yield) HRMS (m/z) (ES<sup>+</sup>) Calculated for C<sub>9</sub>H<sub>19</sub>O<sub>4</sub> [M+H<sup>+</sup>]<sup>+</sup> m/z = 191.1286, Found 191.1286;  $\delta_{\rm H}$  (CDCl3; 400 MHz): 5.95 (m, 1H, CH=CH<sub>2</sub>), 5.28 (m, 2H, CH=C<u>H</u><sub>2</sub>), 4.06 (m, 2H, C<u>H</u><sub>2</sub>CH=CH<sub>2</sub>), 3.62 (m, 12H, CH<sub>2</sub>);  $\delta_{c}$  (CDCl<sub>3</sub>; 100 MHz): 134.6, 117.1, 72.5, 70.2-70.5, 61.6.; IR  $\nu_{max}$  (cm<sup>-1</sup>) = 3376, 2870, 1648, 1350, 1245, 1116, 1064, 934, 885.

#### 2-(2-(allyloxy)ethoxy)ethoxy)ethyl-4-methylbenzenesulfonate (4):

**3** (500 mg, 2.6 mmol) and 5 equivalents of TsCl (2.5 g, 13 mmol) were dissolved in dichloromethane (20 mL) before the resulting mixture was stirred for 15 minutes. To that solution, pyridine (2.13 mL, 26 mmol) was added drop wise before the resulting mixture was stirred at room temperature for 48h. The pyridine was quenched with 1M HCl (1 mL) before the solvents were removed under reduced pressure. The resulting mixture was extracted with CH<sub>3</sub>Cl (50 mL) before the organic layer was washed with H<sub>2</sub>O (2×50 mL) and dried over MgSO<sub>4</sub>. Compound **4** was isolated as a yellow oil in 45% yield (404 mg, 1.17 mmol), after purification *via* silica column chromatography using CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (9-1) as eluent. HRMS (m/z) (ES<sup>+</sup>) Calculated for C<sub>16</sub>H<sub>24</sub>O<sub>6</sub>S [M+Na<sup>+</sup>]<sup>+</sup> m/z = 367.1191, Found 367.1132;  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 400 MHz): 7.79 (d, 2H, <sup>3</sup>J = 8.0 Hz, Ar-H), 7.33 (d, 2H, <sup>3</sup>J = 8.0 Hz, Ar-H), 5.89 (m, 1H, C<u>H</u>=CH<sub>2</sub>), 5.28 (m, 1H, CH=C<u>H<sub>2</sub></u>), 5.18 (m, 1H, CH=C<u>H<sub>2</sub></u>), 4.16 (m, 2H, C<u>H</u><sub>2</sub>-OTs), 4.01 (m, 2H, C<u>H</u><sub>2</sub>CH=CH<sub>2</sub>), 3.68-3.59 (m, 12H, CH<sub>2</sub>), 2.44 (s, 3H, Ar-C<u>H<sub>3</sub></u>);  $\delta_{\rm c}$  (CDCl<sub>3</sub>; 100 MHz): 144.3, 134.2, 132.5, 129.38, 127.5, 117.1, 71.8, 70.3, 70.2, 68.9, 68.8, 68.2, 21.2; IR v<sub>max</sub> (cm<sup>-1</sup>) = 3389, 2876, 1598, 1452, 1351, 1211, 1188, 1120, 1095, 1033, 916, 816, 683, 662.

#### 3-(2-(2-(2-azidoethoxy)ethoxy)propen-1-ene (5):

#### 3-(2-(2-(2-aminoethoxy)ethoxy)propen-1-ene (2):



To a solution of **5** (1.24 g, 5.5 mmol) in THF (50 mL) at 0°C, PPh<sub>3</sub> (1.66 g, 6.1 mmol) was added portionwise and the resulting mixture was

