Supporting Information

Sulfur–Containing Amide–Based [2]Rotaxanes and Molecular Shuttles

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1. General Remarks

Unless stated otherwise, all reagents and anhydrous solvents were purchased for Aldrich Chemicals and used without further purification. p-Xylylene diamine, was distilled under reduced pressure and then recrystallised from ether. 3,3-Diphenylpropane-1-thiol was prepared as described by Wilkinson et al. Column chromatography was performed using Kiesegel C60 (Merck, Germany) as the stationary phase. 

$^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AV 300 or Bruker AV 400 instrument, at a constant temperature of 25 °C, or at the temperature specified. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. Coupling constants ($J$) are reported in hertz. Standard abbreviations indicating multiplicity are used as follows: br = broad, d = doublet, q = quadruplet, t = triplet, s = singlet.


The sulfur-containing thread (3, 4 or 5, 1.0 equiv.) and Et$_3$N (ten-fold excess) was dissolved in anhydrous CHCl$_3$ and stirred vigorously while solutions of the amine (five-fold excess) and the acid chloride (five-fold excess) in anhydrous CHCl$_3$ were added over 3 hours using motor-driven syringe pumps. The reaction was filtered and the solvent removed under reduced pressure. The crude material was then subjected to column chromatography (silica gel, CHCl$_3$/MeOH as eluent) to give the [2]rotaxane 6, 7 or 8 in 12, 43 or 10% yield, respectively. Further details are given in the Supporting Information.
3. Experimental Procedures, Synthesis and Characterization


\[
\begin{aligned}
\text{HSCH}_2\text{OH} \quad \xrightarrow{\text{(i)}} \quad \text{S1} \\
\text{S2} \quad \xrightarrow{\text{iii}} \quad \text{S3}
\end{aligned}
\]

Reagents and conditions: (i) bromodiphenylmethane, 100 °C, 89%; (ii) DCC, N-hydroxysuccinimide, THF, 0 °C, 97%; (iii) Et₃N, glycine ethyl ester hydrochloride, CHCl₃, RT, 61%; (iv) diphenylethanol, bis(chlorodibutyltin)oxide, toluene, reflux, 88%; (v) MCPBA, CHCl₃, –20 °C, 90 min, 70% (4, 1.0 equiv. MCPBA), 98% (5, from 4: 1.0 additional equiv. MCPBA).

3-Benzhydrylmercaptopropionic acid (S1). 3-Mercaptopropionic acid (1.10 g, 10.4 mmol) was slowly added to bromodiphenyl methane (2.51 g, 10.4 mmol). After the initial reaction had subsided the mixture was heated to 100 °C until there was no further evolution of HBr. The reaction mixture was then allowed to cool to room temperature and extracted with a saturated NaHCO₃ solution. The aqueous layer was acidified with 1M HCl and extracted with CHCl₃. The organic layer was dried with MgSO₄ and the solvent removed under reduced pressure. Recrystallization from aqueous ethanol yielded S1 as a colorless solid 2.64 g (89 %). mp 90-91 °C (lit. S2 88-90 °C); ¹H NMR (300 MHz, CDCl₃): δ = 7.43-7.20 (m, 10H, Ar H), 5.19 (s, 1H, Ar₂CH), 2.65 (m, 2H, CH₂COOH) and 2.56 (m, 2H, CH₂S); ¹³C NMR (75 MHz, CDCl₃): δ = 177.8, 141.0, 128.9, 128.5, 127.6, 54.3, 34.2, 26.8; Anal. Calc. for C₁₅H₁₄O₂S: C 70.6, H 5.9; found: C 70.3, H 6.1.
3-Benzhydrylsulfanylpropionic acid succinimidyl ester (S2). N,N’-Dicyclohexylcarbodiimide (2.32 g, 11.0 mmol) was added to a solution of S1 (3.01 g, 11.0 mmol) and N-hydroxysuccinimide (1.30 g, 11.0 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 8 h before being filtered and the solvent removed under reduced pressure. The urea by-product was removed by crystallisation from ethyl acetate and the filtrate was then evaporated to yield the product as a colorless solid 3.96 g (97 %). mp 109-110 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.45-7.21 (m, 10H, ArCH), 5.23 (s, 1H, Ar 2CH) and 2.85-2.72 (m, 8H, 4· CH₂); ¹³C NMR (75 MHz, CDCl₃): δ = 169.3, 167.5, 141.0, 129.1, 128.7, 127.8, 54.9, 31.9, 27.0, 26.0; LRMS (FAB): m/z = 369 [M+H]⁺; Anal. calc. for C₂₀H₁₉O₄SN: C 65.0, H 5.2; found : C 65.1, H 5.4.

