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Supporting Information

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Rotaxane Building Blocks bearing Blocked Isocyanate Stoppers – Polyrotaxanes through Post-Assembly Chain Extension**

Timothy J. Kidd, Ton Loontjens,* David A. Leigh* and Jenny K. Y. Wong

Experimental Section:

Crystallographic data

Rotaxane **3**: C₇₀H₇₆N₁₀O₁₀Cl₄, $M=1359.21$, crystal size 0.56×0.30×0.24mm, triclinic P-1, $a=10.59560(10)$, $b=11.5272(2)$, $c=15.3861(2)$ Å, $\alpha=110.5020(10)$, $\beta=101.6830(10)$, $\gamma=92.5240(10)^\circ$, $V=1710.13(4)$ Å³, $Z=1$, $\rho_{\text{calcd}}=1.320$ Mg m⁻³; MoK_α radiation (graphite monochromator, $\lambda=0.71073$ Å), $\mu=0.239$ mm⁻¹, $T=180(2)$ K. 15779 data (8127 unique, $R_{\text{int}}=0.0284$, $1.90<\theta<29.13^\circ$); Rotaxane **4**: C₉₂H₁₂₂N₁₀O₁₄, $M=1592.00$, crystal size 0.96×0.22×0.10mm, triclinic P-1, $a=10.9198(2)$, $b=14.0083(2)$, $c=14.80100(10)$ Å, $\alpha=88.35$, $\beta=88.44$, $\gamma=70.6730(10)^\circ$, $V=2121.95(5)$ Å³, $Z=1$, $\rho_{\text{calcd}}=1.246$ Mg m⁻³; MoK_α radiation (graphite monochromator, $\lambda=0.71073$ Å), $\mu=0.084$ mm⁻¹, $T=180(2)$ K. 13810 data (9853 unique, $R_{\text{int}}=0.0181$, $1.39<\theta<29.11^\circ$). Rotaxane **5**: C_{76.50}H₉₅ClN₁₀O₁₂, $M=1382.07$, crystal size 0.40 x 0.27 x 0.19 mm, monoclinic, $P2_1/c$, $a=20.5953(16)$, $b=20.3996(16)$, $c=18.8652(15)$ Å, $\beta=115.0790(10)^\circ$, $V=7178.7(10)$ Å³, $Z=4$, $\rho_{\text{calcd}}=1.279$ Mg m⁻³; MoK_α radiation (graphite monochromator, $\lambda=0.71073$ Å), $\mu=0.123$ mm⁻¹,

$T = 150(2)\text{K}$. 44134 data (17301 unique, $R_{\text{int}} = 0.0661$, $1.48 < \theta < 28.93^\circ$), All three structures 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 0.88-1.00 **3**; 0.63-1.00 **4**; 0.74-1.00 **5**). The structures were 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 for **3**: $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} = 0.2347$, conventional $R = 0.0754$ for F values of 8127 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.081$ for 436 parameters. Residual electron density extremes were 0.885 and $-1.068 \text{ \AA}^{-3}$. For **4**: $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} = 0.1982$, conventional $R = 0.0608$ for F values of 9853 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.067$ for 539 parameters. Residual electron density extremes were 0.664 and $-0.367 \text{ \AA}^{-3}$. For **5**: $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} = 0.2031$, conventional $R = 0.0704$ for F values of 17301 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.019$ for 938 parameters. Residual electron density extremes were 0.059 and $-0.952 \text{ \AA}^{-3}$. Amide hydrogen atoms in all three structures were refined isotropically with the all other hydrogen atoms constrained to a Riding model; anisotropic displacement parameters were used for all non-hydrogen atoms. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 188836, 188837 and 197400. 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: teched@chemcryst.cam.ac.uk).

