Supporting Information

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Remarkable Positional Discrimination in Bistable, Light and Heat-Switchable, Hydrogen Bonded Molecular Shuttles

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Details of X-Ray Crystal Structure Determination

Crystallographic data for E-4, S2, S4 and S7 (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-157383, 157381, 199285 and 199286 respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: eched@chemcrys.cam.ac.uk).

General procedure for the preparation of benzylic amide macrocycle containing [2]rotaxanes and shuttles

The thread (1 equiv.) and Et3N (24 equiv.) in anhydrous CHCl3 [or for E-4 and E-1, CH3CN/CHCl3 (1/9)] (100 mL) were stirred vigorously whilst solutions of para-xylylene diamine (12 equiv.) in anhydrous CHCl3 (40 mL) and isophthaloyl dichloride (12 equiv.) in anhydrous CHCl3 (40 mL) were simultaneously added over a period of 2 h using motor-driven syringe pumps. After a further 2 h the resulting suspension was filtered and the solvent removed under reduced pressure. The resulting solid was subjected to column chromatography (silica gel) to yield unconsumed thread, [2]rotaxane, [2]catenane and, in some cases, [3]rotaxane.

General procedure for the photoisomerization of fumaramide derivatives:

The fumaramide derivative (0.05 mmol) was dissolved in CH2Cl2 (30 mL) [except for solubility reasons E-4 and E-2, MeOH/CHCl3 (1/9)] in a quartz vessel. The solution was directly irradiated at 254 nm using a multilamp photo-reactor. The progress of the photoisomerization was monitored by TLC [CHCl3/EtOAc (4/1)] or 1H NMR. Different photostationary states were reached in a range of times not exceeding 30 min, after which the reaction mixture was concentrated under reduced pressure to afford the crude product.

General procedure for the thermal-isomerization of maleamide derivatives:

The maleamide derivative (0.02 mmol) was dissolved in C5D5Cl4 or d6-DMSO (30 mL) and heated at 400K for 4-7 days, resulting in the conversion to the more thermodynamically stable fumaramide derivative in good-to-excellent (80-95%) yields as indicated by 1H NMR.
Rotaxane E-1 has been made using the general procedure for the preparation of benzylic amide macrocycle containing [2]rotaxane from the thread E-5 (0.19 g, 0.25 mmol). The crude material was subjected to column chromatography on silica gel using a gradient of CH₂Cl₂ to CH₂Cl₂/EtOAc (80/20) as eluent to obtain the desired compound as a colourless powder (E-1, 0.19 g, 57%).

Rotaxane E-1 has been also obtained using the general procedure for the thermal-isomerization from rotaxane Z-1 (70% in C₂H₂Cl₄). m.p. 186-187 °C. ¹H NMR (400 MHz, CDCl₃,): δ = 8.31 (br t, 4J(Hₖ,Hₜ) = 1.2 Hz, 2H, ArCHₙ), 8.08 (dd, 4J(Hₜ,Hₖ) = 1.2 Hz, 3J(Hₜ,Hₖ) = 7.8 Hz, 4H, ArCHₖ), 7.68 (br t, 3J(H,H) = 5.4 Hz, 4H, NHₘ), 7.60 (br t, 3J(H,H) = 5.7 Hz, 4H, NHₖ), 7.56 (t, 3J(Hₗ,Hₘ) = 7.8 Hz, 2H, ArCHₗ), 7.45 (br t, 3J(H,H) = 5.7 Hz, 4H, NHₗ), 7.31-7.14 (m, 20H, ArCHₖ), 6.95 (s, 8H, ArCHₐ), 5.86 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₗ); 5.77 (d, 3J(H,H) = 14.8 Hz, 1H, CHₗ or CHₘ), 5.69 (d, 3J(H,H) = 14.8 Hz, 1H, CHₕ or CHₗ), 4.59 (d, 3J(H,H) = 7.7 Hz, 2H, CHₖ), 4.42 (br d, 3J(H,H) = 5.4 Hz, 8H, CHₛ), 4.32 (t, 3J(H,H) = 7.7 Hz, 1H, CHₙ), 4.24 (t, 3J(H,H) = 8.0 Hz, 1H, CHₘ), 3.84 (dd, 3J(H,H) = 8.0 Hz, 3J(H,H) = 5.7 Hz, 2H, CHₜ), 3.17-3.07 (m, 4H, CHₜ and CHₖ), 2.47 (br t, 3J(H,H) = 7.0 Hz, 2H, CHₜ), 2.23 (br t, 3J(H,H) = 7.0 Hz, 2H, CHₗ), 1.51-1.36 (m, 16H, CHₕ and -CH₂-CHₚ) and 1.31-1.10 (m, 16H, CHₜ (alkyl chain)); ¹³C NMR (100 MHz, CDCl₃,): δ = 173.0 (CHₙ-CO-O), 171.3 (CHₚ-CO-NH), 166.6 (CO macrocycle), 165.5 (CO fumaric), 165.2 (CO fumaric), 141.4 (ArCH (ipso thread)), 141.0 (ArCH (ipso thread)), 137.0 (ArC-CHₚ), 134.6 (ArC-CO), 131.3 (CHₖ), 130.3 (CH₈ or CH₆), 129.8 (CH₉ or CH₇), 129.1 (ArCHₜ), 129.0 (ArCHₖ), 128.9 (ArCH (meta thread), 128.6 (ArCH (meta thread), 128.2 (ArCH (ortho thread),
127.8 (ArCH (ortho thread), 127.2 (ArCH (para thread), 126.8 (ArCH (meta thread), 124.5 (ArCH), 67.0 (CH), 50.3 (CH), 49.8 (CH)), 44.8 (CH), 44.2 (CH or CH), 39.6 (CH or CH), 30.8 (-CH\textsubscript{2}-), 29.6 (-CH\textsubscript{2}-), 29.5 (-CH\textsubscript{2}-), 29.3 (-CH\textsubscript{2}-), 29.1 (-CH\textsubscript{2}-), and 26.8 (-CH\textsubscript{2}-); 1H NMR (400 MHz, d\textsubscript{6}-DMSO): δ = 8.59 (br t, 3 J(H,H) = 5.7 Hz, 1H, NH\textsubscript{H}), 8.53 (br t, 3 J(H,H) = 5.6 Hz, 4H, NH\textsubscript{D}), 8.41 (s, 2H, ArCH\textsubscript{C}), 8.26 (br t, 3 J(H,H) = 5.8 Hz, 1H, NH\textsubscript{k}), 8.03 (d, 3 J(H\textsubscript{B},H\textsubscript{A}) = 7.6 Hz, 4H, ArCH\textsubscript{B}), 7.64 (t, 3 J(H\textsubscript{A},H\textsubscript{B}) = 7.6 Hz, 3H, ArCH\textsubscript{A} and NH\textsubscript{k}), 7.36-7.28 (m, 16H, ArCH\textsubscript{H}), 7.26-7.19 (m, 4H, ArCH\textsubscript{H}), 6.99 (s, 8H, ArCH\textsubscript{F}), 6.27 (s, 2H, CH\textsubscript{I} and CH\textsubscript{J}), 4.56 (d, 3 J(H,H) = 7.6 Hz, 2H, CH\textsubscript{B}), 4.40-4.29 (br m, 9H, CH\textsubscript{E} and CH\textsubscript{H}), 4.22 (t, 3 J(H,H) = 7.5 Hz, 1H, CH\textsubscript{m}), 3.81 (dd, 3 J(H,H) = 5.3 Hz, 3 J(H,H) = 7.5 Hz, 4H, CH\textsubscript{I} and CH\textsubscript{J}), 2.32 (br t, 3 J(H,H) = 6.8 Hz, 2H, CH\textsubscript{c}), 2.20 (br t, 3 J(H,H) = 7.0 Hz, 2H, CH\textsubscript{d}), 1.19-1.11 (m, 4H, -CH\textsubscript{2}-CH\textsubscript{f} and -CH\textsubscript{2}-CH\textsubscript{g}) and 0.99-0.87 (m, 16H, CH\textsubscript{2} (alkyl chain)); MS (FAB): m/z = 1290 [(M+H\textsuperscript{+})]; Anal. Calcd. for C\textsubscript{80}H\textsubscript{87}N\textsubscript{7}O\textsubscript{9}: C 74.45, H 6.79, N 7.60. Found C 74.53, H 6.92, N 7.66.

[2]-(1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-((E)-but-2-enedioic acid 2,2-diphenylethylamide {12-[3-(2,2-diphenylethylcarbamoyl)-propionylamino]-dodecyl}-amide)-rotaxane, E-2.

Rotaxane E-2 was obtained using the general procedure for the thermal-isomerization from rotaxane Z-2 (80% in C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}, isolated by preparative TLC).

m.p. 186-187°C. 1H NMR (400 MHz, CDCl\textsubscript{3}, 320K): δ = 8.39 (br t, 4 J(H\textsubscript{C},H\textsubscript{B}) = 1.2 Hz, 2H, ArCH\textsubscript{C}), 8.11 (dd, 4 J(H\textsubscript{B},H\textsubscript{C}) = 1.2 Hz, 3 J(H\textsubscript{B},H\textsubscript{A}) = 7.6 Hz, 4H, ArCH\textsubscript{B}), 7.63 (br t, 3 J(H,H) = 5.4 Hz, 4H, NH\textsubscript{D}), 7.71 (t, 3 J(H\textsubscript{A},H\textsubscript{B}) = 7.6 Hz, 2H, ArCH\textsubscript{A}), 7.30-7.14 (m, 21H, ArCH (thread) and NH\textsubscript{k}), 6.93 (s, 8H, ArCH\textsubscript{F}), 6.86 (br t, 3 J(H,H) = 5.7 Hz, 1H, NH\textsubscript{a}), 6.27 (br t, 3 J(H,H) = 5.7 Hz, 1H,
(E)-N-{12-[3-(2,2-Diphenylethylcarbamoyl)acryloylamino]-dodecyl}-succinamic acid 2,2-diphenylethyl ester, E-5.

To a stirred solution of S10 (0.52 g, 0.89 mmol) in anhydrous CHCl₃ (30 mL) was added TFA (5 mL) and the solution allowed to stir for 2 h. The solution was reduced in volume and the excess of TFA removed in vacuo over 16 h. The resulting oil was taken up in anhydrous DMF (40 mL) and S12 (0.36 g, 1.2 mmol), 4-DMAP (0.20 g, 1.7 mmol) and EDCI·HCl (0.42 g, 2.2 mmol) added in order under argon at 0°C whilst stirring. After 16 h the solution was reduced in volume and the resulting oil taken up with CHCl₃ and washed with 0.5N HCl (3 x 100 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the filtrate reduced in volume to obtain a compound that was purified by column chromatography (CH₂Cl₂/EtOAc) to obtain the desired compound as a colourless solid (E-5, 0.51 g, 76%).