(3-Benzhydrylsulfanyl-propionylamino)acetic acid ethyl ester (S3). Triethylamine (0.6 mL), was added to a slurry of glycine ethyl ester hydrochloride (0.64 g, 4.59 mmol) in chloroform (10 mL) and the reaction mixture allowed to stir for 5 minutes. 3-Benzhydrylsulfanyl propionic acid N-hydroxysuccinimidyl ester S2 (1.65 g, 4.47 mmol) was then added and the mixture was stirred for 30 minutes. The reaction mixture was then washed with water, dried with MgSO₄ and the solvent removed to give S3 as a colorless solid 1.59 g (61 %). mp 46-47 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.28 (m, 10H, ArH), 6.13 (bt, 1H, NHCH₂), 5.23 (s, 1H, Ar₂CH), 4.22 (qt, J = 7.0 Hz, 2H, CH₂CH₃), 4.04 (d, J = 7.0 Hz, 2H, NH-CH₂-CO-), 2.77 (t, J = 7.0 Hz, 2H, SCH₂CH₂), 2.45 (t, J = 7.0 Hz, 2H, SCH₂CH₂) and 1.32 (t, J = 7.0 Hz, 3H, CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 170.3, 141.6, 129.0, 128.7, 127.7, 62.0, 55.1, 41.8, 36.3, 28.3, 14.5; LRMS (FAB): m/z = 357 [M⁺]; HRMS (FAB): m/z = 357.1406 (calc. for C₂₀H₂₃O₃NS, 357.1399).

(3-Benzhydrylsulfanyl-propionylamino) acetic acid 2,2-diphenyl ethyl ester (3). (3-Benzhydrylsulfanyl-propionylamino) acetic acid ethyl ester S3 (966 mg, 2.70 mmol), diphenylethanol (536 mg, 2.70 mmol), and bis(chlorodibutyltin)oxide (10 mg) in toluene (50 mL) were refluxed for 8 hours with...
the continual distillation to remove liberated ethanol. After this time toluene was removed in vacuo, and the crude product was purified by column chromatography to give 1 as a colorless oil 1.21 g (88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.46$-$7.28$ (m, 20H, ArCH), 6.00 (t, $J = 7.0$ Hz, 1H, NHCH$_3$), 5.21 (s, 1H, Ph$_2$CH), 4.74 (d, $J = 7.0$ Hz, 2H, CH$_2$CHAr$_2$), 4.40 (t, $J = 7.0$ Hz, 1H, CH$_2$CHAr$_2$), 3.95 (d, $J = 7.0$ Hz, 2H, NHCH$_3$), 2.72 (t, $J = 7.0$ Hz, 2H, SCH$_2$CH$_2$) and 2.39 (t, $J = 7.0$ Hz, 2H, SCH$_2$CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 170.9$, 170.0, 135.6, 135.3, 129.8, 129.7, 129.4, 129.2, 129.1, 129.0, 73.2, 67.8, 50.1, 41.7, 36.2, 28.3; LRMS (FAB): $m/z = 510$ [M+H]$^+$; HRMS (FAB): $m/z = 510.2097$ (calc. for C$_{32}$H$_{32}$NO$_3$S, 510.2103).

(+,-) 3-(Benzhydrylmethanesulfinyl)propionylaminoacetic acid 2,2-diphenylethyl ester (4). To a solution of 3 (1.17 g, 2.29 mmol) in chloroform (10 mL) at -20 °C under an argon atmosphere, was added a solution of MCPBA (460 mg, 2.29 mmol) in chloroform (5 mL). The reaction mixture was stirred at -20 °C for 90 minutes then diluted with chloroform (30 mL) and allowed to warm to room temperature. The reaction mixture was washed with 5% NaHCO$_3$(aq) (3 x 30 mL) and H$_2$O (3 x 30 mL). The organic layer was then dried with MgSO$_4$ and the solvent removed under reduced pressure to give 2 as a colorless solid 85 mg (70 %). mp 110-111 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.51$-7.29 (m, 20H, ArH), 6.53 (t, 1H, NHCH$_3$), 4.89 (s, 1H, Ar$_2$CHS), 4.71 (d, $J = 7.0$ Hz, 2H, CH$_2$CHAr$_2$), 4.38 (t, $J = 7.0$ Hz, 1H, CH$_2$CHAr$_2$), 3.89 (dd, $J = 6.0$ Hz, $J = 18.0$ Hz, 2H, NHCH$_3$) and 2.93-2.67 (m, 4H, SCH$_2$CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 170.9$, 170.0, 135.6, 135.3, 129.4, 129.1, 129.0, 128.8, 128.6, 127.3, 73.2, 67.8, 50.1, 46.0, 41.7, 29.1; LRMS (FAB): $m/z = 526$ [M+H]$^+$; HRMS (FAB): $m/z = 526.2047$ (calc. for C$_{32}$H$_{32}$O$_4$NS, 526.2052).

3-(Benzhydrylmethanesulfonyl)propionylaminoaceticacid 2,2-diphenyl ethyl ester (5). To a solution of 4 (2.66 g, 5.06 mmol) in chloroform (10 mL) at -20 °C under argon, was added a solution of MCPBA (873 mg, 5.06 mmol) in chloroform (8 mL). The reaction mixture was allowed to stir at –
20 °C for 1.5 hours before being warmed to room temperature. The reaction mixture was then diluted with chloroform and washed with 5% NaHCO₃(aq) (3 x 30 mL) and H₂O (3 x 30 mL). The organic layer was then dried with MgSO₄ and the solvent removed under reduced pressure to give the product as a colorless solid 2.68 g (98%). mp 138-139 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.48-7.23 (m, 20H, ArH), 6.17 (t, J = 5.0 Hz, 1H, NH), 5.43 (s, 1H, Ph₂CH-SO₂-), 4.72 (d, J = 7.0 Hz, 2H, Ph₂CHCH₂), 4.39 (t, J = 7.0 Hz, 1H, Ph₂CHCH₂), 3.92 (d, J = 5.0 Hz, 2H, NHC H₂), 3.23 (t, J = 7.0 Hz, 2H, SCH₂CH₂) and 2.70 (t, J = 7.0 Hz, 2H, SCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 170.9, 170.0, 135.6, 135.3, 129.4, 129.1, 129.0, 128.8, 128.6, 127.3, 74.2, 67.0, 50.1, 47.8, 41.9, 28.1; LRMS (FAB): m/z = 542 [M+H]+; HRMS (FAB): m/z = 542.2005 (calc. for C₃₂H₃₂NO₅S, 542.2001).