Synthesis

N-[2-(Benzylamino)ethyl]-2-oxo-1-azepanecarboxamide **1**

To a stirred solution of *N*-benzylethylenediamine (5.00 g, 33.3 mmol) in dry toluene (100 mL) at 60 °C was added 1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone (CBC) (8.39 g, 33.3 mmol). The reaction was stirred for eighteen hours at 60 °C and cooled to room temperature. The mixture was washed with distilled water (4 x 200 mL) followed by saturated aqueous calcium chloride solution (2 x 200 mL). Drying of the organic layer with anhydrous magnesium sulfate followed by removal of the solvent under reduced pressure afforded the desired product as a pale yellow oil. Yield: 9.23 g, 92 %; ¹H NMR (300 MHz, CDCl₃) δ = 1.74 (6H, bs, CH₂), 2.71 (2H, bm, CH₂NCONH), 2.81 (2H, t, *J* = 6.5 Hz, CH₂NH), 3.35 (2H, q, *J* = 6 Hz, CH₂NHCO), 3.81 (2H, s, CH₂Ar), 3.97 (2H, bm, CH₂CON), 7.27 (5H, m, ArCH), 9.45 (1H, bt, CONH); ¹³C NMR (75 MHz, CDCl₃) δ = 23.37, 29.30, 29.34, 38.61, 39.05, 39.89, 50.20, 51.31, 129.96, 130.20, 130.40, 139.53, 157.35, 176.78; MS (EI): *m/z* 290 [M+H]⁺; anal. calcd. for C₁₆H₂₃N₃O₂: C, 66.4 %; H, 8.0 %; N, 14.5 %, found: C, 65.6 %; H, 7.8 %; N, 14.3 %.

***N*-{2-[(2-amino-3-phenylpropanoyl)(benzyl)amino]ethyl}-2-oxo-1-azepanecarboxamide -
Phenylalanine derivative of stopper **1** (mixture of isomers)**

1,3-Dicyclohexylcarbodiimide (0.78 g, 3.8 mmol) was added to a stirred solution of *t*-BOC-DL-phenylalanine (1.00 g, 3.8 mmol), stopper **1** (1.09 g, 3.8 mmol) and 4-dimethylaminopyridine (0.23 g, 1.8 mmol) in dichloromethane (10 mL) under an atmosphere of nitrogen at 0 °C. The reaction was stirred at 0 °C for half an hour followed by a further hour at room temperature before being filtered to remove precipitated dicyclohexylurea. The solvent was removed under reduced pressure to afford a colorless oil which was taken up in ethyl acetate (100 mL). 4 M hydrochloric acid (100 mL) was added and was stirred at room temperature for 15 hours under an atmosphere of nitrogen, cooled to 0 °C and neutralized using 3 M sodium hydroxide. Extraction of the product with ethyl acetate (3 x 100 mL) followed by drying of the organic portion (MgSO₄) and removal of the solvent under reduced pressure gave the product as a colorless oil. Yield: 1.46 g, 89 %; ¹H NMR (300 MHz, CDCl₃) δ = 1.74 (6H, bs, CH₂), 2.69 (2H, bm, CH₂NCONH), 3.02 (2H, m, CH₂Ar), 3.19 (2H, m, CH₂N), 3.38 (2H, m, CH₂NH), 3.74 & 4.04 (1H, m, CHCH₂Ar), 3.94 (bm, 2H, CH₂CON), 4.34 (2H, m, NH₂), 5.30 (m, 2H, CH₂Ar), 7.25 (10H, m, ArCH), 9.31 (1H, bm, CONH); ¹³C NMR (75 MHz, CDCl₃) δ = 23.73, 29.37, 29.40,

38.61, 39.11, 39.95, 43.07, 44.17, 49.20, 53.17, 127.68, 128.40, 128.85, 129.28, 129.67, 137.53, 138.20, 155.47, 176.21, 179.92; MS (EI): m/z 437 $[M+H]^+$, 324 $[(M\text{-caprolactam})+H]^+$; anal. calcd. for $C_{25}H_{32}N_4O_3$: C, 68.8 %; H, 7.4 %; N, 12.8 %, found: C, 68.6 %; H, 7.3 %; N, 12.3 %.

2-oxo-N-{6-[(6-[(2-oxo-1-azepanyl)carbonyl]amino}hexyl)amino]hexyl}-1-azepanecarboxamide 2