Compound E-5 has been also obtained using the general procedure for the thermal-isomerization from thread Z-5 (75% in C₂D₂Cl₄). m.p. 151-152 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.34-7.18
(E)-But-2-enedioic acid 2,2-diphenyl ethylamide{12-[3-(2,2-diphenylethylcarbamoyl)-propionylamino]-dodecyl}-amide, E-6.

\[
\begin{align*}
\text{To a stirred solution of } \text{S12} & \text{ (0.50 g, 1.7 mmol) in } \text{CH}_2\text{Cl}_2 \text{ was added thionyl chloride (0.124 mL, 1.7 mmol). The solution was heated until complete dissolution of } \text{S12} \text{ had occurred and the resulting solution was added dropwise to a solution of } \text{S14} \text{ (0.81 g, 1.7 mmol) and Et}_3\text{N (0.17 g, 1.7 mmol) in } \text{CH}_2\text{Cl}_2 \text{ at 0 } ^\circ\text{C and allowed to stir for 30 min. The solution was then filtered and the solid} 
\end{align*}
\]
recrystallized from hot DMSO to give a colourless solid (E-6, 0.56 g, 44%). m.p. 213-214 °C. $^1$H NMR (400 MHz, $d_6$-DMSO, 400K): $\delta = 8.12$ (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_a$), 8.01 (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_b$), 7.52 (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_c$), 7.40 (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_d$), 7.32-7.15 (m, 20H ArC$_H$), 6.76 (d, $^3$J(H,H) = 15.3 Hz, 1H, CH$_l$ or CH$_m$), 6.71 (d, $^3$J(H,H) = 15.3 Hz, 1H, CH$_l$ or CH$_m$), 4.26 (t, $^3$J(H,H) = 8.0 Hz, 1H, CH$_p$), 4.20 (t, $^3$J(H,H) = 8.0 Hz, 1H, CH$_a$), 3.82 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_o$), 3.70 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_b$), 3.12 (td, $^3$J(H,H) = 7.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_i$), 3.00 (td, $^3$J(H,H) = 7.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_i$), 2.22 (s, 4H, CH$_d$ and CH$_e$), 1.48-1.34 (m, 4H, CH$_h$ and CH$_i$) and 1.32-1.20 (br m, 16H, -CH$_2$- (alkyl chain)); $^{13}$C NMR was not possible to be recorded for the low solubility of the compound; MS (FAB): m/z = 757 [(M+H)$^+$]; Anal. Calcd. for C$_{48}$H$_{60}$N$_4$O$_4$: C 76.16, H 7.99, N 7.40. Found C 75.89, H 8.04, N 7.65.

(E)-Hexanedioic acid 2,2–diphenylethylamide\{12-[3-(2,2-diphenylethylcarbamoyl)-acyrloylamino]-dodecyl\}-amide, E-7.

A solution of S12 (0.053 g, 0.18 mmol), S18 (0.1 g, 0.2 mmol) and 4-DMAP (0.02 g, 0.18 mmol) in CHCl$_3$ (10 mL) was stirred at 0 °C for 10 mins. EDC·HCl (0.034 g, 0.18 mmol) was added and the reaction mixture allowed to stir for 16 h at rt. The reaction was diluted with CHCl$_3$ (10 mL) and the combined organic phase washed with 1N HCl (3 x 10 mL), saturated NaHCO$_3$ (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated to give the product as a colourless solid (E-7, 69 mg, 45%). $^1$H NMR (400 MHz, $d_6$-DMSO, 400K): $\delta = 8.47$ (br t, 1H, NH$_p$), 8.34 (br t, 1H, NH$_m$), 7.82 (br t, 1H, NH$_c$), 7.69 (br t, 1H, NH$_b$), 7.31-7.19 (m, 20H, ArC$_H$), 6.80 (d, $^3$J(H,H) = 15.3 Hz, 1H, CH$_n$ or CH$_o$), 6.73 (d, $^3$J(H,H) = 15.3 Hz, 1H, CH$_n$ or CH$_o$), 4.24 (t, $^3$J(H,H) = 8.0 Hz, 1H, CH$_i$), 4.19 (t, $^3$J(H,H) = 8.0 Hz, 1H, CH$_i$), 3.82 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_o$), 3.69 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_i$), 3.01 (td, $^3$J(H,H) = 7.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_i$), 1.96 (m, 4H, CH$_d$ and CH$_e$), 1.35 (m, 8H, CH$_j$, CH$_k$, CH$_c$ and CH$_f$), 1.25 (m, 16H, CH$_2$ (alkyl chain)). $^{13}$C NMR was not possible to be recorded for the low solubility of the

\[\text{[2]}-(1,7,14,20-\text{Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(\(\text{Z}\)-\(\text{N}\)\{-12-[3-(2,2-diphenylethylcarbamoyl)-acryloylmino]-dodecyl\}-succinamic acid 2,2-diphenylethyl ester)-rotaxane, Z-1.\]

Rotaxane Z-1 was obtained using the general procedure for the photo-isomerization from rotaxane E-1. The crude was subjected to column chromatography using a solvent gradient of CH\(_2\)Cl\(_2\) to CH\(_2\)Cl\(_2\)/EtOAc (70/30) to obtain the desired compound as a colourless solid (Z-1, 35 mg, 54%). m.p. 152-154 °C. 1H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.55 \) (br t, \( 3J(H,H) = 5.7 \) Hz, 1H, \( NH_h \), 8.28 (br t, \( 4J(H_C,H_B) = 1.2 \) Hz, 2H, ArCH\(_C\), 8.18 (dd, \( 4J(H_B,H_C) = 1.2 \) Hz, \( 3J(H_B,H_A) = 7.8 \) Hz, 4H, ArCH\(_B\), 7.82 (br t, \( 3J(H,H) = 5.7 \) Hz, 1H, \( NH_h \), 7.60 (t, \( 3J(H_A,H_B) = 7.8 \) Hz, 2H, ArCH\(_A\), 7.38 (br dd, 4H, \( NH_D \), 7.32-7.10 (m, 20H, ArCH\(_H\)), 7.00 (s, 8H, ArCH\(_F\)), 6.36 (t, \( 3J(H,H) = 5.7 \) Hz, 1H, \( NH_e \), 5.90 (d, \( 3J(H,H) = 13.4 \) Hz , 1H, \( CH_i \) or \( CH_j \)), 5.82 (d, \( 2J(H,H) = 13.4 \) Hz, 1H, \( CH_i \) or \( CH_j \)), 4.55 (dd, \( 2J(H_E,H'_E) = 14.1 \) Hz, \( 3J(H_E,H_D) = 5.8 \) Hz, 4H, CHH\(_E'\)_E), 4.44 (d, \( 3J(H,H) = 7.7 \) Hz, 2H, CH\(_B\)), 4.40 (dd, \( 2J(H_E,H'_E) = 14.1 \) Hz, \( 3J(H_E,H_D) = 5.0 \) Hz, 4H, CHH\(_E'\)_E), 4.20 (m, \( CH_a \) and \( CH_m \), 3.88 (dd, \( 3J(H,H) = 8.0 \) Hz, \( 3J(H,H) = 5.7 \) Hz, 2H, \( CH_i \)), 3.04 (td, \( 3J(H,H) = 7.0 \) Hz, \( 3J(H,H) = 5.7 \) Hz, 2H, \( CH_i \)), 2.94 (td, \( 3J(H,H) = 7.0 \) Hz, \( 3J(H,H) = 5.7 \) Hz, 2H, \( CH_i \)), 1.47 (m, 2H, \( CH_d \)), 1.16 (m, 2H, \( CH_d \)), 0.61-1.00 (m, 18H, -CH transports (alkyl chain)), \( ^{13} \)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): \( \delta = 174.7 \) (CH\(_C\)-CO-O), 172.6, (-CO-NH\(_E\)) 166.9 (CO macrocycle), 166.0 (CO maleic), 165.4 (CO maleic), 142.7 (ArC-CH- (ipso thread)), 141.9 (ArC-CH- (ipso thread)), 138.5 (ArC-CH\(_E\)), 135.0 (ArC-CO), 134.2 (CH\(_i \) or \( CH_j \)), 132.1 (CH\(_i \) or \( CH_j \)), 132.0
(ArCH₆), 130.0 (ArCH₆), 129.8 (ArCH₆), 129.5 (ArCH (meta thread)), 129.4 (ArCH (meta thread)), 128.8 (ArCH (ortho thread)), 128.6 (ArCH (ortho thread)), 127.8 (ArCH (para thread)), 127.6 (ArCH (para thread)), 124.8 (ArCH₂), 68.1 (CHb), 51.2 (Chₐ or CHₐm), 50.5 (CHₐ or CHₐm), 44.9 (CH₁), 44.8 (CH₂), 40.7 (CH₉ or CH₂), 40.6 (CH₉ or CH₂), 30.2 (CH₃), 30.1 (CH₃), 29.9 (-CH₂-), 29.8-29.6 (-CH₂-), 29.5 (-CH₂-), 29.4 (-CH₂-), 27.5 (-CH₂-), 27.3 (-CH₂-); MS (FAB): m/z = 1291 [(M+H)+]; Anal. Calcd. for C₈₀H₇₇N₇O₉: C 74.45, H 6.79, N 7.60. Found C 74.62, H 6.68, N 7.49.


Rotaxane Z-2 was obtained using the general procedure for the preparation of the benzylid amide macrocycle containing [2]rotaxane from the thread Z-6 (0.50 g, 0.66 mmol). Column chromatography of the crude obtained using a solvent gradient of CHCl₃ to CHCl₃/MeOH (95/5) gave a colourless solid (Z-2, 0.34 g, 40%).