Scheme 2. Synthesis of Rotaxanes 6–8.

![Scheme 2](image)

[Reagents and conditions: (i) isophthaloyl dichloride, p-xylylenediamine, Et₃N, CHCl₃, RT, 4 h, 12% (6), 43% (7), 10% (8); (ii) MCPBA (1.0 equiv.), CHCl₃, –20 °C to RT, 90 min., 95%; (iii) MCPBA (1.0 equiv.), CHCl₃, –20 °C to RT, 90 min., 97%; (iv) Lawesson’s reagent (1.0 equiv.), THF, –20 °C to RT, 1 h, 87%.

[2]-(1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-((3-benzhydrylsulfanyl-propionylamino)acetic acid 2,2-diphenylethyl ester)- rotaxane (6).

Method a): Rotaxane 6 was synthesized using the general procedure for the preparation of benzylic amide [2]rotaxanes from thread 3 (500 mg, 0.98 mmol). The crude obtained was subjected to column
Method b): To a solution of rotaxane 7 (37 mg, 0.04 mmol) in THF (2 mL) at −20 °C was added Lawesson’s reagent (14 mg, 0.04 mmol). The reaction mixture was allowed to stir at room temperature for 1 hour before the solvent removed under reduced pressure. The crude product was purified by column chromatography (5% MeOH/CHCl₃) to give the desired product as a colorless solid 32 mg (87%). mp 115-116 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.21 (d, J = 7.0 Hz, 4H, CH₆), 8.11 (br t, 2H, CH₆C), 7.67 (t, J = 7.0 Hz, 2H, CH₆A), 7.31 (br t, 4H, CH₆D), 7.29–7.12 (m, 28H, ArH), 6.43 (br t, 1H, CH₂CONHCH₂COO), 4.66 (s, 1H, Ph₂CHS), 4.57 (d, J = 7.0 Hz, 2H, COOCH₂), 4.53 (AA′BB′ system, 4H, J = 5.0 and 14.0 Hz, 4H, CH₂E), 4.27 (t, J = 7.0 Hz, 1H, Ph₂CHCH₂O), 3.31 (d, J = 6.0 Hz, 2H, CH₂COO), 1.72 (t, J = 8.0 Hz, 2H, S-CH₂-CH₂ or S-CH₂-CH₂), 1.43 (t, J = 8.0 Hz, 2H, S-CH₂-CH₂ or S-CH₂-CH₂); LRMS (FAB): m/z = 1080 [M+K]+; HRMS (FAB): m/z = 1042.4210 (calc. for C₆₄H₆₀O₇N₅S, 1042.4213).

(+,-) [2]-((1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacoseno)–((benzhydrylmethanesulfinyl)-propionylaminoacetic acid 2,2-diphenyl ethyl ester)-rotaxane (7). Method a): Rotaxane 7 was synthesized from 4 (440 mg, 0.84 mmol) using the general procedure. Column chromatography (CHCl₃) afforded the product as a white solid 379 mg (43%).

Method b): To a solution of rotaxane 6 (25 mg, 0.024 mmol) in CHCl₃ (1 mL) under an argon atmosphere at −20 °C was added a solution of MCPBA (4.00 mg, 0.02 mmol) in CHCl₃ (0.5 mL). The reaction mixture was stirred at −20 °C for 90 minutes before being allowed to warm to room temperature. The reaction mixture was then diluted with CHCl₃ and washed with 5% NaHCO₃(aq) (3 x 30 mL) and H₂O (3 x 30 mL). The organic layer was dried with MgSO₄ and the solvent removed in vacuo to give 5 as a colorless solid 24 mg (95%). mp 127-128 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.22 (t, J = 8.0 Hz, 4H, ArH₆B), 7.97 (s, 2H, ArH₆C), 7.63 (t, J = 8.0 Hz, 4H, NH₆D), 7.33-7.27 (m, 28H,
ArH), 7.24 (bt, 2H, ArH\textsubscript{A}), 4.60 (m, 11H, CH\textsubscript{2}CONHCH\textsubscript{2}COO, CH\textsubscript{E} and COOCH\textsubscript{2}), 4.38 (s, 1H, Ph\textsubscript{3}CH-SO\textsubscript{2}), 4.30 (t, J = 8.0 Hz, 1H, Ph\textsubscript{2}CH-CH\textsubscript{2}), 3.70 (t, J = 5.0 Hz, 2H, CH\textsubscript{2}COO) and 1.29-0.92 (m, 4H, SO-CH\textsubscript{2}-CH\textsubscript{2}); LRMS (FAB): m/z = 1059 [M+H\textsuperscript{+}]; HRMS (FAB): m/z = 1058.4154 (calc. for C\textsubscript{64}H\textsubscript{60}O\textsubscript{8}N\textsubscript{5}S, 1058.4162).