To a solution of bis-(hexamethylene)triamine (100.00 g, 0.466 mol) in dry toluene (400 mL) at 80 °C was added 1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone (CBC) (246.84 g, 0.980 mol) and the resultant mixture stirred for eighteen hours. The reaction was then cooled to room temperature, concentrated under reduced pressure to half its original volume and washed with distilled water (8 x 250 mL) followed by saturated aqueous calcium chloride solution (5 x 250 mL). Drying of the organic layer with anhydrous magnesium sulfate followed by the complete removal of the solvent under reduced pressure afforded the desired product as a brown waxy solid. Yield: 198.32 g, 94 %; 1H NMR (300 MHz, $CDCl_3$) δ = 1.35 (8H, m, $\underline{CH_2}$), 1.56 (8H, m, $\underline{CH_2}$), 1.83 (14H, m $\underline{CH_2}$), 2.68 (8H, m, $\underline{CH_2}NCONH$), 3.26 (4H, m, $\underline{CH_2}$), 3.98 (4H, m, $\underline{CH_2}CON$), 9.26 (2H, bt, $CONH$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 23.45, 26.52, 26.74, 28.31, 29.09, 29.38, 39.75, 40.45, 43.68, 46.86, 48.24, 154.78, 179.32; MS (EI): m/z 494 $[M+H]^+$; anal. calcd. for $C_{26}H_{47}N_5O_4$: C, 63.3 %; H, 9.6 %; N, 14.2 %, found: C, 63.0 %; H, 9.5 %; N, 13.9 %.

Ethyl-4-[(2,5-dioxo-1-pyrrolidinyl)oxy]-4-oxo-2-butenolate

Dicyclohexylcarbodiimide (31.49 g, 0.153 mol) was added to a solution of fumaric acid mono-ethyl ester (20.00 g, 0.139 mol) and *N*-hydroxysuccinimide (17.57 g, 0.153 mol) in anhydrous tetrahydrofuran (200 mL). The mixture was stirred for one hour and then filtered. The organic solvent was removed under reduced pressure to afford an oil which was recrystallized from ethyl acetate to further remove residual dicyclohexylurea. Removal of the solvent under reduced pressure afforded the desired product as a light brown waxy solid. Yield: 33.12 g, 98 %, mp 30.1-32.0 °C; ¹H NMR (300 MHz, CDCl₃) δ = 1.43 (3H, t, *J* = 6.9 Hz, CH₂CH₃), 2.88 (4H, s, CH₂), 4.23 (2H, q, *J* = 6.9 Hz, CH₂CH₃), 7.05 (2H, dd, *J* = 14.5 Hz, CH=CH); ¹³C NMR (75 MHz, CDCl₃) δ = 13.87, 25.52, 62.83, 137.36, 138.54, 163.76, 164.95, 167.73; MS (EI): *m/z* 242 [M+H]⁺; anal. calcd. for C₁₀H₁₁N₁O₆: C, 49.8 %; H, 4.6 %; N, 5.8 %, found: C, 49.7 %; H, 4.7 %; N, 5.5 %.

4-[(2,2-Diphenylethyl)amino]-4-oxo-2-butenoic acid

Ethyl-4-[(2,5-dioxo-1-pyrrolidinyl)oxy]-4-oxo-2-butenoate (6.11 g, 25.3 mmol) in tetrahydrofuran (60 mL) was added dropwise to a stirred solution of 2,2-diphenylethylamine (5.00 g, 25.3 mmol) in tetrahydrofuran (75 mL) and the resultant solution was refluxed at 86 °C for one and a half hours. After which time the reaction cooled and the solvent removed under reduced pressure to give a brown solid. This solid was dissolved in ethanol (100 mL) followed by the addition of 4 M sodium hydroxide solution (100 mL). The mixture was refluxed for 3 hours, cooled to 0 °C and acidified to pH 6, producing a light brown precipitate. The precipitate was filtered and washed with distilled water (3 x 200 mL) then dried under reduced pressure. Recrystallization of the precipitate from toluene afforded the pure product as a colorless solid. Yield: 4.56 g, 61 %; ¹H NMR (300 MHz, [D₆]DMSO) δ = 3.74 (2H, bt, CH₂NH), 4.23 (1H, t, *J* = 6.0 Hz, Ar₂CH), 6.49 (1H, d, *J* = 14.5 Hz, CHCO₂H), 6.78 (1H, d, *J* = 14.5 Hz, CHCONH), 7.29 (10H, m, ArCH), 8.67 (1H, bt, CONH), 12.85 (bs, CO₂H); ¹³C NMR (75 MHz, [D₆]DMSO) δ = 43.35, 46.21, 126.55, 127.64, 128.39, 133.41, 141.23, 163.98, 166.45; MS (EI): *m/z* 318 [M+Na]⁺; anal. calcd. for C₁₈H₁₇N₁O₃: C, 73.2 %; H, 5.8 %; N, 4.7 %, found: C, 72.9 %; H, 5.9 %; N, 4.8 %.