Rotaxane Z-2 was also obtained using the general procedure for the photo-isomerization from rotaxane E-2 (48% by ¹H NMR). m.p. 171-172 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₐ), 8.31 (br t, 4J(Hc,Hb) = 1.2 Hz, 2H, ArCH₄C), 8.16 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₐ), 8.14 (dd, 4J(Hb,HC) = 1.2 Hz, 3J(Hb,HA) = 7.8 Hz, 4H, ArCH₄B), 7.67 (br t, 3J(H,H) = 5.4 Hz, 4H, NHₐ), 7.56 (t, 3J(Hₐ,Hₐ) = 7.8 Hz, 2H, ArCH₃A), 7.31-7.10 (m, 20H, ArCH₂(thread)), 7.02 (s, 8H, ArCH₉), 6.53 (br t, 3J(H,H) = 5.7 Hz, 1H, NH₁), 6.15 (br t, 3J(H,H) = 5.7 Hz, 1H, NH₁), 5.92 (d, 3J(H,H) = 13.6 Hz, 1H, CH₁ or CH₉m), 5.83 (d, 3J(H,H) = 13.6 Hz, 1H, CH₁ or CH₉m), 4.50
(dd, $^2J(H_E, H'_E) = 14.1$ Hz, $^3J(H_E, H_D) = 5.4$ Hz, 4H, $CHH'_E$), 4.43 (dd, $^2J(H_E, H'_E) = 14.1$ Hz, $^3J(H'_E, H_D) = 5.4$ Hz, 4H, $CHH'_E$), 4.23 (t, $^3J(H_H, H) = 8.0$ Hz, 1H, $CH_p$), 4.06 (t, $^3J(H_H, H) = 8.0$ Hz, 1H, $CH_o$), 3.67 (dd, $^3J(H_H, H) = 8.0$ Hz, 2H, $CH_g$), 3.15 (td, $^3J(H_H, H) = 8.0$ Hz, 1H, $CH_p$), 3.09 (t, $^3J(H_H, H) = 8.0$ Hz, 1H, $CH_a$), 3.06 (t, $^3J(H_H, H) = 8.0$ Hz, 2H, $CH_g$), 2.99 (td, $^3J(H_H, H) = 8.0$ Hz, 2H, $CH_p$), 1.48 (m, 2H, $CH_i$), 1.38 (m, 2H, $CH_h$), 1.33-1.16 (m, 16H, -$C_H_2$ (alkyl chain)) and 1.07 (m, 4H, $C_H_d$ and $C_H_e$); $^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta = 173.0$ (CO succinic), 172.9 (CO succinic), 166.6 (CO macrocycle), 165.0 (CO maleic), 164.7 (CO maleic), 141.7 (ArC-CH (ipso thread)), 141.6 (ArC-CH (ipso thread)), 137.5 (ArC-CH$_E$), 133.8 (ArC-CH$_F$), 133.1 (CH$_l$ or CH$_m$), 131.5 (ArCH$_n$), 131.4 (CH$_l$ or CH$_m$), 129.2 (ArCH$_i$), 129.1 (ArCH$_A$), 128.8 (ArCH (meta thread)), 128.7 (ArCH (meta thread)), 127.9 (ArCH (ortho thread)), 127.8 (ArCH (ortho thread)), 127.1 (ArCH (para thread)), 126.8 (ArCH (para thread)), 124.0 (ArCH$_C$), 50.5 (CH$_p$), 50.3 (CH$_a$), 44.2 (CH$_b$), 44.1 (CH$_b$), 44.0 (CH$_E$), 39.7 (CH$_l$ and CH$_b$), 29.8 (CH$_d$ or CH$_e$), 29.4 (CH$_d$ or CH$_e$), 29.3 (-CH$_2$), 29.2 (-CH$_2$), 29.1 (-CH$_2$), 29.0 (-CH$_2$), 28.8 (-CH$_2$) and 28.7 (-CH$_2$); MS (FAB): $m/z = 1289 [(M+H)^+]$; Anal. Calcd. for C$_{80}$H$_{88}$N$_8$O$_8$: C 74.51, H 6.88, N 8.69. Found C 74.69, H 6.94, N 8.76.


Rotaxane Z-3 has been made using the general procedure for the formation of the benzylic amide macrocycle containing [2]rotaxane from thread Z-7 (1.5 g, 1.9 mmol). Column chromatography of the crude product (silica gel, 3:97, MeOH/CHCl$_3$) gave the product as a colourless solid (Z-3, 0.5 g, 20 %). m.p. 115 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.82$ (br t, $^3J(H_H, H) = 5.7$ Hz, 1H, NH$_m$), 8.24
(br s, 3H, ArCH and NH₆), 8.13 (dd, 4J(H₆,H₇) = 1.5 Hz, 3J(H₆,H₈) = 7.8 Hz, 4H, ArCH₆), 7.63 (t, 3J(H,H) = 5.3 Hz, 4H, NH₆D), 7.53 (t, 3J(H₆,H₇) = 7.8 Hz, 2H, ArCH₆), 7.32-7.15 (m, 20H, ArCH), 7.05 (s, 8H, ArCH₆F), 6.20 (br t, 3J(H,H) = 5.6 Hz, 1H, NHO₆), 6.03 (br t, 3J(H,H) = 5.1 Hz, 1H, NH₆), 5.71 (d, 3J(H,H) = 13.4 Hz, 1H, CH₆n or CH₆o), 5.71 (d, 3J(H,H) = 13.4 Hz, 1H, CH₆n or CH₆o), 4.55 (dd, 2J(H,E, H′E) = 14.4 Hz, 3J(H,E, HD) = 5.3 Hz, 4H, CH₆E), 4.45 (dd, 2J(H,E, H′E) = 14.4 Hz, 3J(H,E, HD) = 5.3 Hz, 4H, CH₆E), 4.19 (t, 3J(H,H) = 7.8 Hz, 1H, C₆r), 4.13 (t, 3J(H,H) = 7.8 Hz, 1H, C₆a), 3.87 (2d, 3J(H,H) = 7.8 Hz, 2H, C₆q), 3.66 (2d, 3J(H,H) = 7.8 Hz, 2H, C₆b), 2.94 (m, 4H, C₆i and C₆l), 1.41 (br m, 2H, -C₆H₂- (alkyl chain)), 1.33 (br m, 4H, C₆d and C₆g), 1.25-1.18 (m, 22H, -C₆H₂- (alkyl chain)), 0.76 (br m, 4H, C₆d and C₆g); 13C NMR (100 MHz, CDCl₃): δ = 173.4 (CO adipamide), 173.3 (CO adipamide), 166.4 (CO macrocycle), 165.4 (CO maleic), 164.6 (CO maleic), 142.1 (ArC- (ipso thread)), 141.5 (ArC- (ipso thread)), 137.6 (ArC-CH₂), 133.9 (ArC-CO-), 133.2 (CH₆n or CH₆o), 131.9 (CH₆n or CH₆o), 131.8 (ArCH₆), 131.4 (ArCH₆F), 129.2 (ArCH₆A), 128.4 (ArCH (meta thread)), 128.0 (ArCH (ortho thread)), 126.91 (ArCH (para thread)), 124.4 (CH₆), 50.7 (CH₆), 50.2 (CH₆), 44.4 (CH₆), 44.3 (CH₆), 44.0 (CH₆), 40.1 (CH₆), 39.7 (CH₆), 35.5 (CH₆d or CH₆e), 35.4 (CH₆d or CH₆e), 29.4 (-CH₂-), 29.3 (-CH₂-), 29.2 (-CH₂-), 29.1 (-CH₂-), 29.0 (-CH₂-), 28.9 (-CH₂-), 28.6 (-CH₂-), 26.8 (-CH₂-), 26.7 (-CH₂-), 24.7 (-CH₂-), 24.5 (-CH₂-). HRMS (FAB, NBA matrix): m/z = 1317.70829 [(M+H)+] (Anal. Calcd. for C₈₂H₉₃N₈O₈: m/z = 1317.71164).

(Z),₆N-{12-[3-(2,2-Diphenyl-ethylcarbamoyl)-acryloylamino]-dodecyl]-succinamic acid 2,2-diphenylethyl ester, Z-5.

To a stirred solution of S10 (0.25 g, 0.43 mmol) in anhydrous CHCl₃ (30 mL) was added TFA (5 mL) and the solution stirred for 2 h. The solution was reduced in volume and the excess of TFA was removed in vacuo over 16 h. The resulting oil was taken up in anhydrous CHCl₃ (200 mL) and Et₃N (1 mL), S8 (0.14 g, 0.47 mmol) and EDCI·HCl (0.10 g, 0.51 mmol) added sequentially under cooling with an ice bath. After 16 h the solution was reduced in volume and the resulting oil taken up with CHCl₃ and washed with 0.5N HCl (3 x 100 mL). The organic layer was dried over
anhydrous MgSO₄, filtered and the filtrate reduced in volume to give a colourless solid that was purified by column chromatography CHCl₃/MeOH (90/10) (Z-5, 0.23 g, 70%).

Compound Z-5 has also been obtained using the general procedure for the photo-isomerization from the thread E-5 (57% by ¹H NMR), m.p. 54-56 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.45 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₖ), 7.91 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₖ), 7.28-7.08 (m, 20H, ArCH), 5.90 (d, 3J(H,H) = 13.4 Hz, 1H, CHₖ or CHₗ), 5.82 (d, 3J(H,H) = 13.4 Hz, 1H, CHₖ or CHₗ), 5.53 (br t, 3J(H,H) = 5.7 Hz, 1H, NHₖ), 4.55 (d, 3J(H,H) = 7.7 Hz, 2H, CHₖ), 4.27 (t, 3J(H,H) = 7.7 Hz, 1H, CHₖ or CHₗ), 4.17 (t, 3J(H,H) = 8.0 Hz, 2H, CHₖ), 3.87 (dd, 3J(H,H) = 8.0 Hz, 3J(H,H) = 5.7 Hz, 2H, CHₖ), 3.16 (td, 3J(H,H) = 7.0 Hz, 3J(H,H) = 5.7 Hz, 2H, CHₖ), 2.48 (t, 3J(H,H) = 7.0 Hz, 2H, CHₖ), 2.24 (t, 3J(H,H) = 7.0 Hz, 2H, CHₖ), 1.51-1.40 (m, 2H, CH₂-CH₉g), 1.40-1.31 (m, 2H, CH₂-CH₉), 1.30-1.12 (m, 16H, -CH₂-, (alkyl chain)); ¹³C NMR (100 MHz, CDCl₃): δ = 173.3 (CHc-CO-O), 171.6 (CO-NHe), 165.4 (CO maleic), 165.0 (CO maleic), 142.2 (ArC- (ipso)), 141.4 (ArC- (ipso)), 133.9 (CHₖ or CHₗ), 131.7 (CHₖ or CHₗ), 129.1 (ArCH- (meta)), 129.0 (ArCH- (meta)), 128.6 (ArCH- (ortho)), 128.4 (ArCH- (ortho)), 127.2 (ArCH- (para)), 67.3 (CHₖ), 50.7 (CHₖ), 50.2 (CHₖ), 44.6 (CHₖ), 40.2 (CHₖ or CHₗ), 40.0 (CHₖ or CHₗ), 31.4 (CHₖ or CHₗ), 30.1 (CHₖ or CHₗ), 29.9 (-CH₂-), 29.8-29.7 (-CH₂-), 29.6 (-CH₂-), 29.5 (-CH₂-), 27.4 (-CH₂-) and 27.3 (-CH₂-); MS(FAB): m/z = 758 [(M+H)⁺]; Anal. Calcd. for C₄₈H₅₉N₃O₅: C 76.06, H 7.85, N 5.54. Found C 76.09, H 8.11, N 5.63.