[2]-(1,4,7,14,17,20-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25–terabenzocyclohexacosane)-((3-benzhydrylsulfonyl-propionylamino) acetic acid 2,2-diphenylethyl ester)-rotaxane (8).

**Method a):** Rotaxane 8 was synthesized using the general procedure for the preparation of benzylic amide [2]rotaxanes from thread 5 (500 mg, 0.92 mmol). The crude material obtained was subjected to column chromatography on silica gel using CHCl\textsubscript{3} as eluent to obtain the desired compound as colorless solid 99 mg (10%).

**Method b):** To a solution of rotaxane 7 (100 mg, 0.09 mmol) in CHCl\textsubscript{3} (2 mL) under an Ar atmosphere at –20 °C was added a solution of MCPBA (16 mg, 0.09 mmol) in CHCl\textsubscript{3} (0.5 mL). The reaction mixture was allowed to stir at –20 °C for 90 minutes before being warmed to room temperature. The reaction mixture was diluted with chloroform and washed with 5% NaHCO\textsubscript{3}(aq) (3 x 30 mL) and H\textsubscript{2}O (3 x 30 mL). The organic layer was dried with MgSO\textsubscript{4} and the solvent removed under reduced pressure to give 8 as a colorless solid 94 mg (97 %). mp 110-111 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textdelta = 8.11 (d, J = 8.0 Hz, 4H, ArH\textsubscript{B}), 7.91 (s, 2H, ArH\textsubscript{C}), 7.62 (t, J = 6.0 Hz, 1H, CH\textsubscript{2}CONHCH\textsubscript{2}COO), 7.56 (bt, 2H, ArH\textsubscript{A}), 7.42 (t, J = 4.0 Hz, 4H, NH\textsubscript{D}), 7.32-7.02 (m, 28H, ArH), 4.86 (s, 1H, Ph\textsubscript{3}CH-SO\textsubscript{2}-), 4.66 (d, J = 8.0 Hz, 2H, COOCH\textsubscript{2}), 4.56 (m, 8H, CH\textsubscript{E}), 4.32 (t, J = 8.0 Hz, 1H, Ph\textsubscript{2}CHCH\textsubscript{2}O), 3.57 (d, J = 6.0 Hz, 2H, NHCH\textsubscript{2}COO), 2.00 (t, J = 7 Hz, 2H, SO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} or SO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} and 1.57 (t, J = 7.0 Hz, 2H, SO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} or SO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}); LRMS (FAB): m/z = 1074 [M+H\textsuperscript{+}]; HRMS (FAB): m/z = 1074.4106 (calc. for C\textsubscript{64}H\textsubscript{60}N\textsubscript{5}O\textsubscript{8}S, 1074.4111).

Reagents and conditions: (i) propiolic acid, pyridine, 3 hours, 88%; (ii) oxalyl chloride, benzene, then 2,2-diphenylethylamine, CH₂Cl₂, 92% over 2 steps; (iii) MCPBA, CH₂Cl₂, 90%; (iv) isophthaloyl dichloride, p-xylylenediamine, Et₃N, CHCl₃, RT, 63% (11); (v) MCPBA, CH₂Cl₂, RT, 18 h, 83% (12); (vi) Ph₂CHCH₂CH₂SNa, DMF, 120 °C, 15 h, 85% (10); (vii) Ph₂CHCH₂CH₂SNa, DMF, 120 °C, 16 h, 92% (10).

(E)-3-(3,3-Diphenyl-propylsulfanyl)-acrylic acid (S4). 3,3-diphenylpropane-1-thiol (5.00 g, 22.0 mmol) was dissolved in dry pyridine (100 mL), and the solution was cooled in an ice bath. Propiolic acid (1.49 mL, 1.10 equiv) was then added dropwise and the solution was stirred at 0 °C for 3 hours. After a further 18 hours stirring at room temperature the solvent was removed in vacuo. The resulting black solid was then triturated with CH₂Cl₂ (300 mL), before water (250 mL) followed by 1M HCl (50 mL, 2.3 equiv.) was added. The triphasic mixture was vigorously stirred and upon complete dissolution of the solid, the aqueous layer was extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were dried with MgSO₄, filtered and the solvent removed in vacuo. The crude residue was purified using flash column chromatography on silica gel (eluent: CH₂Cl₂ to 5% MeOH/CH₂Cl₂) to yield the corresponding pure (E)-acid as a colorless amorphous solid 5.75 g (88%). $^1$H NMR (400
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MHz, CDCl₃): δ = 7.77 (d, J = 13.2 Hz, 1H, SCH=CH), 7.17-7.34 (m, 10H, H-Ar), 5.65 (d, 1H, SCH=CH), 4.07 (t, J = 7.8 Hz, 1H, Ph₂CH), 2.72-2.77 (m, 2H, SCH₂CH₂), 2.39-2.47 (m, 2H, SCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 169.4, 149.6, 143.4, 128.7, 127.8, 126.7, 112.7, 50.0, 34.2, 30.3; LRMS (ESI-): m/z = 297 [M-H]⁻; HRMS (FAB, NBA matrix): m/z = 298.1036 (calc. for C₁₈H₁₈O₂S, 298.1027).

