

## **Electronic Supplementary Information**

# Redox divergent conversion of a [2]rotaxane into two distinct degenerate partners with different shuttling dynamics

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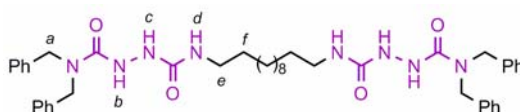
## 1. General Experimental Section

Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. HPLC grade solvents (Scharlab) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Column chromatography was carried out using silica gel (60 Å, 70-200 µm, SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminum cards (0.25 mm thick, with fluorescent indicator 254 nm, Fluka) and observed under UV light. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded as nujol emulsions on a Nicolet Impact 400 spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded at 298 K on a Bruker Avance 300, 400 MHz and 600 MHz instruments. <sup>1</sup>H NMR chemical shifts are reported relative to Me<sub>4</sub>Si and were referenced via residual proton resonances of the corresponding deuterated solvent whereas <sup>13</sup>C NMR spectra are reported relative to Me<sub>4</sub>Si using the carbon signals of the deuterated solvent. Signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the synthesized compounds were assigned with the aid of DEPT, APT, or two-dimensional NMR experiments (COSY, HMQC and HMBC). Abbreviations of coupling patterns are as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. Mass spectra were recorded with Agilent 5973 (EI), Agilent VL (ESI) and HPLC/MS TOF 6220 mass spectrometers. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

## 2. Synthesis of the bis(hydrazodicarboxamide) [4H]-3

To a stirred solution of 1,12-dodecanediamine (0.27g, 1.34 mmol) in  $\text{CHCl}_3$  (25 mL) were added phenyl *N,N*-dibenzylaminocarbonylhydrazinecarboxylate (**2**) (1.0 g, 2.77 mmol) and triethylamine (0.6 mL, 3.96 mmol) were added. The reaction mixture was stirred for 15 hours at reflux temperature after which time the reaction was concentrated under reduced pressure and purified by column chromatography on silica gel using a  $\text{CHCl}_3/\text{MeOH}$  (97/3) mixture as eluent to give the title product as a white solid (0.73 g, 71%).

$N^1, N^{1'}$ -(dodecane-1,12-diyl)bis( $N^2, N^2$ -dibenzylhydrazine-1,2-dicarboxamide), [4H]-3

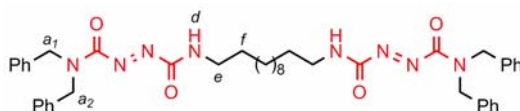


Yield= 71 %; M.p. 182-184 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.40-7.05 (m, 22H, 20Ph + 2 NH), 5.69 (br s, 1H, NH), 4.47 (s, 8H,  $\text{CH}_a$ ), 3.04 (t,  $J$  = 7.2 Hz, 4H,  $\text{CH}_e$ ), 1.45-1.29 (m, 4H,  $\text{CH}_f$ ), 1.28-1.12 (m, 16H, alkyl chain);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.78 (CO), 159.44 (CO), 136.92 ( $\text{C}_{Ar}$ ), 128.93( $\text{C}_{Ar}\text{H}$ ), 127.71( $\text{C}_{Ar}\text{H}$ ), 127.50( $\text{C}_{Ar}\text{H}$ ), 50.19 ( $\text{C}_a\text{H}_2$ ), 40.26 ( $\text{C}_e\text{H}_2$ ), 29.95, 29.28, 29.25, 29.17, 26.80; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{59}\text{N}_8\text{O}_4$  [ $\text{M} + \text{H}$ ] $^+$  763.46593, found 763.46550.

## 3. Synthesis of the bis(azodicarboxamide) 3

To a stirred solution of the bis(hydrazodicarboxamide) [4H]-3 (0.58 g, 0.77 mmol) in dichloromethane (20 mL) were added pyridine (150  $\mu\text{L}$ , 1.69 mmol) and *N*-bromosuccinimide (0.29 g, 1.61 mmol). The resulting orange solution was stirred at room temperature for 1 h. Then the reaction mixture was diluted with dichloromethane (20 mL) and sequentially washed with water (40 mL), 5% aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (35 mL) and saturated solution of  $\text{NaHCO}_3$  (2 x 35 mL). The organic phase was dried with anhydrous  $\text{MgSO}_4$ , and concentrated *in vacuo* to afford a crude material which was purified by column chromatography on silica gel eluting with a  $\text{CHCl}_3/\text{MeOH}$  (98/2) mixture as eluent to give the title product as an orange solid (0.50 g, 85%).

(1*E*,1'*E*)- $N^1, N^{1'}$ -(dodecane-1,12-diyl)bis( $N^2, N^2$ -dibenzylidiazene-1,2-dicarboxamide), **3**



Yield= 85 %; M.p. 118-120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.40-7.29 (m, 16H, Ph), 7.18-7.14 (m, 4H, Ph), 6.54 (t, 2H, *J*=5.4 Hz, NH<sub>d</sub>), 4.65 (s, 4H, CH<sub>a1</sub>), 4.48 (s, 4H, CH<sub>a2</sub>), 3.45 (dd, 4H, *J*=13.3, 7.0 Hz, CH<sub>e</sub>), 1.68-1.57 (m, 4H, CH<sub>f</sub>), 1.41-1.20 (m, 16H, alkyl chain); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 162.37 (CO), 159.44 (CO), 135.44 (C<sub>Ar</sub>), 135.34 (C<sub>Ar</sub>), 129.00 (x 2), 128.63, 128.25, 128.21, 127.79, 49.18 (C<sub>a1</sub>/C<sub>a2</sub>), 49.11 (C<sub>a1</sub>/C<sub>a2</sub>), 41.21, 29.80, 29.49, 29.30, 29.22, 26.80; HRMS (ESI) calcd for C<sub>44</sub>H<sub>54</sub>KN<sub>8</sub>O<sub>4</sub> [M + K]<sup>+</sup> 797.39051, found 797.39030.