stirred at room temperature for 12h. The resulting oil was dissolved in H<sub>2</sub>O and washed with toluene (2 × 20mL). **2** was obtained as a yellow oil after evaporation of the aqueous layer under reduced pressure (759 mg, 4.0 mmol, 73%).  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 400 MHz): 5.89 (m, 1H, C<u>H</u>=CH<sub>2</sub>), 5.28 (m, 1H, CH=C<u>H<sub>2</sub></u>), 5.16 (m, 1H, CH=C<u>H<sub>2</sub></u>), 4.01 (m, 2H, C<u>H</u><sub>2</sub>CH=CH<sub>2</sub>), 3.65-3.49 (m, 12H, CH<sub>2</sub>), 2.85 (m, 2H, H<sub>2</sub>N-C<u>H<sub>2</sub></u>);  $\delta_{\rm c}$  (CDCl<sub>3</sub>; 100 MHz): 134.3, 116.7, 114.8, 71.8, 70.3, 70.2, 69.6, 69.0, 50.2, 42.3; IR  $\nu_{\rm max}$  (cm<sup>-1</sup>)= 3360, 2666, 1665, 1565, 1445, 1348, 1297, 1248, 1091, 995, 924, 881, 818.

## *N*,*N*'-bis(2-(2-(allyloxy)ethoxy)ethoxy)pyridine-2,6-dicarboxamide (L1):

To a solution of **1** (300 mg, 1.5 mmol) and triethylamine (270 mg, 6 mmol, 4 eq) at 0°C in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added a solution of **2** (612 mg, 3.2 mmol, 2.2 eq) and triethylamine (148 mg, 1.6 mmol, 1.1 eq) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) dropwise over a period of 15 min. The resulting mixture was allowed to reach room temperature before being stirred for 48h. The solvent was removed under reduced pressure before the resulting brown oil was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with distilled H<sub>2</sub>O (2 × 50 mL). The organic layer was dried over MgSO<sub>4</sub> before the solvent was removed and L1 was then obtained as an yellow oil in 48% yield (360 mg, 0.7 mmol). HRMS (m/z) (ES<sup>+</sup>) Calculated for C<sub>25</sub>H<sub>39</sub>O<sub>8</sub>N<sub>3</sub> [M+Na<sup>+</sup>]<sup>+</sup> m/z = 532.2635, Found 532.2812;  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 400 MHz):8.57 (s, 2H, N<u>H</u>), 8.35 (d, <sup>3</sup>J = 7.6 Hz, 1H, Pyr-H), 8.03 (t, <sup>3</sup>J = 8.2 Hz, 2H, Pyr-H), 5.88 (m, 2H, C<u>H</u>=CH<sub>2</sub>), 5.26 (m, 2H, CH=C<u>H<sub>2</sub></u>), 5.15 (m, 2H, CH=C<u>H<sub>2</sub></u>), 3.98 (m, 2H, C<u>H</u>=CH<sub>2</sub>), 3.72-3.66 (m, 20H, CH<sub>2</sub>), 3.59 (m, 2H, HN-C<u>H<sub>2</sub></u>);  $\delta_{\rm c}$  (CDCl<sub>3</sub>; 100 MHz): 169.4, 151.3, 134.6, 126.5, 117.2, 72.0, 70.3, 70.2, 70.0, 69.2, 67.3, 45.4, 39.3; IR v<sub>max</sub> (cm<sup>-1</sup>)= 3550, 3320, 2867, 1665, 1532, 1445, 1349, 1247, 1093, 998, 926, 846, 749, 679.

## Complex, L1<sub>3</sub>.Eu:

Ligand L1 (50 mg, 0.098 mmol) and Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (19.6 mg; 0.032 mmol) were refluxed in CH<sub>3</sub>CN (10 mL) for 12h. The solvent was removed under reduced pressure. The resulting concentrated solution was poured over diethylether before complex L1<sub>3</sub>.Eu was collected in 32% yield as pale yellow oil (22.2 mg; 0.012 mmol).  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 600 MHz): 8.53; 8.37; 8.05; 7.36; 5.88; 5.29; 4.04; 3.74-3.59; 3.52. IR  $\nu_{\rm max}$  (cm<sup>-1</sup>): 3510, 3285; 1667; 1547; 1346; 1260; 1093; 1005; 980; 937; 752; 677.