(Z)-But-2-enedioic acid 2,2-diphenylethylamide {12-[3-(2,2-diphenylethylcarbamoyl)-propionylamino]-dodecyl}-amide, Z-6.

To a stirred solution of S14 (0.50 g, 1.0 mmol) in anhydrous CHCl₃ (50 mL) at 0 °C was added S8 (0.34 g, 1.2 mmol), 4-DMAP (0.15 g, 1.2 mmol) and EDCl-HCl (0.24 g, 1.2 mmol) and the resulting reaction mixture stirred for 16 h at rt. The solution was then washed with a solution of 1N NaOH (3 x 100 mL), 1N HCl (3 x 100 mL) and H₂O (1 x 100 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the solvent removed under reduced pressure to obtain a
colourless solid that was subjected to column chromatography using a solvent gradient of CH₂Cl₂ to
CH₂Cl₂/MeOH (95/5) (Z-6, 0.63 g, 70%). m.p. 68-69 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.40 (br t, ³J(H,H) = 5.7 Hz, 1H, NHₖ), 7.80 (br t, ³J(H,H) = 5.7 Hz, 1H, NHₗ), 7.25-7.09 (m, 20H, ArCH), 5.91-6.00 (br m, 2H, NHₐ and NHₐ), 5.92 (d, ³J(H,H) = 13.3 Hz, 1H, CHₐ or CHₐ), 5.83 (d, ³J(H,H) = 13.3 Hz, 1H, CH₈ or CH₈), 5.91-6.00 (br m, 2H, NHₐ and NHₐ), 5.92 (d, ³J(H,H) = 13.3 Hz, 1H, CH₉ or CH₉), 5.83 (d, ³J(H,H) = 13.3 Hz, 1H, CH₈ or CH₈), 4.18 (t, ³J(H,H) = 8.0 Hz, 1H, CH₉), 4.09 (t, ³J(H,H) = 8.0 Hz, 1H, CH₈), 3.87 (dd, ³J(H,H) = 8.0 Hz, 3J(H,H) = 5.7 Hz, 2H, CH₁₀ or CH₁₀), 3.79 (dd, ³J(H,H) = 8.0 Hz, 3J(H,H) = 5.7 Hz, 2H, CH₇ or CH₇), 2.29 (s, 4H, CH₉ and CH₉), 1.45 (m, 2H, CH₁₀), 1.37 (m, 2H, CH₂ or CH₂) and 1.12-1.29 (m, 16H, -CH₂-(alkyl chain)); ¹³C NMR (100 MHz, CDCl₃): δ = 172.6 (CO succinic), 172.4 (CO succinic), 165.4 (CO maleic), 164.9 (CO maleic), 142.2 (Ar- (ipso)), 142.1 (Ar- (ipso)), 133.9 (CH₈ or CH₉), 131.6 (CH₇ or CH₇), 129.1 (ArCH (meta)), 128.4 (ArCH (ortho)), 127.2 (ArCH (para)), 51.0 (CH₉), 50.7 (CH₈), 44.6 (CH₁₀), 44.2 (CH₉), 40.2 (CH₉ or CH₉), 40.0 (CH₉ or CH₉), 32.2 (CH₂ or CH₂), 32.1 (CH₂ or CH₂), 29.9-29.8 (-CH₂- (alkyl chain)), 29.6-29.5 (-CH₂- (alkyl chain)), 27.3 (-CH₂- (alkyl chain)) and 27.2 (-CH₂- (alkyl chain)); MS (FAB): m/z = 757 [(M+H)+]; Anal. Calcd. for C₄₈H₆₀N₄O₄: C 76.16, H 7.99, N 7.40. Found C 75.98, H 8.10, N 7.45.

(Z)-Hexanedioic acid 2,2-diphenylethylamide[12-[3-(2,2-diphenylethylcarbamoyl)-acryloylamino]-dodecyl]-amide, Z-7.

A solution of S₈ (0.16 g, 0.54 mmol), S₁₈ (0.3 g, 0.59 mmol) and 4-DMAP (0.07 g, 0.54 mmol) in CHCl₃ (10 mL) was stirred at 0 °C for 10 mins followed by addition of EDCI-HCl (0.10 g, 0.54 mmol). The reaction mixture was stirred for 16 h at rt. The solution was diluted with CHCl₃ (10 mL) and the combined organic phase washed with 1N HCl (3 x 10 mL), saturated NaHCO₃ (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the filtrate concentrated to give the product as a colourless solid (Z-7, 0.35 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.45 (br t, ³J(H,H) = 5.7 Hz, 1H, NH₆), 7.88 (br t, ³J(H,H) = 5.7 Hz, 1H, NH₆), 7.33-7.20 (m, 20H, ArCH), 6.02 (d, ³J(H,H) = 13.3 Hz, 1H, CH₉ or CH₉), 5.92 (d, ³J(H,H) = 13.3 Hz, 1H, CH₉ or CH₉), 5.72 (br m, 2H, NH₆ and NH₆), 4.26 (t, ³J(H,H) = 8.0 Hz, 1H, CH₉), 4.20 (t,
$^3J(H,H) = 8.0$ Hz, 1H, $CH_a$, 3.96 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, $CH_b$), 3.89 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, $CH_b$), 3.23 (m, 4H, $CH_i$ and $CH_l$), 2.10 (t, $^3J(H,H) = 7.3$ Hz, 2H, $CH_d$ or $CH_g$), 2.07 (t, $^3J(H,H) = 7.3$ Hz, 2H, $CH_d$ or $CH_g$), 1.55-1.47 (m, 8H, $CH_e$, $CH_f$, $CH_j$ and $CH_k$), 1.32-1.27 (m, 16H, -$CH_2-$ (alkyl chain)); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 172.8 (CO adipamide), 172.6 (CO adipamide), 165.0 (CO maleic), 164.6 (CO maleic), 141.9 (ArC- (ipso)), 141.8 (ArC- (ipso)), 133.4 ($CH_n$ or $CH_o$), 131.4 ($CH_n$ or $CH_o$), 128.7 (ArCH (meta)), 128.6 (ArCH (meta)), 128.0 (ArCH (ortho)), 126.8 (ArCH (para)), 50.6 ($CH_i$), 50.3 ($CH_o$), 44.2 ($CH_q$), 43.8 ($CH_b$), 39.8 ($CH_h$), 39.5 ($CH_i$), 36.2 ($CH_d$ or $CH_g$), 36.1 ($CH_d$ or $CH_g$), 29.5 (-$CH_2-$), 29.3 (-$CH_2-$), 29.1 (-$CH_2-$), 29.0 (-$CH_2-$), 26.9 (-$CH_2-$), 26.8 (-$CH_2-$) and 24.9 (-$CH_2-$). HRMS (FAB, NBA matrix): $m/z =$ 785.49929 [(M+H)$^+$] (Anal. Calcd. for C$_{50}$H$_{65}$N$_4$O$_4$: $m/z =$ 785.50058).

$N,N'$-bis-(2,2-Diphenylethyl)-succinamide, S1.

To a stirred solution of 2,2-diphenylethylamine (0.50 g, 2.5 mmol) and Et$_3$N (0.26 g, 2.5 mmol) in CH$_2$Cl$_2$ (20 mL) at 0 °C was added dropwise a solution of succinyl dichloride (0.2 g, 1 mmol) in CH$_2$Cl$_2$. The obtained solution was allowed to stir for 3 h and then washed with 1N HCl (2 x 20 mL), 1N NaOH (2 x 20 mL) and H$_2$O (1 x 20 mL). The organic layer was dried over anhydrous MgSO$_4$, filtered and the solvent removed under reduced pressure to obtain a solid that was recrystallized from acetone to give colourless needles (S1, 0.59 g, 97%), m.p. 168-169 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.34-7.18 (m, 20H, Ar$CH$), 5.84 (br t, $^3J(H,H) = 5.7$ Hz, 2H, $NH_c$), 4.14 (t, $^3J(H,H) = 8.0$ Hz, 2H, $CH_b$), 3.83 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, $CH_b$), 2.28 (s, 4H, $CH_d$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 172.0 (CO), 141.8 (ArC-CH- (ipso)), 128.9 (ArCH (meta)), 128.0 (ArCH (ortho)), 126.8 (ArCH (para)), 50.5 ($CH_i$), 43.8 ($CH_b$) and 31.6 ($CH_d$); MS(FAB): $m/z =$ 477 [(M + H)$^+$]; Anal. Calcd. for C$_{32}$H$_{32}$N$_2$O$_2$: C 80.64, H 6.77, N 5.88. Found C 81.03, H 6.92, N 6.09.
Rotaxane S2 was obtained using the general procedure for the preparation of benzylic amide macrocycle containing [2]rotaxane from the thread S1 (0.50 g, 1.05 mmol). The crude obtained was subjected to column chromatography on silica gel [CH3Cl/MeOH (5/95)] to obtain a colourless solid (S2, 0.55 g, 52%). m.p. 230-232 °C; 1H NMR (400 MHz, CDCl3): δ = 8.31 (br t, 4J(Hc,Hb) = 1.3 Hz, 2H, ArCHc), 8.19 (dd, 4J(Hb,HC) = 1.3 Hz, 3J(Hb,HA) = 7.7 Hz, 4H, ArCHb), 7.62 (t, 3J(HA,Hb) = 7.7 Hz, 2H, ArCHA), 7.47 (br t, 3J(H,H) = 7.1 Hz, 4H, NH), 7.30-7.15 (m, 12H, ArCH (para and meta thread)), 7.12 (d, 3J(H,H) = 7.1 Hz, 8H, ArCH (ortho thread)), 6.85 (s, 8H, ArCHF), 5.87 (br t, 3J(H,H) = 5.6 Hz, 2H, NH), 4.43 (d, 3J(H,H) = 5.4 Hz, 8H, CHE), 4.04 (t, 3J(H,H) = 5.6 Hz, 2H, CHF), 3.5 (dd, 3J(H,H) = 7.8 Hz, 3J(H,H) = 5.6 Hz, 4H, CHF) and 0.89 (s, 4H, CHF); 13C NMR (100 MHz, CDCl3): δ = 172.8 (CO thread), 166.5 (CO macrocycle), 141.4 (Ar-C-CH- (ipso thread)), 137.6 (Ar-C-CH), 134.0 (Ar-C-CO-), 130.8 (ArCHB), 129.3 (ArCHF), 129.0 (ArCHA), 128.9 (ArCH (meta)), 127.8 (ArCH (ortho)), 127.2 (ArCH (para)), 125.4 (ArCCH), 49.4 (CHa), 44.3 (CHb), 43.9 (CHED) and 28.4 (CHd); MS(FAB): m/z = 1009 [(M+H)+]. Anal. Calcd. for C64H80N10O10: C 76.17, H 5.99, N 8.33. Found C 76.28, H 5.85, N 8.16.