#### 4. Preparation of benzylic amide macrocycle containing [2]rotaxanes 1b and [2H]-1b and shuttles 4 and [4H]-4

##### Method A. Assembly of [2]rotaxanes

The thread (1 equiv.) and Et<sub>3</sub>N (24 equiv.) in anhydrous CHCl<sub>3</sub> (250 mL) were stirred vigorously whilst solutions of *p*-xylylenediamine (12 equiv.) in anhydrous CHCl<sub>3</sub> (40 mL) and the corresponding acid dichloride (12 equiv.) in anhydrous CHCl<sub>3</sub> (40 mL) were simultaneously added over a period of 4 h using motor-driven syringe pumps. After a further 4 h the resulting suspension was filtered through a Celite pad and the solvent removed under reduced pressure. The resulting solid was subjected to column chromatography (silica gel) using CHCl<sub>3</sub>/MeOH (95/5) mixture as eluent to give the [2]rotaxanes.

##### Method B. Reduction of 1,2-azodicarboxamide [2]rotaxanes

To a degassed solution (or suspension) of the corresponding 1,2-azodicarboxamide [2]rotaxane in chloroform (10 mL) was added hydrazine monohydrate (1 or 2 equiv) in one go. The orange solution was transformed to a colourless solution in less than 5-10 min. The reaction mixture was dried with a high vacuum pump to afford the corresponding 1,2-hydrazidedicarboxamide [2]rotaxane as a colorless solid. Occasionally it was necessary to purify the crude material by column chromatography using a solvent gradient of CHCl<sub>3</sub> to CHCl<sub>3</sub>/MeOH (95/5).

##### Method C. Oxidation of 1,2-hydrazodicarboxamide [2]rotaxanes

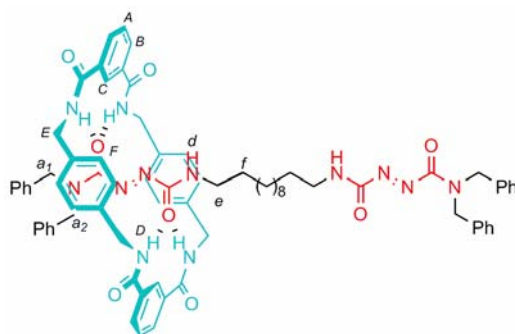
To a solution (or suspension) of the corresponding 1,2-hydrazodicarboxamide [2]rotaxane in dichloromethane (15 mL) were added pyridine (1.1 equiv) and *N*-bromosuccinimide (1 equiv). The resulting orange solution was stirred at room temperature for 30 min. Then the reaction mixture was diluted with dichloromethane (10 mL) and sequentially washed with water (25 mL), 5% aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL) and saturated solution of NaHCO<sub>3</sub> (2 x 20 mL). The organic phase was dried with anhydrous MgSO<sub>4</sub>, and concentrated *in vacuo* to afford a crude material which was purified by column chromatography on silica gel eluting with a CHCl<sub>3</sub>/MeOH (98/2) mixture as eluent to give the title product as an orange solid.

#### 4.1 Single-binding site rotaxanes **1b** and [2H]-**1b**

Rotaxanes **1b** and [2H]-**1b** were synthesized as described in our previous publication, see: J. Berná, M. Alajarín and R.-A. Orenes, *J. Am. Chem. Soc.*, 2010, **132**, 10741-10747.

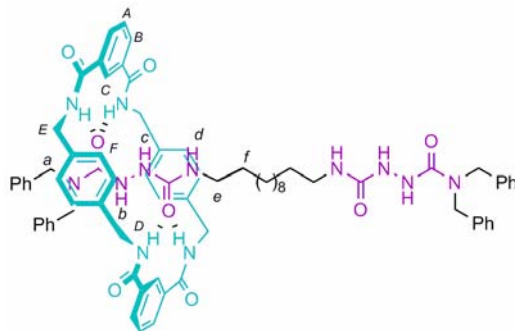
#### 4.2 Two-binding site [2]rotaxanes **4** and [4H]-**4**