(E)-N-(2,2-Diphenyl-ethyl)-3-(3,3-diphenyl-propylsulfanyl)-acrylamide (S5). Acid S₄ (940 mg, 3.15 mmol) was dissolved in dry benzene (30 mL), and the solution was cooled in an ice bath. Oxalyl chloride (555 µL, 2.00 equiv) was then added dropwise, followed by one drop of DMF. The solution was stirred at room temperature for 2 hours before the solvent was removed in vacuo. The resulting yellow oil was dissolved in dry CH₂Cl₂ (5 mL) and added dropwise to an ice-cold solution of 2,2-diphenylethylamine (1.43 g, 2.30 equiv) in dry CH₂Cl₂ (50 mL). The reaction mixture was then stirred at room temperature for 2 hours. After this time water (40 mL) and 1M HCl (10 mL, 3.2 equiv.) were added and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were dried with MgSO₄, filtered and the solvent removed in vacuo. The crude residue was then purified by column chromatography (eluent: petroleum ether/EtOAc 7/3) to yield the corresponding pure amide as a colorless solid 1.47 g (92 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.68 (d, J = 14.9 Hz, 1H, SCH=CH), 7.19-7.45 (m, 20H, H-Ar), 5.61 (t, J = 4.8 Hz, 1H, NH), 5.35 (d, 1H, SCH=CH), 4.26 (t, J = 8.0 Hz, 1H, Ph₂CHCH₂NH), 4.08 (t, J = 7.7 Hz, 1H, Ph₂CHCH₂CH₂S), 3.99-4.05 (m, 2H, CH₂NH), 2.85 (t, J = 7.5 Hz, 2H, SCH₂CH₂), 2.40-2.49 (m, 2H, SCH₂CH₂). ¹³C NMR (100 MHz, CDCl₃) δ = 166.3, 145.6, 143.7, 141.2, 129.2, 128.8, 128.3, 128.0, 127.4, 126.6, 114.4, 50.4, 50.0, 44.4, 34.8, 30.2; LRMS (ESI+): m/z = 478 [M+H]⁺; HRMS (FAB, NBA matrix): m/z = 477.2138 (calc. for C₃₂H₃₁NOS, 477.2126).
(+/-) \((E)\)-N-(2,2-Diphenyl-ethyl)-3-(3,3-diphenyl-propane-1-sulfinyl)-acrylamide (9). Vinyl sulfide S5 (1.47 g, 3.08 mmol) was dissolved in \(\text{CH}_2\text{Cl}_2\) (50 mL), and the solution was cooled to -78 °C. MCPBA (530 mg, 1.00 equiv) was then added and the solution was stirred at room temperature overnight. After this time saturated \(\text{NaHCO}_3\) (50 mL) was slowly added and the aqueous layer was extracted with \(\text{CH}_2\text{Cl}_2\) (3 · 20 mL). The combined organic layers were dried with \(\text{MgSO}_4\), filtered and the solvents removed \textit{in vacuo}. The crude residue was then purified \textit{via} flash column chromatography (eluent: petroleum ether/EtOAc 1:1) to yield the corresponding vinyl sulfoxide 9 as a colorless amorphous solid 1.37 g (90%). \(^1\text{H NMR}\) (400 MHz, \(\text{CDCl}_3\)) \(\delta = 7.48\) (d, \(J = 14.8\) Hz, 1H, SCH=CH), 6.99-7.25 (m, 20H, H-Ar), 5.41 (t, \(J = 4.9\) Hz, 1H, NH), 5.15 (d, 1H, SCH=CH), 4.26 (t, \(J = 8.0\) Hz, 1H, Ph\(_2\)CHCH\(_2\)NH), 4.06 (t, \(J = 7.8\) Hz, 1H, Ph\(_2\)CHCH\(_2\)CH\(_2\)S), 3.79-3.91 (m, 2H, CH\(_2\)NH), 2.55 (t, \(J = 7.7\) Hz, 2H, SCH\(_2\)CH\(_2\)), 2.20-2.29 (m, 2H, SCH\(_2\)CH\(_2\)); \(^{13}\text{C NMR}\) (100 MHz, \(\text{CDCl}_3\)): \(\delta = 166.3, 145.6, 143.7, 141.3, 128.9, 128.7, 128.0, 127.9, 127.2, 126.6, 114.4, 50.4, 50.0, 44.4, 34.8, 30.2; LRMS (ESI+): \(m/z = 494\) [M+H]+; HRMS (FAB, NBA matrix): \(m/z = 493.2081\) (calc. for C\(_{32}\)H\(_{31}\)NO\(_2\)S, 493.2075).