X-ray crystallographic data for compound S2.
C76H88N10O10, M = 1301.56, crystal size 0.24 × 0.06 × 0.06 mm, triclinic P-1, a = 9.8887(5), b = 13.1481(6), c = 15.3131(7) Å, α = 108.0300(10), β = 106.0530(10), γ = 101.9480(10)°, V = 1723.58(14) Å3, Z = 1, ρcalc = 1.254 Mg m-3; MoKa radiation (graphite monochromator, λ = 0.71073 Å), μ = 0.084 mm-1, T = 293(2) K. 8463 data (4770 unique, Rint = 0.0628, 1.50 < θ < 23.31°), were
collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semi-empirically for absorption and incident beam decay (transmission 1.00–0.70). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give \( wR = \left\{ \Sigma [w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)^2] \right\}^{1/2} = 0.2659 \), conventional \( R = 0.0866 \) for \( F \) values of 4770 reflections with \( F_o^2 > 2\sigma(F_o^2) \), \( S = 1.027 \) for 446 parameters. Residual electron density extremes were 0.356 and −0.250 eÅ\(^{-3}\). Amide hydrogen atoms were refined isotropically with the remainder constrained; anisotropic displacement parameters were used for all non-hydrogen atoms.

**Hexanedioic acid bis-[2,2-diphenylethylamide], S3.**

\[
\begin{align*}
\text{Ph} & \quad \text{a} \quad \text{b} \quad \text{N} \quad \text{O} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{N} \quad \text{H} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

To a solution of 2,2-diphenylethylamine (0.42 g, 2.1 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added Et\(_3\)N (0.25 g, 2.5 mmol) followed by dropwise addition of hexanedionyl dichloride (0.18 g, 1 mmol) in CH\(_2\)Cl\(_2\) (5 mL) over 10 min at 0 °C. The reaction mixture was allowed to stir for 16 h at rt and then washed with 1N HCl (2 x 10 mL), saturated aqueous NaHCO\(_3\) (2 x 10 mL) and brine (10 mL). The organic layer was dried over anhydrous MgSO\(_4\), filtered and the solution concentrated under reduced pressure to give a colourless solid that was recrystallized in CH\(_2\)Cl\(_2\)/MeOH to afford colourless needles (S3, 0.40 g, 79%). m.p. 183 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.35-7.22 \) (m, 20H, ArCH), 5.60 (br t, \(^3\)J(H,H) = 5.7 Hz, 2H, NH\(_c\)), 4.21 (t, \(^3\)J(H,H) = 8.0 Hz, 2H, CH\(_a\)), 3.91 (dd, \(^3\)J(H,H) = 8.0 Hz, \(^3\)J(H,H) = 5.7 Hz, CH\(_b\)), 2.03 (m, 4H, CH\(_d\)) and 1.47 (m, 4H, CH\(_e\)); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 172.6 \) (CO), 141.9 (ArC-CH- (ipso)), 128.7 (ArCH (meta)), 128.0 (ArCH (ortho)), 126.8 (ArCH (para)), 50.6 (CH\(_a\)), 43.7 (CH\(_b\)), 36.1 (CH\(_d\)) and 24.7 (CH\(_e\)). HRMS (FAB, THIOG matrix): \( m/z = 505.28550 [(M+H)^+] \) (Anal. Calcd. for C\(_{34}\)H\(_{37}\)N\(_2\)O\(_2\): \( m/z = 505.28695 \)).
Rotaxane S4 was prepared from thread S3 (0.50 g, 0.99 mmol) according to the general procedure for the preparation of benzylic amide macrocycle containing [2]rotaxane. The crude product was purified by column chromatography (CHCl₃/MeOH (97/3)) to give the desired compound as a colourless solid. (S4, 0.08 g, 8%); m.p. 264 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.16 (br t, 4H, ArCH₂), 8.14 (br s, 2H, ArCH₂), 7.59 (t, 3J(H,H) = 7.8 Hz, 2H, ArCH₃), 7.49 (br t, 4H, NH₂), 7.40-7.25 (m, 20H, ArCH₃), 7.06 (s, 8H, ArCH₂), 5.99 (br t, 2H, CH₂), 4.55 (d, 3J(H,H) = 5.6 Hz, 8H, CH₂), 4.12 (t, 3J(H,H) = 7.8 Hz, 2H, CH₂), 3.65 (dd, 3J(H,H) = 7.8 Hz, 4H, CH₂), 0.91 (m, 4H, CH₃) and 0.50 (m, 4H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 173.5 (CO thread), 166.5 (CO macrocycle), 142.0 (ArC-CH (ipso thread)), 137.8 (ArC-CH₂), 134.1 (ArC-CO), 131.1 (ArCH₂), 129.3 (ArCH₃), 128.8 (ArCH₂), 128.7 (ArCH (meta thread)), 128.0 (ArCH (ortho thread)), 126.9 (ArCH (para thread)), 124.5 (ArCH₃), 50.2 (CH₃), 44.2 (CH₂), 43.8 (CH₂), 34.7 (CH₂) and 23.8 (CH₃); HRMS (FAB, THIOG matrix): m/z = 1037.49656 [(M+H)⁺] (Anal. Calcd. for C₆₆H₆₅N₆O₆: m/z = 1037.49395).

X-ray crystallographic data for compound S4.

Crystals of rotaxane grown in CHCl₃/MeOH: C₆₆H₇₂N₆O₆, M = 1101.32, crystal size 0.10 × 0.06 × 0.05 mm, monoclinic, C2/c, a = 30.939(6), b = 11.3129(18), c = 18.568(3) Å, β = 118.147(17)°, V = 5730.5(17) Å³, Z = 4, ρcalcd = 1.277 Mg m⁻³; synchrotron radiation (CCLRC Daresbury Laboratory Station 9.8, silicon monochromator, λ = 0.69230 Å), μ = 0.084 mm⁻¹, T = 150(2) K. 18920 data (7604 unique, Rint = 0.0348, 2.42 < θ < 29.30°), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in θ), and were corrected semi-empirically for absorption
and incident beam decay (transmission 1.00–0.60). The structure was solved by direct methods and refined by full-matrix least-squares on \( F^2 \) values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give \( wR = \left( \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right)^{1/2} = 0.1361 \), conventional \( R = 0.0541 \) for \( F \) values of 7604 reflections with \( F_o^2 > 2 \sigma (F_o^2) \), \( S = 1.070 \) for 384 parameters. Residual electron density extremes were 0.429 and \(-0.411 \) eÅ\(^{-3}\). Amide hydrogen atoms were refined isotropically with the remainder constrained; anisotropic displacement parameters were used for all non-hydrogen atoms.

**2,2-Diphenylethyl succinic acid mono ester, S5.**

![Structure of 2,2-Diphenylethyl Succinic Acid Mono Ester](image)

To a stirred solution of 2,2-diphenylethanol (3.00 g, 15.0 mmol) in CH\(_2\)Cl\(_2\) (150 mL) was added one drop of Et\(_3\)N and a solution of succinic anhydride (1.66 g, 16.7 mmol) in CH\(_2\)Cl\(_2\) (25 mL) added slowly over 30 mins. After 16 h the solution was reduced in volume and recrystallized from CH\(_2\)Cl\(_2\) (10 mL) to obtain a colourless solid (S5, 4.00 g, 90\%). m.p. 103-104 °C. \(^1\)H NMR (400 MHz, \( d_6 \)-DMSO): \( \delta = 7.38\text{-}7.21 \) (m, 10H, ArCH), 4.61 (d, \( ^3 J(H,H) = 7.7 \) Hz, 2H, CH\(_b\)), 4.35 (t, \( ^3 J(H,H) = 7.7 \) Hz, 1H, CH\(_a\)) and 2.40 (m, 4H, CH\(_c\) and CH\(_d\)); \(^{13}\)C NMR (100 MHz, \( d_6 \)-DMSO): \( \delta = 173.9 \) (CO), 172.4 (CO), 141.8 (ArC-CH- (ipso)), 128.8 (ArCH (meta)), 128.3 (ArCH (ortho)), 127.0 (ArCH (para)), 66.5 (CH\(_b\)), 49.6 (CH\(_a\)), 29.1 (CH\(_c\) or CH\(_d\)) and 28.9 (CH\(_c\) or CH\(_d\)); MS (FAB): \( m/z = 299 \text{ [(M+H)^+]} \); Anal. Calcd. for C\(_{18}\)H\(_{18}\)O\(_4\): C 72.47, H 6.08. Found C 73.01, H 6.22.

**N-(2,2-Diphenylethyl)-succinamic acid 2,2-diphenyl-ethyl ester, S6.**

![Structure of N-(2,2-Diphenylethyl)-succinamic Acid 2,2-Diphenyl-ethyl Ester](image)

To a stirred solution of S5 (1.0 g, 3.4 mmol), 2,2-diphenylethylamine (0.66 g, 3.4 mmol) and 4-DMAP (0.49 g, 4 mmol) in CH\(_2\)Cl\(_2\) (350 mL) cooled in an ice bath was added EDCI.HCl (0.71 g, 3.7 mmol) and the solution allowed to stir for 16 h. The reaction mixture was washed with a
saturated solution of citric acid (3 x 50 mL) and H₂O (3 x 50 mL). The organic layer was dried over anhydrous MgSO₄, filtrated and the filtrate reduced in volume and the resulting solid purified by chromatography on silica gel using a gradient of CH₂Cl₂ to CH₂Cl₂/EtOAc (80/20) to obtain the desired compound as a colourless powder (S6, 1.16 g, 71%). m.p. 150-153 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.22 (m, 20H, ArCH), 5.60 (br, 1H, NH₄), 4.64 (d, ³J(H,H) = 7.8 Hz, 2H, CH₆), 4.38 (t, ³J(H,H) = 7.8 Hz, 1H, CH₆), 4.21 (t, ³J(H,H) = 8.0 Hz, 1H, CH₆), 3.90 (dt, ³J(H,H) = 8.0 Hz, 1H, CH₆), 2.55 (t, ³J(H,H) = 7.0 Hz, 2H, CH₆), 2.27 (t, ³J(H,H) = 7.0 Hz, 2H, CH₆); ¹³C NMR (100 MHz, CDCl₃): δ = 173.1 (CHc-CO-O), 171.6 (-CO-NH₄), 142.3 (ArC-CH (ipso)), 141.5 (ArC-CH (ipso)), 129.2 (ArCH (meta)), 129.0 (ArCH (meta)), 128.6 (ArCH (ortho)), 128.5 (ArCH (ortho)), 127.3 (ArCH (para)), 67.3 (CHb), 51.0 (CHa), 50.0 (CHg), 44.3 (CHf), 31.3 (CHc) and 29.9 (CHd); FABMS: m/z 478 [M+H]⁺; Anal. Calcd. for C₃₂H₃₁NO₃: C 80.48, H 6.54, N 2.93. Found C 80.70, H 6.68, N 3.02.