##### Bis(azodicarboxamide) rotaxane **4**



Yield = 28% (Met. A), 79% (Met C);; M.p. 169-171 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.11 (br s, 2H, CH<sub>C</sub>), 8.07 (dd, 4H, *J*=7.8, 1.4 Hz, CH<sub>B</sub>), 7.65 (br s, 2H, NH<sub>d</sub>), 7.46 (t, 2H, *J*=7.7 Hz, CH<sub>A</sub>), 7.37-7.31 (m, 6H, Ph), 7.28- 7.17 (m, 14H, 10Ph + 4NH<sub>D</sub>), 6.95-6.86 (m, 4H, Ph), 6.89 (s, 8H, CH<sub>F</sub>), 4.45 (s, 4H, CH<sub>a1</sub>), 4.44 (s, 4H, CH<sub>a2</sub>), 4.40 (d, 8H, *J*=4.9 Hz), 3.37 (dd, 4H, *J*=13.3, 6.7 Hz, CH<sub>e</sub>) 1.71-1.58 (m, 4H, CH<sub>f</sub>), 1.42-1.20 (m, 16H, alkyl chain); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 8.09 (br s, 2H, CH<sub>C</sub>), 8.03 (dd, 4H, *J*=7.8, 1.5 Hz, CH<sub>B</sub>), 7.88 (br s, 2H, NH<sub>d</sub>), 7.46 (t, 2H, *J*=7.7 Hz, CH<sub>A</sub>), 7.39-7.16 (m, 20H, 16Ph + 4NH<sub>D</sub>), 7.01-6.86 (m, 4H, Ph), 6.95 (s, 8H, CH<sub>F</sub>), 4.46 (s, 8H, CH<sub>a</sub>), 4.40 (d, 8H, *J*=4.9 Hz, CH<sub>E</sub>), 3.37 (dd, 4H, *J*=13.3, 6.6 Hz, CH<sub>e</sub>), 1.71-1.56 (m, 4H, CH<sub>f</sub>), 1.42-1.15 (m, 16H, alkyl chain); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 166.44 (CO macrocycle), 159.25 (CO), 157.73 (CO), 137.29 (C<sub>Ar</sub>), 135.20 (C<sub>Ar</sub>), 134.80 (C<sub>Ar</sub>), 133.69 (C<sub>Ar</sub>), 131.55, 129.15, 129.08, 128.98, 128.65, 128.56, 128.31, 127.27, 123.91, 49.73 (CH<sub>a</sub>), 44.17 (CH<sub>E</sub>), 41.57 (CH<sub>e</sub>), 29.38, 29.15, 26.90. HRMS (ESI) calcd for C<sub>76</sub>H<sub>83</sub>N<sub>12</sub>O<sub>8</sub> [M + H]<sup>+</sup> 1291.6457, found 1291.6474.

##### Bis(hydrazodicarboxamide) rotaxane [4H]-**4**



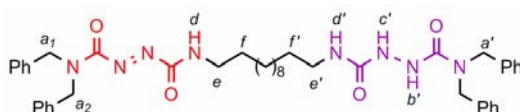
Yield= 95% (Met B); M.p. 264-266 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.37 (br s, 2H, CH<sub>C</sub>), 8.14 (br s, 4H, NH<sub>D</sub>), 8.09 (d, 4H, *J*=7.7 Hz, CH<sub>B</sub>), 7.45 (t, 2H, *J*=7.7 Hz, CH<sub>A</sub>), 7.36-7.17 (m, 16H, Ph), 7.05 (m, 4H, Ph), 7.03 (s, 8H, CH<sub>F</sub>), 6.43 (br s, 2H, NH), 5.52 (br s, 2H, NH), 4.41 (br s, 4H, CH<sub>E</sub>), 4.32 (br s, 4H, CH<sub>a</sub>), 2.81 (br s, 4H, CH<sub>e</sub>), 1.19-1.11 (m, 20H, alkyl chain); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 166.99 (CO macrocycle), 159.39 (CO), 158.24(CO), 137.27 (C<sub>Ar</sub>), 136.61 (C<sub>Ar</sub>), 133.97 (C<sub>Ar</sub>), 131.27, 129.13, 129.02 (x2), 127.91, 127.14, 125.52, 50.19 (CH<sub>a</sub>), 44.61 (CH<sub>E</sub>), 40.23 (CH<sub>e</sub>), 29.73, 28.85 (x3), 26.53; HRMS (ESI) calcd for C<sub>76</sub>H<sub>87</sub>N<sub>12</sub>O<sub>8</sub> [M + H]<sup>+</sup> 1295.67698, found 1295.68050.

## 5. Preparation of compounds with an intermediate oxidation level

### 5.1. Synthesis of the thread [2H]-3 and [2]rotaxane [2H]-4

#### Azo-hydrazo thread [2H]-3

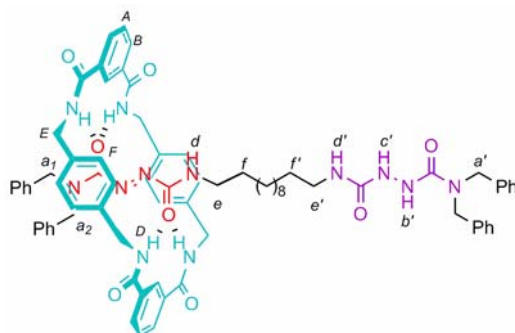
(*E*)-*N*<sup>1</sup>,*N*<sup>1</sup>-dibenzyl-*N*<sup>2</sup>-(12-(2-(dibenzylcarbamoyl)hydrazinecarboxamido)dodecyl)diazene-1,2-dicarboxamide ([2H]-3)