Thread of Rotaxane 3

Fumaroyl chloride (1.54 g, 10.0 mmol) in dichloromethane (50 mL) was added dropwise to a stirred solution of **2** (10.00 g, 22.1 mmol) in dichloromethane (50 mL) at 0 °C under an atmosphere of nitrogen. After one hour, triethylamine (2.24 g, 22.1 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for a further one hour at room temperature before being filtered and the solvent washed with 0.1M hydrochloric acid (2 x 100 mL), followed by saturated sodium hydrogen carbonate solution (2 x 100 mL). The organic fraction was dried over magnesium sulfate and the solvent removed under reduced pressure to give a dark brown oil. Column chromatography (methanol/dichloromethane, 3:97) afforded the pure product as an orange oil. Yield: 6.35 g, 55 %; ¹H NMR (300 MHz, CDCl₃) δ = 1.35 (16H, m, CH₂), 1.56 (16H, m, CH₂), 1.83 (28H, m CH₂), 2.68 (8H, m, CH₂NCONH), 3.26 (16H, m, CH₂), 3.98 (8H, m, CH₂CON), 7.34 (2H, s, CH), 9.26 (4H, bt, CONH); ¹³C NMR (75 MHz, CDCl₃) δ = 23.46, 26.51, 26.72, 28.36, 29.09, 29.38, 39.75, 40.45, 43.68, 46.86, 48.24, 131.28, 154.78, 164.67,

179.32; MS (EI): m/z 1090 $[M+Na]^+$; anal. calcd. for $C_{56}H_{94}N_{10}O_{10}$: C, 63.0 %; H, 8.9 %; N, 13.1 %, found: C, 63.1 %; H, 9.2 %; N, 13.5 %.

***N*¹-(2,2-Diphenylethyl)-*N*⁴,*N*⁴-bis(6-[(2-oxo-1-azepanyl)carbonyl]amino}hexyl)-2-butenediamide 10– Thread of Rotaxane 4**

Dicyclohexylcarbodiimide (0.49 g, 2.4 mmol) was added to a stirred solution of **2** (1.07 g, 2.4 mmol), 4-[(2,2-diphenylethyl)amino]-4-oxo-2-butenic acid (0.70 g, 2.4 mmol) and 4-dimethylaminopyridine (0.15 g, 1.2 mmol) in anhydrous tetrahydrofuran (20 mL). The resultant mixture was stirred for twelve hours at room temperature and filtered to remove precipitated dicyclohexylurea. Removal of the organic solvent afforded a light brown oil, which after recrystallisation from ethyl acetate to remove residual dicyclohexylurea and removal of the solvent under reduced pressure yielded the pure product as a colorless oil. Yield: 1.68 g, 97 %; 1H NMR (300 MHz, $CDCl_3$) δ = 1.33 (8H, bm, $\underline{CH_2}$), 1.54 (8H, bm, $\underline{CH_2}$), 1.73 (14H, bm, $\underline{CH_2}$), 2.68 (4H, bm, $\underline{CH_2}NCONH$), 3.27 (8H, m, $\underline{CH_2}$), 3.97 (6H, m, $\underline{CH_2}$), 4.24 (1H, t, J = 8.0 Hz, $\underline{CHCH_2}Ar_2$), 6.07 (1H, bt, J = 5.7 Hz, $CONH$), 6.70 (1H, d, J

= 14.5 Hz, CH=CHCONR), 7.27 (11H, m, CH=CHCONH & ArCH), 9.25 (2H, m, CH₂HNCON); ¹³C NMR (75 MHz, CDCl₃) δ = 23.11, 26.08, 26.32, 26.40, 27.21, 27.97, 28.75, 29.04, 39.42, 40.03, 43.37, 46.25, 47.81, 126.55, 127.65, 128.41, 130.17, 133.41, 141.26, 154.46, 163.96, 164.25, 179.01; MS (EI): *m/z* 794 [M+Na]⁺; anal. calcd. for C₄₄H₆₂N₆O₆: C, 68.5 %; H, 8.1 %; N, 10.9 %, found: C, 68.1 %; H, 8.2 %; N, 10.8 %.