\(+,-\)[2]-(1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclo hexacosane)--((E)-N-(2,2-diphenylethyl)-3-(3,3-diphenyl-propane-1-sulfinyl)-acrylamide)-rotaxane (11). Rotaxane 11 was synthesized from thread 9 (390 mg, 0.79 mmol) using the general procedure. The crude residue obtained was purified \textit{via} flash column chromatography on silica gel (eluent gradient pet. ether/EtOAc 1 :1, EtOAc then 1% MeOH/EtOAc) to give unreacted thread 9 (95 mg, 24%) and the desired vinyl sulfoxide [2]rotaxane 11 as a colorless solid 510 mg (63%). \(^1\text{H NMR}\) (400 MHz, \(\text{CD}_2\text{Cl}_2\)): \(\delta = 8.21\) (br s, 2H, CH\(_C\)), 8.05 (d, \(J = 7.8\) Hz, 4H, CH\(_B\)), 7.87 (br t, 1H, NHCH\(_2\)CHPH\(_2\)), 7.55 (br t, 2H, NH\(_D\)), 7.52 (t, 2H, CH\(_A\)), 7.55 (br t, 2H, NH\(_D'\)), 7.26–6.98 (m, 20H, ArH), 6.83 (d, \(J = 7.8\) Hz, 4H, CH\(_E\)), 6.67 (d, \(J = 7.8\) Hz, 4H, CH\(_F\)), 6.11 (d, \(J = 14.4\) Hz, 1H, SOCH=CH), 5.39 (d, 1H, SOCH=CH), 4.49-4.18 (m, 9H, CH\(_E\), CH\(_E'\) and Ph\(_2\)CHCH\(_2\)NH), 4.00-3.89 (m, 1H, Ph\(_2\)CHCH\(_2\)NH),
3.72 (m, 2H, Ph₂CHCH₂CH₂S and Ph₂CHCH₂NH), 2.17-1.90 (m, 4H, SOCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃):  δ = 169.5, 169.4, 167.2, 146.1, 145.8, 140.6, 140.4, 137.0, 136.7, 134.9, 134.7, 132.6, 132.4, 132.3, 132.2, 131.1, 130.8, 130.7, 130.5, 130.2, 130.0, 127.2, 55.2, 53.8, 53.5, 47.2, 47.0, 32.3; HRMS (FAB, NBA matrix): m/z = 1025.4175 (calc. for C₆₄H₅₉N₅O₆S, 1025.4186).


Vinyl sulfoxide rotaxane 11 (50 mg, 49 µmol) was dissolved in CH₂Cl₂ (3 mL). MCPBA (16 mg, 1.5 equiv.) was then added and the solution was allowed to stir at room temperature for 18 h. A saturated NaHSO₃ solution (3 mL) was then slowly added, and the resulting biphasic mixture was vigorously stirred at room temperature for 15 min. The aqueous layer was extracted with CH₂Cl₂ (3 x 3 mL). The combined organic layers were then washed with a saturated sodium bicarbonate solution (3 x 2 mL), water (2 mL) and brine (2 mL), dried with magnesium sulfate and the solvent removed in vacuo. The resulting white solid was purified using flash column chromatography on silica gel (eluent: petroleum ether/EtOAc 1/1 to EtOAc) to yield the corresponding vinyl sulfone rotaxane 12 as a colorless solid 42 mg (83 %). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.94 (dd, Jₐ-B = 7.6 Hz, Jₖ-B = 1.5 Hz, 4H, CHₖ), 7.88 (br s, 2H, CHC), 7.64 (br t, 1H, NHCH₂CHPh₂), 7.50 (t, 2H, CHₖ), 7.23-7.00 (m, 24H, ArH and NH₃), 6.80 (m, 8H, CH F), 5.78 (d, J = 15.2 Hz, 1H, SO₂CH=CH), 5.39 (d, 1H, SO₂CH=CH), 4.39 (dd, Jₕ₂H = 14.4 Hz, Jₕ₅H = 5.6 Hz, 4H, CHₕ₁), 4.22 (dd, Jₕ₅H = 5.1 Hz 4H, CHₕ₁), 4.05 (t, J = 7.6 Hz, 1H, Ph₂CHCH₂NH), 3.72 (t, J = 7.8 Hz, 1H, Ph₂CHCH₂CH₂S), 3.53 (dd, Jₕ₂H = 5.6 Hz, 2H, CHCH₂NH), 2.40-2.34 (t, J = 7.5 Hz, 2H, SO₂CH₂CH₂), 2.06-1.98 (m, 2H, SCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃):  δ = 167.0, 163.2, 158.8, 142.5, 141.6, 137.5, 135.2, 134.5, 130.8, 129.3, 128.9, 128.8, 128.7, 127.9, 127.5, 127.1, 127.0, 125.0, 52.6, 49.7, 49.6, 45.2, 44.2, 27.1; HRMS (FAB, NBA matrix): m/z = 1041.4148 (calc. for C₆₄H₅₉N₅O₆S, 1041.4135).

**Method a):** 3,3-Diphenylpropane-1-thiol (111 mg, 10.0 equiv) was dissolved in dry DMF (2 mL) and the solution was cooled to 0 °C. NaH (60% suspension in oil, 19.5 mg, 10.0 equiv) was then added and the resulting solution was stirred for 30 min. Vinyl sulfoxide rotaxane 11 (50 mg, 49 µmol) dissolved in dry DMF (1 mL) was then added and the solution was heated to 120 °C for 16 h. After this time the solvent was removed *in vacuo*, and the resulting residue purified *via* column chromatography (eluent: petroleum ether/EtOAc 7/3 to 1/1) to yield the vinyl sulfide rotaxane 10 as a colorless amorphous solid 42 mg (92 %).