To a stirred solution of the bis(hydrazodicarboxamide) [4H]-3 (100 mg, 0.13 mmol) cooled in dichloromethane (20 mL) at -20°C were added pyridine (11 mg, 0.14 mmol) and *N*-bromosuccinimide (23 mg, 0.13 mmol). The resulting orange solution was stirred at room temperature for 30 min. Then the reaction mixture was diluted with dichloromethane (10 mL) and washed with water (2 x 15 mL). The organic phase was dried with anhydrous MgSO<sub>4</sub>, and concentrated *in vacuo* to afford a crude material which was purified by column chromatography on silica gel eluting with a CHCl<sub>3</sub>/MeOH (98/2) mixture as eluent to give the title product as an orange solid (43 mg, 41 %). M.p. 131-133 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 7.40-7.27 (m, 14H, Ph),

7.26-7.23 (m, 4H, Ph), 7.20-7.17 (m, 2H, Ph), 7.15 (t, 2H,  $J=5.3$  Hz,  $\text{NH}_d$ ), 6.64 (br s, 2H,  $\text{NH}_b$  +  $\text{NH}_c$ ), 5.28 (t, 2H,  $J=5.6$  Hz,  $\text{NH}_d$ ), 4.61 (s, 2H,  $\text{CH}_{a1}$ ), 4.51 (s, 4H,  $\text{CH}_{a'}$ ), 4.49 (s, 2H,  $\text{CH}_{a2}$ ), 3.38 (dd, 2H,  $J=13.2, 7.0$  Hz;  $\text{CH}_e$ ), 3.06 (dd, 2H,  $J=13.2, 6.9$  Hz,  $\text{CH}_e$ ), 1.61 (dt, 2H,  $J=14.6, 7.4$  Hz,  $\text{CH}_f$ ), 1.43-1.21 (m, 18H, alkyl chain);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 162.15$  (CO), 159.51 (CO), 159.28 (2xCO), 136.66 ( $C_{Ar}$ ), 135.38 ( $C_{Ar}$ ), 129.60-126.90 ( $C_{ArS}$ ), 50.55 ( $C_a$ ), 49.34 ( $C_{a1}/C_{a2}$ ), 49.18 ( $C_{a1}/C_{a2}$ ), 41.32, 40.18, 30.72- 26.09 (alkyl chain); HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{54}\text{KN}_8\text{O}_4$  [ $\text{M} + \text{K}$ ] $^+$  797.39051, found 797.39030.; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{56}\text{N}_8\text{NaO}_4$  [ $\text{M} + \text{Na}$ ] $^+$  783.43222, found 783.43180.

### Azo-hydrazo rotaxane [2H]-4



Rotaxane [2H]-4 was obtained from [4H]-4 (60 mg, 0.046 mmol) following the experimental procedure employed to prepare the thread [4H]-3. The solid crude was subjected to column chromatography on silica gel using  $\text{CHCl}_3/\text{MeOH}$  (95/5) mixture as eluent to give the title product as an orange solid (31 mg, 0.024 mmol, 52%). Alternatively [2H]-4 was obtained in 39% yield by partial reduction with hydrazine at  $-10^\circ\text{C}$  of rotaxane 4. M.p. 242-246  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.86$  (br s, 1H,  $\text{NH}_d$ ), 8.12 (br s, 2H,  $\text{CH}_C$ ), 8.05 (dd, 2H,  $J=7.8, 1.2$  Hz,  $\text{CH}_B$ ), 7.50-7.38 (m, 6H,  $4\text{NH}_D + 2\text{CH}_A$ ), 7.37-7.25 (m, 8H, Ph), 7.24-7.10 (m, 10H, Ph), 6.91 (s, 8H,  $\text{CH}_F$ ), 6.90 (br s, 1H, NH) 6.83-6.77 (m, 2H, Ph), 6.19 (br s, 1H, NH), 4.91 (br s, 1H, NH), 4.51 (s, 4H,  $\text{CH}_{a'}$ ), 4.49 (dd, 4H,  $J=14.2, 4.4$  Hz,  $\text{CH}_{E'}$ ), 4.45 (s, 2H,  $\text{CH}_{a1}$ ), 4.35 (s, 2H,  $\text{CH}_{a2}$ ), 4.31 (dd, 4H,  $J=14.2, 4.4$  Hz,  $\text{CH}_{E'}$ ), 3.33 (dd, 2H,  $J=13.8, 6.9$  Hz,  $\text{CH}_e$ ), 2.93-2.73 (m, 2H,  $\text{CH}_{e'}$ ), 1.74-1.59 (m, 2H,  $\text{CH}_f$ ), 1.46-1.07 (m, 18H, alkyl chain);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 166.64$  (CO macrocycle), 159.47 (CO), 159.06 (CO), 158.34 (CO), 158.30 (CO), 137.23 ( $C_{Ar}$ ), 136.97 ( $C_{Ar}$ ), 135.10 ( $C_{Ar}$ ), 134.48 ( $C_{Ar}$ ), 133.80 ( $C_{Ar}$ ), 131.45, 129.37, 129.14, 129.01, 128.91, 128.75, 128.30, 127.87, 127.36, 126.88, 123.98, 50.53 ( $\text{CH}_a$ ), 50.11 ( $\text{CH}_a$ ), 50.01 ( $\text{CH}_a$ ), 44.15 ( $\text{CH}_E$ ), 41.97 ( $\text{CH}_e$ ), 39.83 ( $\text{CH}_{e'}$ ), 29.60, 29.38, 29.14, 28.86, 28.84, 28.70, 28.62, 28.56, 26.76, 26.22;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 8.62$  (br s, 1H,  $\text{NH}_d$ ), 8.15 (br s, 2H,  $\text{CH}_C$ ), 8.09-7.90 (m, 4H), 7.44 (t, 2H,  $J=7.7$  Hz,  $\text{CH}_A$ ), 7.43 (br s, 4H,  $\text{NH}_D$ ) 7.39-7.11 (m, 18H, Ph), 6.95 (s, 8H,  $\text{CH}_F$ ), 6.93 (br s, 1H, NH), 6.90-6.79 (m, 2H, Ph),