***N*¹,*N*⁴-bis{1-benzyl-2-[benzyl(2-[(2-oxo-1-azepanyl)carbonyl]amino)ethyl]amino}-2-oxoethyl}-2-butenediamide 11 - Thread of Rotaxane 5 (mixture of diastereoisomers)**

Fumaroyl chloride (0.25 g, 1.6 mmol) in dichloromethane (10 mL) was added dropwise to a stirred solution of *N*-{2-[(2-amino-3-phenylpropanoyl)(benzyl)amino]ethyl}-2-oxo-1-azepanecarboxamide (1.43 g, 3.3 mmol) in dichloromethane (10 mL) at 0 °C under an atmosphere of nitrogen. After one hour, triethylamine (0.33 g, 3.3 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for one hour at room temperature before being filtered and the solvent washed with 0.2 M hydrochloric acid (2 x 150 mL), followed by saturated sodium hydrogen carbonate solution (2 x 100 mL). The organic fraction was dried over magnesium sulfate and the solvent removed

under reduced pressure to yield a dark brown oil. Column chromatography (methanol/dichloromethane, 3:97) gave the pure product as a light brown glassy solid. Yield: 1.29 g, 85 %; ^1H NMR (300 MHz, CDCl_3) δ = 1.73 (12H, bs, CH_2), 2.68 (4H, bm, CH_2NCONH), 3.30 (14H, bm, mixture of H), 3.95 (4H, bm, CH_2CON), 5.28 (4H, m, CH_2Ar), 6.85 (4H, m, $\text{CH}=\text{CH}$ & CONH), 7.23 (20H, m, ArCH), 9.28 (2H, bt, CH_2HNCON); ^{13}C NMR (75 MHz, CDCl_3) δ = 23.75, 29.34, 29.38, 38.61, 39.10, 39.89, 43.06, 44.20, 49.22, 53.18, 127.70, 128.40, 128.85, 129.28, 129.67, 131.30, 137.53, 138.20, 155.47, 164.21, 176.21, 179.92; MS (EI): m/z 954 $[\text{M}+\text{H}]^+$, 976 $[\text{M}+\text{Na}]^+$; anal. calcd. for $\text{C}_{54}\text{H}_{64}\text{N}_8\text{O}_8$: C, 68.1 %; H, 6.8 %; N, 11.8 %, found: C, 68.3 %; H, 6.7 %; N, 11.5 %.

Rotaxane 3

Separate solutions of isophthaloyl chloride (1.90 g, 9.4 mmol) and *p*-xylylene diamine (1.28 g, 9.4 mmol) in anhydrous chloroform (50 mL each) were added dropwise *via* syringe to a stirred solution of thread 9 (1.00 g, 0.9 mmol) and triethylamine (1.90 g, 18.7 mmol) also in anhydrous chloroform (150 mL) over a period of two hours. Ethanol (10 mL) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 200 mL) followed by 0.1M hydrochloric acid (2 x 200 mL) and then saturated aqueous sodium hydrogen carbonate solution (2 x 200 mL). The organic portion was dried over magnesium sulfate and the solvent removed under reduced pressure to afford a pale brown solid. This solid was taken up in chloroform (2.5 mL) and precipitated into diethyl ether (100 mL). The precipitate was washed with diethyl ether (2 x 10 mL) and dried to give the pure rotaxane as a colorless solid. Yield: 1.05 g, 0.66 mmol, 70 %, mp 164.4-166.7 °C; ^1H