#### Catenation of L1<sub>3</sub>.Eu (Cat•L2<sub>3</sub>.Eu):

Anhydrous complex L1<sub>3</sub>.Eu (26 mg, 0.013 mmol) was dissolved in distilled CH<sub>2</sub>Cl<sub>2</sub> (20 mL), under an inert atmosphere. To this solution the  $2^{nd}$  generation Grubb's catalyst (3.1 mg, 3.6 ×10<sup>-3</sup> mmol, 0.3 eq) was added drop wise over a period of 5 minutes. The resulting mixture was stirred at room temperature for 3 days under an inert atmosphere. The CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure and the resulting brown oil was dissolved in H<sub>2</sub>O. The aqueous layer was washed with ethyl acetate (20 mL) before the H<sub>2</sub>O was removed under reduced pressure. The resulting orange oil was triturated in CH<sub>2</sub>Cl<sub>2</sub> and Cat•L2<sub>3</sub>.Eu was obtained as a crude white solid (7 mg). The dichloromethane was removed under reduced pressure and the compound Cat•L2<sub>3</sub> was obtained as crude yellow oil (10 mg).

**Cat**•L2<sub>3</sub>.**Eu:** HRMS: Calculated for  $C_{70}H_{106}N_9F_9O_{28}SEu [M^{3+} + CF_3SO_3^- + OH^-]^+ 1762.6044$ , Found 1761.6688  $\delta_H$  (CDCl<sub>3</sub>; 600 MHz): 8.93; 8.34; 7.02; 7.36; 5.88; 5.29; 4.06; 3.73-3.69; 3.50. IR  $\nu_{max}$  (cm<sup>-1</sup>): 3510, 3285; 1667; 1547; 1346; 1260; 1093; 1005; 980; 937; 752; 677.

**Cat**•L2<sub>3</sub>: HRMS: Calculated for C<sub>69</sub>H<sub>105</sub>N<sub>9</sub>O<sub>24</sub> [M + Na<sup>+</sup>]<sup>+</sup> 1466.7170, Found 1466.7152  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 600 MHz): 8.30; 8.15; 5.82; 4.00; 5.88; 5.29; 4.06; 3.73-3.71; 3.24. IR  $\nu_{\rm max}$  (cm<sup>-1</sup>): 3552, 3314; 2865; 1665; 1532; 1445; 1345; 1310; 1245; 1099; 998; 852, 740.

#### Macrocyle L2:



Ligand L1 (50.8 mg, 0.1 mmol) was dissolved in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (100 mL), under inert atmosphere. To this solution the 2<sup>nd</sup> generation Grubb's catalyst (12.7 mg, 1.4 ×10<sup>-3</sup> mmol, 0.14 eq) was added drop wise over a period of 5 minutes. The CH<sub>2</sub>Cl<sub>2</sub> is removed under reduced pressure and the resulting mixture is washed with H<sub>2</sub>O (2×50 mL). The organic layer was washed over MgSO<sub>4</sub> and L2 was obtained as brown oil (38.4 mg, 0.08 mmol, 80%). HRMS:

Calculated for C<sub>23</sub>H<sub>35</sub>N<sub>3</sub>O<sub>8</sub> [M + Na<sup>+</sup>]<sup>+</sup>: 504.2322, Found 504.2316;  $\delta_{\rm H}$  (CDCl<sub>3</sub>; 400 MHz): 8.57 (s, 2H, N<u>H</u>), 8.34 (d, <sup>3</sup>*J* = 7.7 Hz, 2H, Pyr-H), 8.02 (t, <sup>3</sup>*J* = 7.8 Hz, 1H, Pyr-H), 5.89 (s, 2H, C<u>H</u>=C<u>H</u>), 4.07 (m, 4H, C<u>H</u><sub>2</sub>CH=CH), 3.74-3.66 (m, 22H, CH<sub>2</sub>), 3.59 (m, 2H, HN-C<u>H</u><sub>2</sub>);  $\delta_{\rm c}$  (CDCl<sub>3</sub>; 100 MHz): 163.6, 148.4, 138.2, 128.9, 124.2, 70.2, 70.1, 69.9, 69.7, 68.6, 39.0, 29.2; IR  $\nu_{\rm max}$  (cm<sup>-1</sup>) = 3550, 3314, 2864, 1663, 1534, 1446, 1349, 1305, 1245, 1176, 1098, 999, 847, 749, 662.