6.33 (br s, 1H, NH), 5.19 (br s, 1H, NH), 4.49 (s, 4H, CH<sub>a</sub>'), 4.46 (s, 2H, CH<sub>al</sub>), 4.45 (dd, 4H, *J*=14.1, 4.3 Hz, CH<sub>E</sub>), 4.37 (s, 2H, CH<sub>a2</sub>), 4.32 (dd, 1H, *J*=14.1, 4.3 Hz, CH<sub>E</sub>'), 3.33 (dd, 2H, *J*=13.5, 6.7 Hz, CH<sub>e</sub>), 2.89 (dd, 2H, *J*=8.1, 5.0 Hz, CH<sub>e</sub>'), 1.67 (dd, 2H, *J*=14.2, 7.2 Hz, CH<sub>f</sub>), 1.52–1.00 (m, 18H, alkyl chain); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 166.81 (CO macrocycle), 159.95 (CO), 159.68 (CO), 159.60 (CO), 158.90 (CO), 137.80 (C<sub>Ar</sub>'), 137.69 (C<sub>Ar</sub>'), 135.82 (C<sub>Ar</sub>'), 135.26 (C<sub>Ar</sub>'), 134.46 (C<sub>Ar</sub>'), 131.58, 129.71, 129.43, 129.33, 129.25, 129.19, 129.09, 128.97, 128.55, 128.13, 127.78, 127.52, 124.76, 50.82 (CH<sub>a</sub>), 50.59 (CH<sub>a</sub>), 50.57 (CH<sub>a</sub>), 44.61 (CH<sub>E</sub>), 42.34 (CH<sub>e</sub>), 40.39 (CH<sub>e</sub>), 30.28, 29.95, 29.90, 29.58, 29.53, 29.49, 29.41, 29.35, 27.34, 26.97; HRMS (ESI) calcd for C<sub>76</sub>H<sub>85</sub>N<sub>12</sub>O<sub>8</sub> [M + H]<sup>+</sup> 1293.66133, found 1293.66170.

## 5.2 Estimation of macrocycle positional integrity in the [2]rotaxane [2H]-4

Considering that the oxidation of the [2]rotaxane [2H]-1b to 1b causes a variation of chemical shift of the hydrogen H<sub>F</sub> of the macrocycle of 0.152 ppm<sup>1</sup> keeping a ring occupational level of a 100%, the variation of chemical shift of the same nucleus, after the oxidation of [4H]-4 to [2H]-4 (0.137 ppm, Figure 3) gives arise to the following occupational level for the azo binding site in [2H]-4:

$$\frac{\delta(H_F)_{[4H]-4} - \delta(H_F)_{[2H]-4}}{\delta(H_F)_{[2H]-1b} - \delta(H_F)_{1b}} \times 100 = \frac{0.137}{0.152} \times 100 = 90\%$$

By doing the same reasoning but considering the inner hydrogen of the macrocycle, H<sub>C</sub>, the ring occupational level obtained for the azo binding site in [2H]-4 is:

$$\frac{\delta(H_C)_{[4H]-4} - \delta(H_C)_{[2H]-4}}{\delta(H_C)_{[2H]-1b} - \delta(H_C)_{1b}} \times 100 = \frac{0.239}{0.263} \times 100 = 91\%$$

## 6. Energy barriers for the rotation of the tertiary amide bonds of the corresponding threads of rotaxanes 1b and [2H]-1b