NMR (300 MHz, CDCl₃) δ = 0.57 (4H, m, CH₂), 1.01 (4H, m, CH₂), 1.24 (XH, m, CH₂), 1.34 (XH, m, CH₂), 1.73 (XH, m, CH₂), 2.70 (8H, m, CH₂NCONH), 2.93 (4H, m, CH₂), 3.22 (12H, m, CH₂), 3.72 (4H, bd, J = 13.8 Hz, Ar-CH₂), 3.98 (8H, m, CH₂CON), 5.25 (4H, bdd, J = 14.3 Hz, Ar-CH₂), 5.97 (2H, s, CH=CH), 7.0 (8H, s, ArCH), 7.70 (6H, m, ArCH & CONH), 8.34 (4H, d, J = 7.8 Hz, ArCH), 8.85 (2H, bs, ArCH), 9.24 (4H, bt, CONH); ¹³C NMR (75 MHz, CDCl₃) δ = 23.72, 26.89, 28.13, 28.58, 29.39, 29.54, 40.06, 40.48, 43.63, 43.97, 48.35, 49.40, 122.79, 128.44, 129.17, 129.98, 132.43, 133.59, 138.32, 155.05, 165.23, 165.45, 179.64; MS (EI): m/z 1623 [M+Na]⁺; anal. calcd. for C₈₈H₁₂₂N₁₄O₁₄: C, 66.1 %; H, 7.7 %; N, 12.3 %, found: C, 66.2 %; H, 7.6 %; N, 12.0 %.

Rotaxane 4

Separate solutions of isophthaloyl chloride (1.98 g, 9.7 mmol) and *p*-xylylene diamine (1.32 g, 9.7 mmol) in anhydrous chloroform (50 mL each) were added dropwise *via* syringe to a stirred solution of thread 10 (0.50 g, 0.7 mmol) and triethylamine (1.97 g, 19.5 mmol) also in anhydrous chloroform (100 mL) over a period of two hours. Ethanol (10 mL) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 300 mL) followed by 0.1M hydrochloric acid (2 x 300 mL) and then saturated aqueous sodium hydrogen carbonate solution (1 x 200 mL). The organic portion was dried over magnesium sulfate and the solvent removed under reduced pressure to afford a colourless solid. This solid was dissolved in chloroform (2.5 mL) and precipitated into diethyl ether (100 mL). The precipitate was washed with diethyl ether (2 x 10 mL) and dried to give the rotaxane as a colorless solid. Yield: 0.59 g, 70 %, mp 156.5-157.3 °C; ¹H NMR (300 MHz,

CDCl₃) δ = 0.51 (2H, m, CH₂), 1.08 (10H, m, CH₂), 1.38 (4H, q, J = 7.4 Hz, CH₂), 1.73 (12H, m, CH₂), 2.69 (4H, m, CH₂), 2.79 (2H, m, CH₂), 3.05 (2H, m, CH₂), 3.13 (4H, m, CH₂), 3.97 (6H, m, CH₂), 4.33 (5H, m, Ar-CH₂ & CHAr₂), 4.54 (4H, bd, Ar-CH₂), 5.67 (1H, d, J = 14.5 Hz, CH=CHCONR), 5.93 (1H, d, J = 14.5 Hz, CH=CHCONH), 6.87 (8H, s, ArCH), 7.29 (10H, m, ArCH), 7.64 (2H, t, J = 7.6 Hz, ArCH), 7.70 (4H, bt, J = 4.9, CONH), 8.22 (4H, d, J = 7.6 Hz, ArCH), 8.57 (2H, bs, ArCH), 9.21 (2H, t, J = 5.4 Hz, CH₂HNCON); ¹³C NMR (75 MHz, CDCl₃) δ = 23.56, 26.32, 26.55, 26.62, 27.69, 28.42, 28.45, 29.26, 39.88, 40.31, 43.85, 45.07, 47.52, 48.87, 123.82, 126.27, 127.46, 128.01, 129.07, 129.12, 129.55, 131.83, 132.31, 133.69, 137.49, 141.60, 154.96, 164.46, 166.03, 166.13, 179.58; MS (EI): m/z 1304 [M+H]⁺; anal. calcd. for C₇₆H₉₀N₁₀O₁₀: C, 70.0 %; H, 7.0 %; N, 10.7 %, found: C, 69.3 %; H, 6.9 %; N, 11.6 %.

Rotaxane 5

Separate solutions of isophthaloyl chloride (2.40 g, 11.8 mmol) and *p*-xylylene diamine (1.61 g, 11.8 mmol) in anhydrous chloroform (50 mL each) were added dropwise *via* syringe to a stirred solution of thread 11 (0.75 g, 0.8 mmol) and triethylamine (2.39 g, 23.6 mmol) also in anhydrous chloroform (100 mL) over a period of two hours. Ethanol (10 mL) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 250 mL), followed by 0.2 M hydrochloric acid (2 x 250 mL) and saturated aqueous sodium hydrogencarbonate solution (2 x 250 mL). The organic portion was dried over magnesium sulfate and the solvent removed under reduced pressure to afford a pale yellow solid. This solid was taken up in chloroform (10 mL) and precipitated into diethyl ether