[2]-(1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N-(2,2-diphenylethyl)-succinamic acid 2,2-diphenylethyl ester)-rotaxane, S7.

Rotaxane S7 was obtained using the general procedure for the preparation of benzylic amide macrocycle containing [2]rotaxane from thread S6 (1.16 g, 2.4 mmol). The solid crude was subjected to column chromatography on silica gel using CH₂Cl₂/EtOAc (75/15) as eluent to obtain the desired compound as a colourless powder (S7, 95 mg, 4%). m.p. 204-205 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.21 (dd, ⁴J(Hb,Ha) = 1.5 Hz, ³J(Hb,Hc) = 7.8 Hz, 4H, ArCHb), 8.17 (br t, ⁴J(Hc,Hb) = 1.5 Hz, 2H, ArCHc), 7.66 (t, ³J(Hb,Hc) = 7.8 Hz, 2H, ArCHb), 7.31-7.08 (m, 24H, ArCH(thread) and NH₄), 6.84 (s, 8H, ArCH₆), 7.33 (br t, ³J(H,H) = 5.6 Hz, 1H, NH₆), 4.46 (dd,
$^2J(\text{H}_E,\text{H}'_E) = 14.4 \text{ Hz}$, $^3J(\text{H}_E,\text{H}_D) = 5.6 \text{ Hz}$, 4H, $\text{CHH}'_E$), 4.40 (dd, $^2J(\text{H}_E,\text{H}'_E) = 14.4 \text{ Hz}$, $^3J(\text{H}'_E,\text{H}_D) = 5.3 \text{ Hz}$, 4H, $\text{CHH}'_E$), 4.34 (d, $^3J(\text{H},\text{H}) = 7.3 \text{ Hz}$, 2H, $\text{CH}_b$), 4.14 (t, $^3J(\text{H},\text{H}) = 7.3 \text{ Hz}$, 1H, $\text{CH}_a$), 4.05 (t, $^3J(\text{H},\text{H}) = 7.8 \text{ Hz}$, 1H, $\text{CH}_g$), 4.05 (t, $^3J(\text{H},\text{H}) = 7.8 \text{ Hz}$, 2H, $\text{CH}_d$), 1.26 (br t, $^3J(\text{H},\text{H}) = 7.5 \text{ Hz}$, 2H, $\text{CH}_c$) and 0.86 (br t, $^3J(\text{H},\text{H}) = 7.5 \text{ Hz}$, 2H, $\text{CH}_d$); $^{13}\text{C}$ NMR (100 MHz, $d_6$-DMSO): $\delta = 173.1$ ($\text{CH}_c-\text{CO-O}$), 171.9 ($-\text{CO-NH}_2$), 166.1 ($\text{CO}$ macrocycle), 143.2 ($\text{ArC-CH}$ (ipso thread)), 141.6 ($\text{ArC-CH}$ (ipso thread)), 137.6 ($\text{ArC-CH}_E$), 134.9 ($\text{ArC-CO}$-), 130.7 ($\text{ArCH}_b$), 129.1 ($\text{ArCH}_A$), 128.8 ($\text{ArCH}_F$), 128.7 ($\text{ArCH}$ (meta thread)), 128.0 ($\text{ArCH}$ (ortho thread)), 126.9 ($\text{ArCH}$ (para thread)), 126.7 ($\text{ArCH}$ (para thread)), 125.8 ($\text{ArCH}_C$), 66.3 ($\text{CH}_b$), 50.4 ($\text{CH}_a$ or $\text{CH}_g$), 49.3 ($\text{CH}_a$ or $\text{CH}_d$), 43.6 ($\text{CH}_d$), 43.5 ($\text{CH}_E$), 28.8 ($\text{CH}_c$ or $\text{CH}_i$) and 28.1 ($\text{CH}_c$ or $\text{CH}_d$); MS (FAB): $m/z = 1010$ [M+H]+; Anal. Calcd. for C$_{64}$H$_{59}$N$_5$O$_7$: C 76.09, H 5.89, N 6.93. Found C 76.31, H 5.78, N 6.79.

**X-ray crystallographic data for compound S7.**

$\text{C}_{72}\text{H}_{82}\text{N}_5\text{O}_{11}\text{S}_4$, $M = 1321.67$, crystal size $0.15 \times 0.10 \times 0.08$ mm, triclinic $P-1$, $a = 9.9959(4)$, $b = 12.8280(4)$, $c = 15.1241(6)$ Å, $\alpha = 107.0330(10)$, $\beta = 105.5420(10)$, $\gamma = 99.0490(10)$°, $V = 1726.95(11)$ Å$^3$, $Z = 1$, $\rho_{\text{calc}} = 1.271$ Mg m$^{-3}$; MoK$_\alpha$ radiation (graphite monochromator, $\lambda = 0.71073$ Å), $\mu = 0.201$ mm$^{-1}$, $T = 180(2)$ K. 11064 data (7963 unique, $R_{\text{int}} = 0.0510$, 1.72 $< \theta < 28.97$°), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in $\omega$), and were corrected semi-empirically for absorption and incident beam decay (transmission 1.00–0.45). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2697$, conventional $R = 0.0963$ for $F$ values of 7963 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 0.873$ for 438 parameters. Residual electron density extremes were 0.998 and −0.719 eÅ$^{-3}$. Amide hydrogen atoms were refined isotropically with the remainder constrained; anisotropic displacement parameters were used for all non-hydrogen atoms.
**N-(2,2-Diphenylethyl)-maleamide acid, S8.**

![Chemical Structure](image)

To a stirred solution of 2,2-diphenylethylamine (5.00 g, 25.3 mmol) in anhydrous THF (25 mL) at 0 °C, was added dropwise a solution of maleic anhydride (2.50 g, 25.5 mmol) in anhydrous THF (10 mL). The mixture obtained was allowed to stir at rt for 16 h and then reduced in volume and the resulting oil taken up with CHCl₃ (50 mL) and washed with a solution of 1N NaOH (3 x 20 mL) and H₂O (1 x 20 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the solvent removed under reduced pressure to obtain a colourless solid which was recrystallized from CH₂Cl₂. (S8, 5.62 g, 75%). m.p. 209 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.29-7.23 (m, 4H, ArC₆H₄(meta)), 7.20-7.14 (m, 6H, ArC₆H₄(ortho and para)), 6.43 (br t, ³J(H,H) = 5.7 Hz, 1H, NHc), 6.19 (d, ³J(H,H) = 12.6 Hz, 1H, CHₑ), 6.02 (d, ³J(H,H) = 12.6 Hz, 1H, CH₆), 4.18 (t, ³J(H,H) = 8.0 Hz, 1H, CHₐ) and 3.95 (dd, ³J(H,H) = 8.0 Hz, ³J(H,H) = 5.7 Hz, 2H, CH₇); ¹³C NMR (100 MHz, CDCl₃): δ = 166.0 (-CO-OH), 164.5 (-CO-NH₂), 140.7 (ArC-CH (ipso)), 137.1 (CH₃), 130.2 (CH₆), 129.0 (ArCH (meta)), 127.9 (ArCH (ortho)), 127.4 (ArCH (para)), 50.0 (CH₄) and 44.6 (CH₅); HRMS (FAB, THIOG matrix): m/z = 262.12884 [(M+H)+] (Anal. Calcd. for C₁₈H₁₈NO₃: m/z = 296.12867). Anal. Calcd. for C₁₈H₁₇NO₃: C 73.20, H 5.80, N 4.74. Found C 73.13, H 5.85, N 4.61.

**12-Aminododecylcarbamic acid tert-butyl ester, S9.**

![Chemical Structure](image)

To a stirred solution of 1,12-diaminododecane (20.00 g, 100 mmol) in CHCl₃ (500 mL) was added di-tert-butyl dicarbonate (11 g, 50 mmol). The reaction was allowed to stir for 16 h at rt after which time the solvent was removed under reduced pressure and the residual oil subjected to column chromatography using a solvent gradient of CHCl₃/MeOH (95/5) to CHCl₃/MeOH/NH₄OH (89/10/1) to obtain a colourless solid (S9, 9 g, 60%). m.p. 96-97 °C. ¹H NMR (400 MHz, CDCl₃): δ = 4.50 (br t, ³J(H,H) = 5.7 Hz, 1H, NH₅), 3.10 (td, ³J(H,H) = 7.0 Hz, ³J(H,H) = 5.7 Hz, 2H, CH₆), 2.67 (t, ³J(H,H) = 7.0 Hz, 2H, CH₇), 1.49-1.36 (br, 13H, CH₉, CH₁₀ and CH₁₁) and 1.33-1.20 (br, 16H,
-CH₂- (alkyl chain); ¹³C NMR (100 MHz, CDCl₃): δ = 156.3 (CO), 79.2 (C(CH₃)₃), 42.6 (CH₂), 40.9 (CH₂), 34.2 (-CH₂-), 30.4 (-CH₂-), 30.0 (-CH₂-), 29.9 (-CH₂-), 29.7 (-CH₂-), 29.6 (-CH₂-), 29.2 (-CH₂-), 28.9 (-CH₂-), 28.8 (CH₃), 27.2 (-CH₂-) and 27.1 (-CH₂-); HRMS (FAB, THIOG matrix): m/z = 301.28491 [(M+H)⁺] (Anal. Calcd. for C₁₇H₃₇N₂O₂: m/z = 301.28550). Anal. Calcd. for C₁₇H₃₆N₂O₂: C 67.95, H 12.08, N 9.32. Found C 67.73, H 11.94, N 9.31.

N-(12-tert-Butyloxycarbonylaminododecyl)-succinamic acid 2,2-diphenylethyl ester, S10.