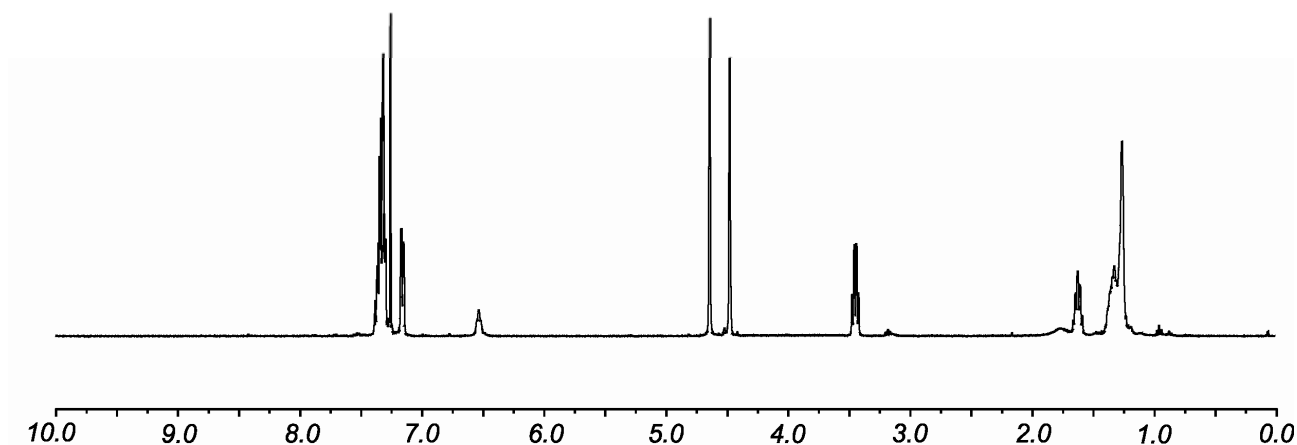
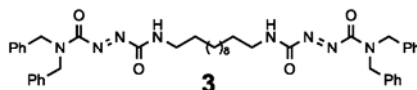
Free energies of activation for the rotation<sup>2</sup> of the tertiary amide bonds of (a) *N,N,N',N'*-tetrabenzyl-1,2-hydrazoazodicarboxamide: Δ*v* (H<sub>a</sub>-H<sub>b</sub>) = 106.65 Hz (measured at 223 K), *k<sub>c</sub>* = 236.92 s<sup>-1</sup>, T<sub>c</sub> = 248 K; Δ*G*<sup>‡</sup> = 11.74 kcal·mol<sup>-1</sup> and (b) *N,N,N',N'*-tetrabenzyl-1,2-azodicarboxamide:

$\Delta\nu$  ( $H_a-H_b$ ) = 81.97 Hz (measured at 295 K),  $k_c = 182 \text{ s}^{-1}$ ,  $T_c = 383 \text{ K}$ ;  $\Delta G^\ddagger = 18.65 \text{ kcal}\cdot\text{mol}^{-1}$ .

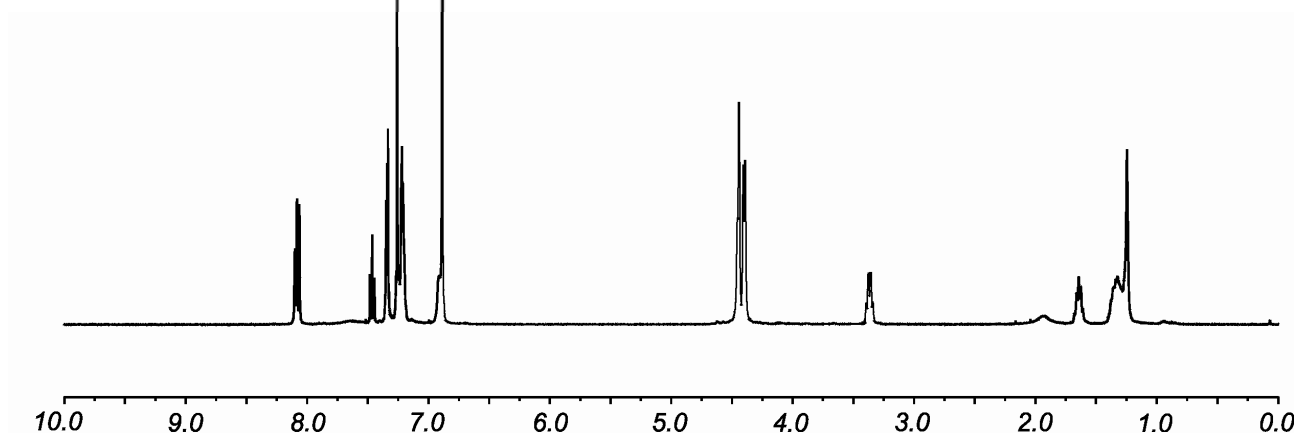
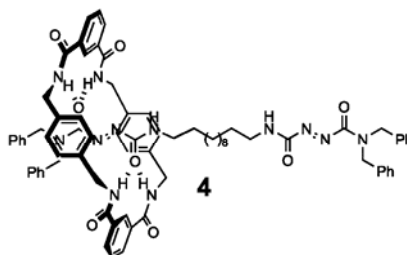
Energy values were calculated using the Eyring equation,  $\Delta G_c^\ddagger = -RT_c \cdot \ln(k_c h / k_b T_c)$ , where  $k_c = (\pi\Delta\nu)/\sqrt{2}$  or  $k_c = \pi\sqrt{(\Delta\nu^2 + 6J^2)}/\sqrt{2}$  and  $R$ ,  $h$  and  $k_b$  are the gas, Planck and Boltzmann constants, respectively.<sup>3</sup>