**Method b):** 3,3-Diphenylpropane-1-thiol (113 mg, 10.0 equiv) was dissolved in dry DMF (2 mL) and the solution was cooled to 0 °C. NaH (60% suspension in oil, 19.7 mg, 10.0 equiv) was then added and the resulting solution was stirred for 30 min. Vinyl sulfone rotaxane 12 (52 mg, 49 µmol) dissolved in dry DMF (1 mL) was then added and the solution was heated to 120 °C for 15 h. After this time the solvent was removed *in vacuo*, and the resulting residue purified *via* column chromatography (eluent: petroleum ether/EtOAc 7/3 to 1/1) to yield the vinyl sulfide rotaxane 10 as a colorless amorphous solid 39 mg (85 %).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 8.06$ (br d, $J_{A-B} = 7.3$ Hz, 4H, CH$_B$), 7.97 (br s, 2H, CH$_C$), 7.59 (t, 2H, CH$_A$), 7.31–6.84 (m, 20H, ArH), 6.83 (m, 8H, CH$_F$), 6.79 (br t, 4H, NHD), 6.56 (d, $J = 14.7$ Hz, 1H, SCH=CH), 6.41 (br t, 1H, NHCH$_2$CH$_2$Ph$_2$), 4.46 (dd, $J_{gem} = 14.2$ Hz, $J_{NH-E} = 5.5$ Hz, 4H, CH$_E$), 4.26 (dd, $J_{NH-E'} = 4.8$ Hz, 4H, CH$_E'$), 4.19 (d, 1H, SCH=CH$_2$), 3.63 (t, $J = 7.8$ Hz, 1H, Ph$_2$CHCH$_2$NH), 3.53 (t, $J = 7.8$ Hz, 1H, Ph$_2$CHCH$_2$CH$_2$S), 3.14 (dd, $J_{NH-CH_2} = 5.8$ Hz, 2H, CHCH$_2$NH), 1.91-1.83 (m, 2H, SCH$_2$CH$_2$), 1.81-1.75 (m, 2H, SCH$_2$CH$_2$); HRMS (FAB, NBA matrix): $m/z = 1009.4245$ (calc. for C$_{64}$H$_{59}$N$_5$O$_5$S, 1009.4237).

1H NMR (400 MHz, CDCl3): 4.62-4.42 (m, 2H, NHBoc), 3.18-3.04 (m, 4H, CH2N), 1.53-1.39 (m, 4H, CH2CH2N), 1.45 (s, 18H, Me3C), 1.33-1.25 (m, 16H, CH2); 13C NMR (100 MHz, CDCl3): δ = 156.8, 79.0, 40.6, 30.1, 29.5, 29.3, 28.4, 26.8; LRMS (ESI+): m/z = 400.5 [M+H]+.

(12-Amino-dodecyl)-carbamic acid tert-butyl ester (S7). Di-boc derivative S6 (70 g, 0.19 mol) was dissolved in CH2Cl2 (280 mL), before a solution of HCl (2M in Et2O, 280 mL, 3 equiv.) was added over 5 min. The solution was vigorously stirred at room temperature for 22 hours. The resulting white precipitate was filtered, washed with Et2O (3 x 200 mL) and dried under vacuum to yield the hydrochloride of the mono-Boc derivative as a colorless solid 55 g (87 %). The crude material was used in the next step without any further purification.
{12-[(E)-3-(3,3-Diphenylpropylsulfanyl)-acryloylamino]-dodecyl}-carbamic acid tert-butyl ester (S8). S4 (940 mg, 3.15 mmol) was dissolved in dry benzene (30 mL), and the solution was cooled in an ice bath. Oxalyl chloride (555 µL, 2.00 equiv) was then added dropwise, followed by one drop of DMF. The solution was stirred at room temperature for 2 hours before the solvent was removed. The resulting yellow oil was dissolved in dry CH₂Cl₂ (5 mL) and added dropwise to an ice-cold solution of the amine S7 (2.17 g, 2.30 equiv) in dry CH₂Cl₂ (50 mL). The reaction mixture was stirred at room temperature for 2 hours before being quenched with water (40 mL) and 1M HCl (10 mL, 3.20 equiv). The aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL), and the combined organic layers were then dried with MgSO₄, filtered and the solvent evaporated. The crude residue was purified by column chromatography (eluent: CH₂Cl₂ to 2% MeOH/CH₂Cl₂) to yield S8 as a colorless amorphous solid 1.64 g (90 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.51 (d, J = 14.9 Hz, 1H, SCH=CH), 7.35-7.18 (m, 10H, H-Ar), 5.50 (d, 1H, SCH=CH), 5.38 (t, J = 4.6 Hz, 1H, CH=CHCONH), 4.61-4.49 (m, 1H, NHBoc), 4.06 (t, J = 7.8 Hz, 1H, Ph₂CH₂CH₂S), 3.32-3.24 (dt, J = 6.4 Hz, 2H, CH₂NHCOCH=CH), 3.15-3.06 (m, 2H, CH₂NHBoc), 2.72 (t, J = 7.8 Hz, 2H, SCH₂CH₂), 2.45-2.38 (m, 2H, SCH₂CH₂), 1.56-1.44 (m, 4H, CH₂), 1.46 (s, 9H, Me₃C), 1.35-1.24 (m, 18H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 164.4, 157.9, 143.8, 141.5, 128.6, 127.9, 126.4, 116.8, 50.0, 40.6, 39.4, 34.9, 30.2, 29.7, 29.5, 29.3, 28.4, 26.9, 26.8; LRMS (ESI+): m/z = 581.5 [M+H]⁺; HRMS (FAB, NBA matrix): m/z = 580.3694 (calc. for C₃₅H₅₂N₂O₃S, 580.3699).