(250 mL). The precipitate was washed with diethyl ether (2 x 50 mL) and dried to give the rotaxane as a colorless solid. Yield: 0.53 g, 45 %, mp 167.1-169.3 °C; ^1H NMR (300 MHz, CDCl_3) δ = 1.71 (12H, bs, CH_2), 2.25-4.50 (20H, bm, mixture of H), 4.68 & 5.38 (8H, m, CH_2Ar), 4.98 & 5.68 (8H, m, CH_2), 5.64 (2H, s, $\text{CH}=\text{CH}$), 6.78 (8H, bm, ArCH), 7.20 (20H, m, ArCH), 7.49 (6H, m, ArCH & CONH), 8.10 (6H, m, ArCH), 8.78 & 9.28 (2H, bt, CH_2HNCON); ^{13}C NMR (75 MHz, CDCl_3) δ = 23.61, 28.39, 29.26, 38.68, 39.03, 39.70, 43.84, 46.01, 50.46, 53.05, 125.21, 126.28, 127.68, 127.98, 128.48, 128.90, 129.11, 129.47, 129.80, 130.43, 131.26, 133.67, 133.81, 136.30, 136.61, 137.06, 137.34, 155.11, 166.68, 171.79, 172.19, 179.31; MS (EI): m/z 1487 $[\text{M}+\text{H}]^+$, 1509 $[\text{M}+\text{Na}]^+$; anal. calcd. for $\text{C}_{86}\text{H}_{92}\text{N}_{12}\text{O}_{12}$: C, 69.5 %; H, 6.2 %; N, 11.3 %, found: C, 68.9 %; H, 6.3 %; N, 10.9 %.

N¹,N⁴-dibenzyl-N¹,N⁴-bis(2-[(2-oxo-1-azepanyl)carbonyl]amino)ethyl)-2-butenediamide

Fumaroyl chloride (1.2 g, 7.8 mmol) in dichloromethane (25 mL) was added dropwise to a stirred solution of **1** (5.00 g, 17.3 mmol) in dichloromethane (50 mL) at 0 °C under an atmosphere of nitrogen. After three hours, triethylamine (1.75 g, 17.3 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for one hour at room temperature before being filtered and the solvent washed with 0.1 M hydrochloric acid (2 x 100 mL), followed by saturated sodium hydrogencarbonate solution

(2 x 100 mL) and water (1 x 150 mL). The organic fraction was dried over magnesium sulfate and the solvent removed under reduced pressure to afford a dark brown oil. Column chromatography (methanol/dichloromethane, 2:98) gave the pure product as a colorless solid. Yield: 2.90 g, 56 %; ^1H NMR (400 MHz, CDCl_3) δ = 1.72 (12H, m, CH_2), 2.67 (4H, m, CH_2CON), 3.55 (8H, m, CH_2), 3.95 (4H, m, CH_2NO), 4.70 (4H, bdd, Ar- CH_2), 7.30 (12H, m, ArCH & $\text{CH}=\text{CH}$), 9.36 (2H, m, CH_2HNCON); ^{13}C NMR (100 MHz, CDCl_3) δ = 23.43, 28.27, 29.04, 38.22, 39.29, 39.56, 43.75, 46.22, 49.49, 51.89, 126.60, 127.75, 128.14, 131.73, 136.30, 155.10, 155.20, 179.37; MS (EI): m/z 659 $[\text{M}+\text{H}]^+$; anal. calcd. for $\text{C}_{36}\text{H}_{46}\text{N}_6\text{O}_6$: C, 65.6 %; H, 7.0 %; N, 12.8 %, found: C, 65.9 %; H, 7.0 %; N, 12.9 %.