## 7. <sup>1</sup>H NMR Spectra of new synthesized compounds

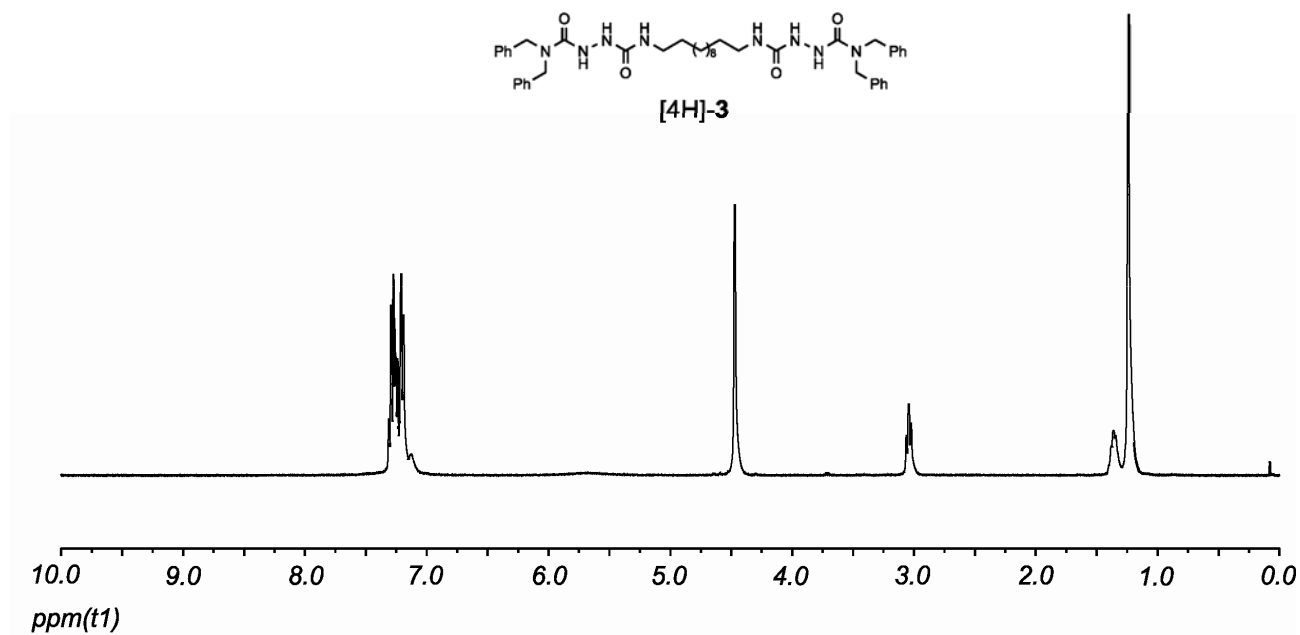
<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>, 298 K



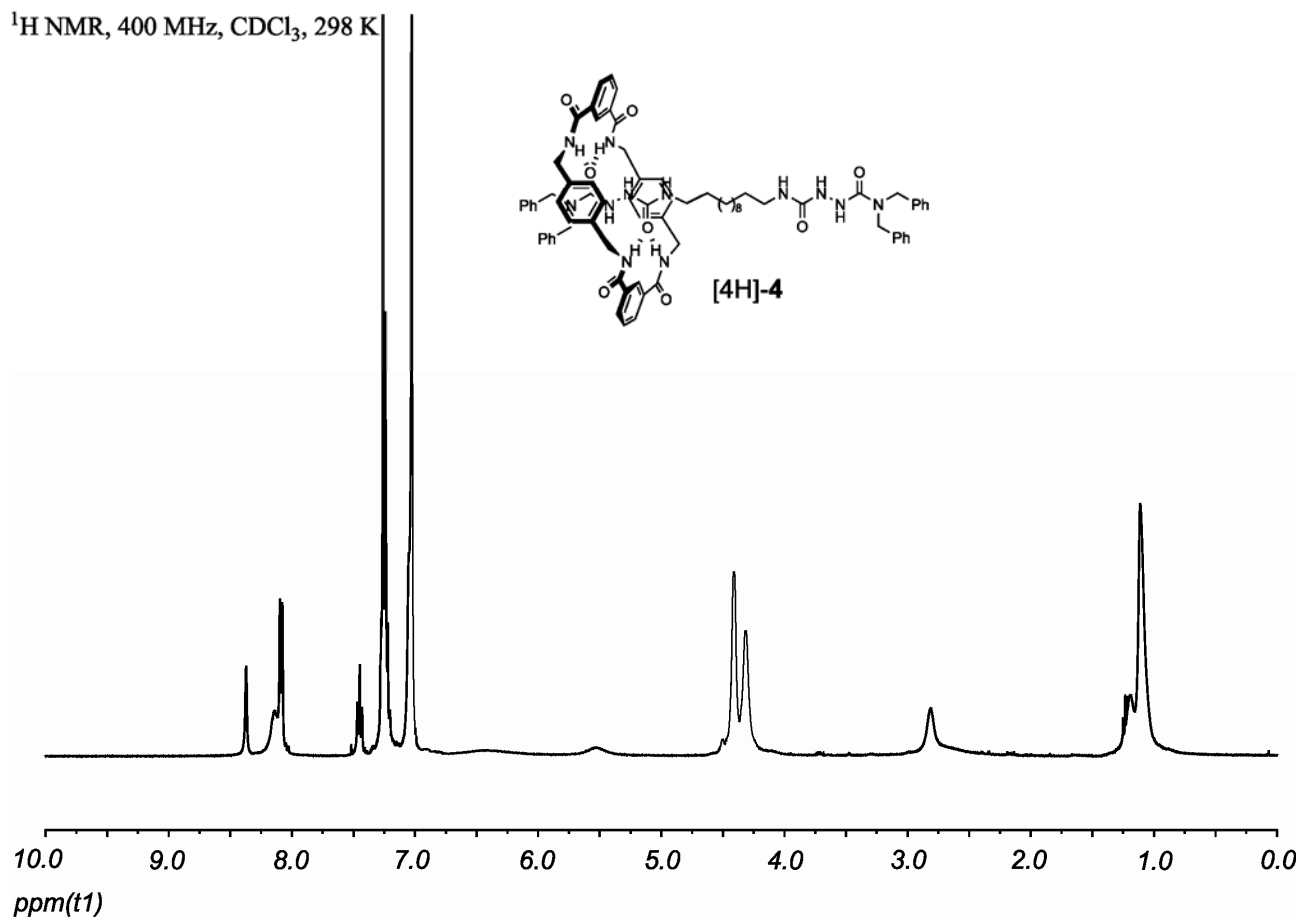
<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>, 298 K