To a stirred solution of S₅ (0.40 g, 1.3 mmol), S₉ (0.40 g, 1.3 mmol) and 4-DMAP (0.20 g, 1.6 mmol) in anhydrous CH₂Cl₂ (200 mL) cooled on an ice bath, was added EDCI-HCl (0.28 g, 1.5 mmol) and the reaction allowed to stir for 48 h at rt. The solution was washed with a saturated solution of citric acid (2 x 50 mL) and H₂O (2 x 50 mL) and the organic layer dried over anhydrous MgSO₄, filtered and the filtrate reduced in volume. The solid obtained was subjected to column chromatography using a solvent gradient of CH₃Cl to CH₃Cl/MeOH (90/10) to obtain a colourless solid (S₁₀, 0.52 g, 68%). m.p. 88-89 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.22-7.18 (m, 4H, ArC₇H₈ (meta)) 7.17-7.09 (m, 6H, ArC₇H₈ (ortho and para)), 5.52 (t br, ³J(H,H) = 5.7 Hz, 1H, NH₆), 4.56 (d, ³J(H,H) = 7.7 Hz, 2H, CH₆), 4.47 (br, 1H, NH₆), 4.28 (t, ³J(H,H) = 7.7 Hz, 1H, CH₆), 3.10 (td, ³J(H,H) = 7.0 Hz, 2H, CH₆), 3.02 (br, 2H, CH₆), 2.50 (t, ³J(H,H) = 7.0 Hz, 2H, CH₆), 2.25 (t, ³J(H,H) = 7.0 Hz, 2H, CH₆), 1.42-1.30 (m, 13H, CH₆, CH₆ and CH₆) and 1.25-1.13 (m, 16H, -CH₂- (alkyl chain)); ¹³C NMR (100 MHz, CDCl₃): δ = 173.2 (CH c-CO-O), 171.6 (CO-NH₆), 156.3 (CO), 141.4 (ArC- (ipso)), 128.9 (Ar(CH₃)₃), 128.6 (Ar(CH (meta))), 128.6 (Ar(CH (ortho))), 127.2 (Ar(CH para)), 79.4 (C(CH₃)₃), 67.3 (CH₃), 50.2 (CH₃), 41.0 (CH₃), 40.0 (CH₃), 32.4 (CH₃), 31.0 (CH₆), 30.4 (-CH₂-), 30.1 (-CH₂-), 30.0-29.9 (-CH₂-), 29.6 (-CH₂-), 29.5 (-CH₂-), 29.4 (-CH₂-), 28.8 (CH₆), 27.3 (-CH₂-) and 27.2 (-CH₂-); MS (FAB): m/z = 581 [(M + H)⁺]; Anal. Calcd. for C₃₅H₅₂N₂O₅: C 72.38, H 9.02, N 4.82. Found C 72.62, H 9.40, N 5.02.
**N-(2,2-Diphenylethyl)-fumaric acid ethyl ester, S11.**

![Chemical Structure](image)

To a stirred solution of 2,2-diphenylethylamine (0.50 g, 2.5 mmol), fumaric acid monoethylester (0.37 g, 2.5 mmol) and 4-DMAP (0.33 g, 2.7 mmol) in anhydrous CH$_2$Cl$_2$ (200 mL) cooled on an ice bath was added EDCI·HCl (0.52 g, 2.7 mmol). After 24 h the solution was washed with a saturated solution of citric acid (3 x 50 mL) and H$_2$O (3 x 50 mL) and the organic layer dried over anhydrous MgSO$_4$, filtered and the filtrate reduced in volume to obtain a colourless solid that was recrystallized from EtOAc (S11, 0.70 g, 85%). m.p. 112-113 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.34-7.27 (m, 4H, ArH (meta)), 7.26-7.19 (m, 6H, ArH (ortho and para)), 6.77 (d, $^3$J(H,H) = 14.4 Hz, 1H, CH$_a$), 6.72 (d, $^3$J(H,H) = 14.4 Hz, 1H, CH$_d$), 5.90 (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_c$), 4.25-4.15 (m, 3H, CH$_b$ and CH$_f$), 3.98 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_b$) and 1.28 (t, $^3$J(H,H) = 7.0 Hz, 3H, CH$_g$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 165.6 (-CO-OEt), 163.6 (-CO-NH), 141.5 (ArC- (ipso)), 136.0 (CH$_e$), 130.6 (CH$_d$), 128.9 (ArCH (meta)), 128.1 (ArCH (ortho)), 127.0 (ArCH (para)), 61.2 (CH$_f$), 50.3 (CH$_a$), 44.1 (CH$_b$) and 14.1 (CH$_g$); MS (FAB): $m/z$ = 324 [(M+H)$^+$]; Anal. Calcd. for C$_{20}$H$_{21}$NO$_3$: C 74.28, H 6.55, N 4.33. Found C 74.83, H 6.91, N 4.38.

**N-(2,2-Diphenylethyl)-fumaramide acid, S12.**

![Chemical Structure](image)

To a stirred solution of S11 (0.70 g, 2.2 mmol) in EtOH (50 mL) was added dropwise a solution of NaOH (0.10 g, 2.4 mmol) in H$_2$O (2.5 mL). After 16 h the solution was reduced in volume and washed several times with Et$_2$O to obtain a colourless powder that was recrystallized from CHCl$_3$ (S12, 0.58 g, 91%), m.p. >270 °C (decomp). $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta$ = 12.83 (br s, 1H, -COOH), 8.57 (br t, $^3$J(H,H) = 5.7 Hz, 1H, NH$_c$), 7.33-7.15 (m, 10H, ArCH), 6.87 (d, $^3$J(H,H) = 15.4 Hz, 1H, CH$_e$), 6.47 (d, $^3$J(H,H) = 15.4 Hz, 1H, CH$_d$), 4.22 (t, $^3$J(H,H) = 8.0 Hz, 1H, CH$_b$) and 3.81 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 5.7 Hz, 2H, CH$_b$); $^{13}$C NMR (100 MHz, $d_6$-DMSO) $\delta$ 168.0 (CO-OH), 164.5 (CO-NH$_c$), 143.1 (ArC- (ipso)), 134.3 (CH$_e$), 134.0 (CH$_d$), 128.8 (ArCH (meta)), 128.2
(ArCH (ortho)), 126.7 (ArCH (para)), 50.3 (CH₆) and 43.7 (CH₇); MS (FAB): m/z = 296 [(M+H)⁺]; Anal. Calcd. for C₁₈H₁₇NO₃: C 73.20, H 5.80, N 4.70. Found C 73.10, H 5.20, N 4.73.

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\text{N-(2,2-Diphenylethyl)-succinamic acid, S13.}
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\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{O} \\
& \quad \text{a} & \quad \text{b} \\
& \quad \text{c} & \quad \text{d} \\
& \quad \text{e} & \quad \text{OH}
\end{align*}
\]

To a stirred solution of succinic anhydride (2.53 g, 25.3 mmol) in anhydrous THF (25 mL) was added at rt dropwise a solution of 2,2-diphenylethylamine (5.00 g, 25.3 mmol) in anhydrous THF (25 mL). After 16 h the solvent was removed under reduced pressure and the resulting oil recrystallized in CH₂Cl₂ to obtain a colourless solid. (S13, 7.16 g, 95%). m.p. 153-154°C. ¹H NMR (400 MHz, CDCl₃): δ = 7.34-7.28 (m, 4H, ArCH (meta)), 7.26-7.19 (m, 6H, ArCH (ortho and para)), 5.63 (br t, 3 J(H,H) = 5.7 Hz, 1H, NHc), 4.18 (t, 3 J(H,H) = 8.0 Hz, 1H, CHa), 3.90 (dd, 3 J(H,H) = 8.0 Hz, 3 J(H,H) = 5.7 Hz, 2H, CHb), 2.63 (t, 3 J(H,H) = 6.5 Hz, 2H, CHa) and 2.39 (t, 3 J(H,H) = 6.5 Hz, 2H, CHa); ¹³C NMR (100 MHz, CDCl₃): δ = 176.2 (CO-OH), 172.1 (CO-NHc), 141.5 (ArC- (ipso)), 128.8 (ArCH (meta)), 128.0 (ArCH (ortho)), 127.0 (ArCH (para)), 50.4 (CH₆), 44.0 (CH₇), 30.6 (CH₆) and 29.6 (CH₇); MS (FAB): m/z = 298 [(M+H)⁺]; Anal. Calcd. for C₁₈H₁₉NO₃: C 72.71, H 6.44, N 4.71. Found C 72.83, H 6.57, N 4.80.

\[
\text{N-(12-Aminododecyl)-N'-(2,2-diphenylethyl)-succinamide, S14.}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{O} \\
& \quad \text{a} & \quad \text{b} \\
& \quad \text{c} & \quad \text{d} \\
& \quad \text{e} & \quad \text{f} \\
& \quad \text{g} & \quad \text{h} \\
& \quad \text{i} & \quad \text{NH₂}
\end{align*}
\]

To a stirred solution of S13 (0.50 g, 1.7 mmol) in CH₂Cl₂ was added thionyl chloride (0.12 mL, 1.7 mmol). The solution was heated until complete dissolution of S13 and the resulting solution added dropwise to a solution of 1,12-diaminododecane (1.68 g, 8.40 mmol) and Et₃N (0.17 g, 1.7 mmol) in CH₂Cl₂ at 0°C. After 30 min the reaction mixture was washed with 1N NaOH (1 x 100 mL) and H₂O (1 x 100 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the filtrate reduced in volume to obtain a solid that was subjected to column chromatography using a solvent gradient of CHCl₃ to CHCl₃/MeOH (90/10) to obtain a colourless solid (S14, 0.28 g, 35%). m.p. 78-
79 °C. 1H NMR (400 MHz, CDCl₃): \[ \delta = 7.36-7.29 \text{ (m, 4H, ArH (meta))}, 7.28-7.21 \text{ (m, 6H, ArH (ortho and para))} \), 6.14 (br t, \[ J(H,H) = 5.7 \text{ Hz, 1H, NHc})], 4.19 (t, \[ J(H,H) = 8.0 \text{ Hz, 1H, CH₆}]], 3.89 (dd, \[ J(H,H) = 8.0 \text{ Hz, } J(H,H) = 5.7 \text{ Hz, 2H, CH₆}]], 3.19 (td, \[ J(H,H) = 7.0 \text{ Hz, J(H,H) = 5.7 Hz, 2H, CH₆}]], 2.41 (m, 4H, CH₆ and CH₇), 1.40-1.54 (m, 4H, CH₇ and CH₈) and 1.20-1.40 (m, 16H, -CH₂- (alkyl chain)); 13C NMR (100 MHz, CDCl₃): \[ \delta = 172.6 \text{ (CO), 172.3 \text{ (CO), 142.3 \text{ (ArC- (ipso), 129.1 \text{ (ArCH (meta), 128.4 \text{ (ArCH (ortho), 127.2 \text{ (ArCH (para), 51.0 \text{ (CH₆}, 44.2 \text{ (CH₇}, 42.7 \text{ (CH₈}, 40.0 \text{ (CH₉}, 34.3 \text{ (CH₉}, 32.2 \text{ (CH₆ or CH₇}, 32.1 \text{ (CH₆ or CH₇}, 30.0 \text{ (-CH₂-), 29.9 \text{ (-CH₂-), 29.8 \text{ (-CH₂-), 29.7 \text{ (-CH₂-), 27.3 \text{ (-CH₂-) and 27.2 \text{ (-CH₂-); MS (FAB): } m/z = 480 [(M+H)⁺]}; Anal. Calcd. for C₃₀H₄₅N₃O₂: C 75.11, H 9.46, N 8.76. Found C 75.23, H 9.65, N 8.87.