Rotaxane 5 without Phenylalanine Residues (X-Ray Crystal Structure, Figure 1c)

Separate solutions of isophthaloyl chloride (3.47 g, 17.1 mmol) and *p*-xylylene diamine (2.33 g, 17.1 mmol) in anhydrous chloroform (50 mL each) were added dropwise *via* syringe to a stirred solution of corresponding thread (0.75 g, 1.1 mmol) and triethylamine (3.46 g, 34.2 mmol) also in anhydrous chloroform (100 mL) over a period of two hours. Ethanol (10 mL) was added and the reaction filtered. The resultant solution was washed

with distilled water (3 x 150 mL) followed by 0.1 M hydrochloric acid (3 x 150 mL) and saturated aqueous sodium hydrogen carbonate solution (2 x 150 mL). The organic portion was then dried over magnesium sulfate and the solvent removed under reduced pressure to afford a creamy solid. This solid was taken up in chloroform (5 mL) and precipitated into diethyl ether (250 mL). The precipitate was washed with diethyl ether (2 x 50 mL) and dried to give the pure rotaxane as a colorless solid. Yield: 0.77 g, 56 %, mp 198.0-199.3 °C; ^1H NMR (400 MHz, CDCl_3) δ = 1.34 (4H, m, CH_2), 1.71 (12H, m, CH_2), 2.63 (4H, m, CH_2CON), 3.24 (8H, bm, CH_2), 3.68 (4H, m, CH_2NO), 4.00 & 4.75 (8H, m, Ar- CH_2), 4.55 (8H, m, Ar- CH_2), 6.41 (2H, m, $\text{CH}=\text{CH}$), 6.93 (8H, s, Ar CH), 7.18 (20H, m, Ar CH), 7.68 (2H, t, J = 7.9 Hz, Ar CH), 7.75 (4H, bt, CONH), 8.28 (4H, m, Ar CH), 8.93 (2H, s, Ar CH), 9.34 (2H, m, CH_2HNCON); ^{13}C NMR (100 MHz, CDCl_3) δ = 23.27, 27.88, 28.94, 38.18, 39.40, 40.06, 43.64, 46.90, 47.92, 48.03, 51.84, 125.33, 127.90, 128.68, 128.86, 129.03, 129.13, 129.25, 131.82, 133.33, 134.49, 137.30, 154.97, 155.26, 166.20, 179.47; MS (EI): m/z 618 $[\text{M}+2\text{Na}]^{2+}$, 1213 $[\text{M}+\text{Na}]^+$; anal. calcd. for $\text{C}_{68}\text{H}_{74}\text{N}_{10}\text{O}_{10}$: C, 68.6 %; H, 6.3 %; N, 11.8 %, found: C, 68.7 %; H, 6.3 %; N, 11.9 %.

General method for the polymerization of rotaxane monomer 3

A mixture of rotaxane **3** (100 mg, 0.06 mmol) and Jeffamine[®] D400 (50 mg, 2.0 eq.) were dissolved in dichloromethane (1 mL) and mixed thoroughly. The solvent was removed under reduced pressure and the dry mixture heated to 175 °C under an atmosphere of nitrogen for one hour. The polymer was cooled rapidly to room temperature and the

resultant gelatinous solid washed repeatedly with dichloromethane (3 x 10 ml). Repeated attempts to dissolve the polymer in common organic solvents were unsuccessful resulting in a swollen suspension of the polymer in the solvents.

General method for the polymerization of rotaxane monomers 4 & 5

A mixture of rotaxane **4** or **5** (100 mg) and Jeffamine[®] D400 (1.0 eq.) were dissolved in dichloromethane (1 mL) and mixed thoroughly. The solvent was removed under reduced pressure and the dry mixture heated to 175 °C under an atmosphere of nitrogen for one hour. The polymer was cooled rapidly to room temperature and the resultant colorless solid dissolved in dichloromethane (1 mL) followed by precipitation into diethylether (100 mL). The resultant solid was filtered and dried under reduced pressure to afford the corresponding polyrotaxane as a colorless solid (typical yields were > 90 %).

Figures for Supporting Information:

Figure S1. 300 MHz ^1H NMR of (a) thread of rotaxane **1** and (b) rotaxane **1** in CDCl_3 .

Figure S2. Dynamic mechanical test (DMTA) on a thin film of polyrotaxane 4.

Figure S3. 300 MHz ^1H NMR of (a) rotaxane **2** and (b) polyrotaxane **5** in CDCl_3 [* denote macrocyclic protons; • denote Jeffamine[®] protons]

Figure S4. 300 MHz ^1H NMR of (a) rotaxane **3** and (b) polyrotaxane **6** in CDCl_3 [* denote macrocyclic protons; • denote Jeffamine[®] protons]