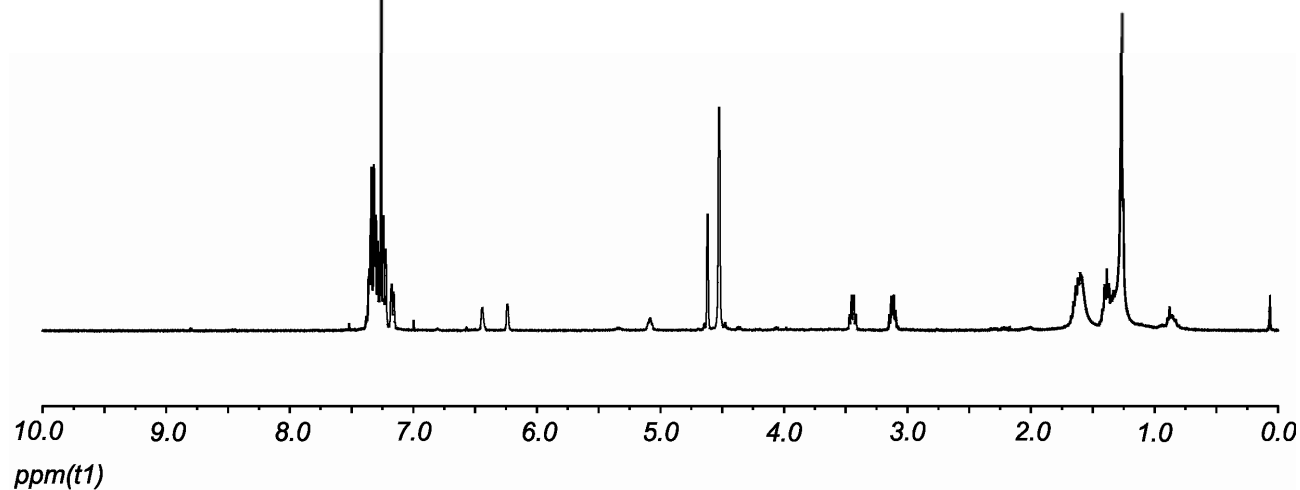
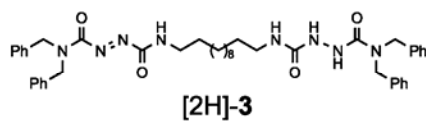
$^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ , 298 K



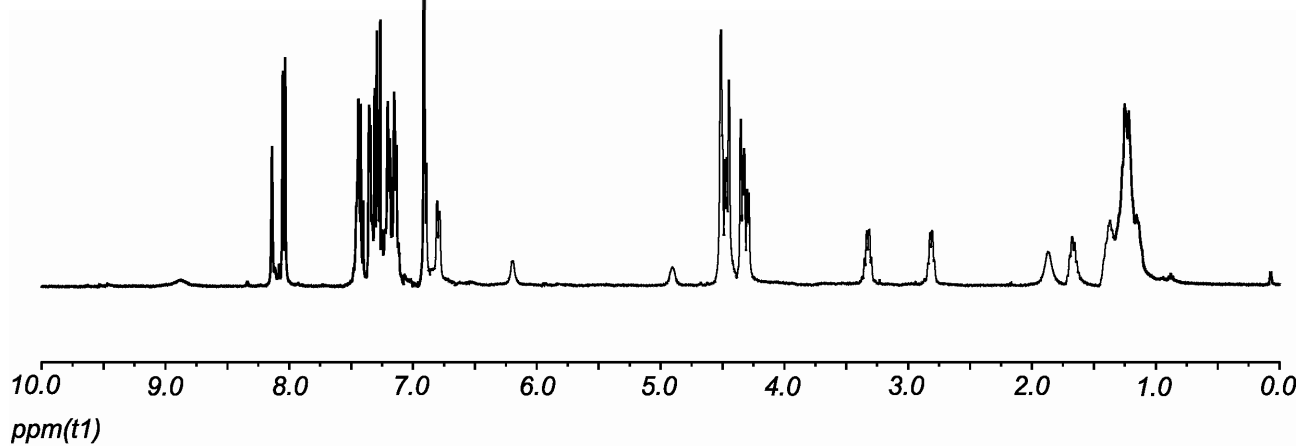
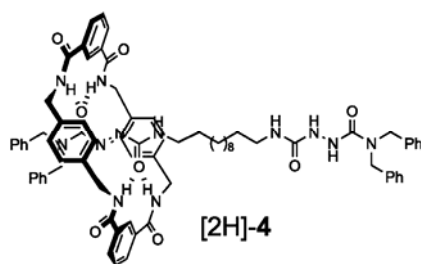
$^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ , 298 K



$^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ , 298 K



$^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ , 298 K



## 8. References

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