5-(2,2-Diphenylethylcarbamoyl)-pentanoic acid ethyl ester, S15.

A solution of adiptic acid monoethyl ester (4.01 g, 23 mmol), 2,2-diphenylethylamine (5.00 g, 25 mmol) and 4-DMAP (2.81 g, 23 mmol) in CH₂Cl₂ (250 mL) was stirred at 0 °C for 10 min followed by addition of EDCI·HCl (4.42 g, 23 mmol). After 16 h the organic phase was washed with 1N HCl (3 x 70 mL), saturated aqueous NaHCO₃ (3 x 70 mL) and brine (1 x 70 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the filtrate concentrated to give the product as a colourless solid. (S15, 7.03 g, 86%). m.p. 44 °C; 1H NMR (400 MHz, CDCl₃): \[ \delta = 7.34-7.21 \text{ (m, 10H, ArCH₆}, 5.70 (br t, \[ J(H,H) = 5.7 \text{ Hz, 1H, NHc})], 4.23 (t, \[ J(H,H) = 8.0 \text{ Hz, 1H, CH₆}]], 4.13 (q, \[ J(H,H) = 7.0 \text{ Hz, 2H, CH₆}]], 3.91 (dd, \[ J(H,H) = 8.0 \text{ Hz, J(H,H) = 5.7 Hz, 2H, CH₆}]], 2.26 (t, \[ J(H,H) = 7.0 \text{ Hz, 2H, CH₆ or CH₇}]], 2.09 (t, \[ J(H,H) = 7.0 \text{ Hz, 2H, CH₆ or CH₇}]], 1.56 (m, 4H, CH₆ and CH₇), 1.27 (t, \[ J(H,H) = 7.0 \text{ Hz, 3H, CH₇}]]; 13C NMR (100 MHz, CDCl₃): \[ \delta = 173.8 \text{ (CO-OEt), 172.9 \text{ (CO-NHc}, 142.3 \text{ (ArC- (ipso), 129.1 \text{ (ArCH (meta), 128.5 \text{ (ArCH (ortho), 127.2 \text{ (ArCH (para), 60.7 \text{ (CH₆}, 51.0 \text{ (CH₇}, 44.2 \text{ (CH₈}, 36.6 \text{ (CH₉ or CH₊}, 34.3 \text{ (CH₊ or CH₁₂}, 25.4 \text{ (CH₂ or CH₁₂}, 24.7 \text{ (CH₇ or CH₁₂} and 14.7 \text{ (CH₁); HRMS (FAB, THIOG matrix): } m/z = 354.20660 [(M+H)⁺]; Anal. Calcd. for C₂₂H₂₈NO₃: m/z = 354.20692).
5-(2,2-Diphenylethylcarbamoyl)-pentanoic acid, S16.

![Chemical structure](image)

To a solution of S15 (7.03 g, 19.9 mmol) in EtOH (50 mL) was added aqueous KOH (5.58 g in 9 mL of H₂O, 99.4 mmol) and the resulting solution stirred for 2 h at 78 °C. The yellow solution was cooled to rt, poured into water and acidified with dropwise addition of concentrated HCl resulting in a colourless precipitate that was filtered and dried in vacuo to give the product as a colourless solid (S16, 6.12 g, 95%). m.p. 124 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.23 (m, 10H, ArCH), 5.55 (br t, ³J(H,H) = 5.7 Hz, 1H, NH), 4.21 (t, ³J(H,H) = 8.0 Hz, 1H, CH₃), 3.92 (dd, ³J(H,H) = 8.0 Hz, ³J(H,H) = 5.7 Hz, 2H, CH₂), 2.33 (t, ³J(H,H) = 7.0 Hz, 2H, CH₂), 2.12 (t, ³J(H,H) = 7.0 Hz, 2H, CH₂), 1.59 (m, 4H, CH₂ and CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 178.2 (-CO-OH), 172.8 (-CO-NH), 141.7 (ArC- (ipso)), 128.7 (ArC- (meta)), 128.0 (ArC- (ortho)), 126.9 (ArC- (para)), 50.6 (CH₃), 43.8 (CH₂), 36.2 (CH₂), 33.5 (CH₃), 24.9 (CH₂ or CH₃), 24.0 (CH₂ or CH₃); HRMS (FAB, THIOG matrix): m/z = 326.17637 [(M+H)+] (Anal. Calcd. for C₂₀H₂₄NO₃: m/z = 326.17562).

(12-[5-(2,2-Diphenylethylcarbamoyl)-pentanoylamino]-dodecyl}-carbamic acid tert-butyl ester, S17.

A solution of S16 (0.50 g, 1.5 mmol), S9 (0.51 g, 1.7 mmol) and 4-DMAP (0.19 g, 1.5 mmol) in CHCl₃ (20 mL) was stirred at 0 °C for 10 min followed by addition of EDCI·HCl (0.29 g, 1.5 mmol). After 16 h the reaction mixture diluted with CHCl₃ (10 mL) and the organic phase washed with 1N HCl (3 x 10 mL), saturated NaHCO₃ (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over anhydrous MgSO₄, filtered and the filtrate concentrated to give the product as a colourless solid (S17, 0.85 g, 92%). m.p. 114 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.33-7.20 (m, 10H, ArCH), 5.84 (br t, ³J(H,H) = 5.7 Hz, 1H, NH), 5.79, (br t, ³J(H,H) = 5.7 Hz, 1H, NH), 4.57
(br t, $^3J(H,H) = 5.7$ Hz, 1H, NH$_m$), 4.22 (t, $^3J(H,H) = 8.0$ Hz, 1H, CH$_a$), 3.90 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, CH$_b$), 2.69 (m, 2H, CH$_h$), 2.11 (t, $^3J(H,H) = 7.3$ Hz, 2H, CH$_d$ or CH$_g$), 2.09 (t, $^3J(H,H) = 7.3$ Hz, 2H, CH$_d$ or CH$_g$), 1.58 (m, 4H, CH$_e$ and CH$_j$), 1.51 (m, 2H, CH$_i$), 1.45 (m, 2H, CH$_i$), 1.28 (brs, 16H, -CH$_2$- (alkyl chain)); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 172.7 (CO), 172.5 (CO), 157.6 (NH m-), 141.9 (Ar (ipso)), 128.7 (Ar (meta)), 128.0 (Ar (ortho)), 126.8 (Ar (para)), 79.4 (CH$_3$), 50.6 (CH$_a$), 43.7 (CH$_b$), 40.6 (CH$_i$), 39.6 (CH$_l$), 36.2 (CH$_d$ or CH$_g$), 36.1 (CH$_d$ or CH$_g$), 30.0 (-CH$_2$-), 29.6 (-CH$_2$-), 29.5 (-CH$_2$-), 29.3 (-CH$_2$-), 28.4 (-CH$_2$-), 26.9 (-CH$_2$-), 26.8 (-CH$_2$-), 24.9 (-CH$_2$-), 24.8 (-CH$_2$-), MS (FAB): $m/z = 608$ [(M + H)$^+$]; HRMS (FAB, THIOG matrix): $m/z = 608.44148$ [(M+H)$^+$] (Anal. Calcd. for C$_{37}$H$_{58}$N$_3$O$_4$: $m/z = 608.44273$).

Hexanedioic acid (12-aminododecyl)-amide (2,2-diphenylethyl)-amide, S18.

A solution of S17 (0.4 g, 0.7 mmol) in TFA (15 mL) was stirred at rt for 30 min. The reaction mixture was washed with 1N NaOH (2x 10 mL), brine (1x 10 mL), dried over anhydrous MgSO$_4$, filtered and the filtrate concentrated to give the product as a colourless solid (S18, 0.22 g, 66%). m.p. 91 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.35-7.22 (m, 10H, ArCH$_i$), 5.77 (br t, $^3J(H,H) = 5.7$ Hz, 1H, NH$_c$ or NH$_h$), 5.75 (br t, $^3J(H,H) = 5.7$ Hz, 1H, NH$_c$ or NH$_h$), 4.22 (t, $^3J(H,H) = 8.0$ Hz, 1H, CH$_a$), 3.91 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, CH$_b$), 3.24 (td, $^3J(H,H) = 7.0$ Hz, $^3J(H,H) = 5.7$ Hz, 2H, CH$_d$ or CH$_g$), 2.69 (m, 2H, CH$_h$), 2.11 (t, $^3J(H,H) = 7.3$ Hz, 2H, CH$_d$ or CH$_g$), 2.09 (t, $^3J(H,H) = 7.3$ Hz, 2H, CH$_d$ or CH$_g$), 1.58 (m, 4H, CH$_e$ and CH$_j$), 1.51 (m, 2H, CH$_i$), 1.45 (m, 2H, CH$_i$), 1.28 (brs, 16H, -CH$_2$- (alkyl)); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 172.7 (CO), 172.6 (CO), 141.9 (Ar (ipso)), 128.7 (Ar (meta)), 128.0 (Ar (ortho)), 126.8 (Ar (para)), 50.6 (CH$_a$), 43.7 (CH$_b$), 42.2 (CH$_i$), 39.5 (CH$_l$), 36.2 (CH$_d$ or CH$_g$), 36.1 (CH$_d$ or CH$_g$), 33.7 (-CH$_2$-), 29.6-29.5 (-CH$_2$-), 29.4 (-CH$_2$-), 29.2 (-CH$_2$-), 26.9 (-CH$_2$-), 26.8 (-CH$_2$-), 24.9 (-CH$_2$-), 24.8 (-CH$_2$-); HRMS (FAB, THIOG matrix): $m/z = 508.39143$ [(M+H)$^+$] (Anal. Calcd. for C$_{32}$H$_{50}$N$_3$O$_2$: $m/z = 508.39030$).
Figure 1. 400 MHz $^1$H NMR spectra of (a) maleamide-adipamide thread Z-7 and (b) rotaxane Z-3 in CDCl$_3$ at 298K.