**ESI.4:** Absorption, excitation ( $\lambda_{em} = 545$  and 615 nm) and Emission ( $\lambda_{ex} = 281$  nm) spectra of L1 and the resulting Eu<sup>3+</sup> and Tb<sup>3+</sup> in acetonitrile at C =  $2 \times 10^{-5}$  M



**ESI.5:** Absorption, excitation ( $\lambda_{em} = 545$  and 615 nm) and Emission ( $\lambda_{ex} = 281$  nm) spectra of L1 and the resulting Eu<sup>3+</sup> and Tb<sup>3+</sup> in acetonitrile at C =  $2 \times 10^{-5}$  M





**ESI.6:** Evolution of the absorption and delayed emission spectra of a solution of L1 ( $2 \times 10^{-5}$  M in acteonitrile) upon the addition of Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>

**ESI.6:** Job's plots experiments, performed by varying the molar fraction of  $Eu(CF_3SO_3)_3$  in solution ( $C_{tot} = 2 \times 10^{-5}$  M in acetonitrile)





**ESI.7:** Evolution of the absorption and delayed emission spectra of a solution of L1 ( $2 \times 10^{-5}$  M in acteonitrile) upon the addition of Tb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>





**ESI.8:** Job's plots experiments, performed by varying the molar fraction of  $Tb(CF_3SO_3)_3$  in solution ( $C_{tot} = 2 \times 10^{-5}$  M in acetonitrile)

**ESI.9:** Speciation diagram and fit resulting from the data obtained from the UV-vis titration of L1 vs  $Eu(CF_3SO_3)_3$ 



**ESI.10:** Speciation diagram and fit resulting from the data obtained from the UV-vis titration of L1 vs  $Tb(CF_3SO_3)_3$ 



ESI.11: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) of L1 and L2 and Mass-spectrum obtained in ESMS for L2



**ESI.12:** <sup>1</sup>H-NMR (MeOD-D<sub>4</sub>, 400 MHz) of Cat•L2<sub>3</sub>



**ESI.13:** MALDI-ToF (DCTB matrix) Mass-Spectrum of the Cat•L2<sub>3</sub> compound resulting from an inter-ligand RCM (inset: calculated spectra for Cat•L2<sub>3</sub> + Na<sup>+</sup> and Cat•L2<sub>3</sub> + K<sup>+</sup>)



**ESI.14:** MALDI-ToF (DCTB matrix) Mass-Spectrum of the Cat•L2<sub>3</sub>.Eu compound resulting from an intra-ligand RCM.



**ESI.15:** MS.MS spectra obtained for the fragment found at m/z = 1280.4 (Top) and 1761.6 (Bottom) for the [2]-Cat•L2<sub>2</sub>.Eu and [3]-Cat•L2<sub>3</sub>.Eu respectively during the MALDI.ToF analyses







**ESI.17:** Mass-spectrum obtained after stirring a solution of L1<sub>3</sub>.Eu with 1 equivalent of DTPA for 30 minutes



**ESI.18:** Mass-spectrum obtained after stirring a solution of **Cat**•L2<sub>3</sub>.Eu with 1 equivalent of DTPA for 30 minutes



**ESI.19:** Mass-spectrum (MALDI-ToF) obtained after stirring a solution of L2 with 0.3 equivalent of  $Eu(CF_3SO_3)_3$  for 30 minutes



**ESI.20:** Mass-spectrum (MALDI-ToF) obtained after stirring a solution of L2 + 0.3 Eu with 1 equivalent of DTPA for 30 minutes