N-(2,2-Diphenyl-ethyl)-N'-{12-[(E)-3-(3-diphenyl-propylsulfanyl)-acryloylamino]-dodecyl}-succinamide (13). Carbamate S8 (950 mg, 1.63 mmol) was dissolved in CH₂Cl₂ (20 mL) and TFA (10 mL) was added dropwise. The solution was then stirred at room temperature for 3 hours before the solvent was evaporated. The crude oil was dissolved in CH₂Cl₂ (50 mL) and washed with saturated NaHCO₃ (50 mL) before being dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting yellow solid was dissolved in dry CH₂Cl₂ (20 mL) and N-(2,2-diphenylethyl)-
succinamic acid (578 mg, 1.20 equiv), DMAP (314 mg, 1.50 equiv) and EDCI (471 mg, 1.50 equiv) were then added. The reaction mixture was stirred at room temperature for 20 hours before being quenched with 1M HCl (10 mL). The organic layer was then washed with 1M HCl (5mL), saturated NaHCO₃(aq) (5 mL) and brine (5 mL), before being dried with MgSO₄, filtered and the solvent removed. The resulting yellow solid was purified by column chromatography (eluent: CH₂Cl₂ to 8% MeOH/CH₂Cl₂) to yield 13 as a colorless solid 1.03 g (83 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.49 (d, J = 14.7 Hz, 1H, SCH=CH), 7.33-7.16 (m, 20H, H-Ar), 5.94-5.85 (m, 2H, CH₂NHCOCH₂), 5.45 (d, 1H, SCH=CH), 5.19 (t, J = 4.8 Hz, 1H, CH=CONH), 4.16 (t, J = 8.1 Hz, 1H, Ph₂CHCH₂NH), 4.04 (t, J = 7.8 Hz, 1H, Ph₂CHCH₂CH₂S), 3.87 (dd, J = 5.8 Hz, 2H, Ph₂CHCH₂NH), 3.32-3.24 (dt, JCH₂-CH₂ = 6.6 Hz, JCH₂-NH = 6.6 Hz, 2H, CH₂NHCOCH₂), 3.20-3.14 (m, 2H, CH₂NHCOCH₂CH₂), 2.71 (t, J = 6.8 Hz, 2H, SCH₂CH₂), 2.44-2.34 (m, 2H, SCH₂CH₂), 2.38 (s, 4H, COCH₂CH₂CO), 1.54-1.40 (m, 4H, CH₂), 1.34-1.22 (m, 16H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ = 172.2, 172.0, 164.4, 143.8, 141.9, 141.5, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 126.8, 126.2, 116.8, 50.6, 50.0, 43.8, 39.6, 39.5, 34.9, 31.8, 31.7, 30.2, 29.7, 29.5, 29.4, 29.2, 26.9, 26.8; LRMS (ESI+): m/z = 760.5 [M+H]⁺; HRMS (FAB, NBA matrix): m/z = 759.4445 (calc. for C₄₈H₆₁N₃O₃S, 759.4434).
**Scheme 5.** Synthesis of Rotaxanes 14–17.

Reagents and conditions: (i) isophthaloyl dichloride, p-xylylenediamine, Et$_3$N, CHCl$_3$, RT, 23% (14) + 8% (15); (ii) MCPBA, CH$_2$Cl$_2$, -78 °C to RT, 2 h, 90% (16); (iii) MCPBA, CH$_2$Cl$_2$, -78 °C to RT, 2 h, 92% (17); (iv) Ph$_2$CHCH$_2$CH$_2$SNa (10 equiv.), DMF, 120 °C, 16 h, 93% (14); (v) Ph$_2$CHCH$_2$CH$_2$SNa (10 equiv.), DMF, 120 °C, 18 h, 90% (14).
[2]-{(1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N-(2,2-diphenylethyl)-N’-{12-[(E)-3-(3,3-diphenylpropylsulfanyl)-acryloylamino]-do-decyl}-succinamide)-rotaxane (14). Method a): Rotaxane 14 was synthesized from thread 13 (760 mg, 1.00 mmol) using the general procedure. The crude obtained was subjected to a flash column chromatography on silica gel (eluent: petroleum ether/EtOAc 1:1, to 1% MeOH/EtOAc) to give first the [3]rotaxane 15 144 mg (8 %) then the vinyl sulfide [2]rotaxane 14 as a colorless solid 291 mg (23%).

Method b): 3,3-Diphenylpropane-1-thiol (52 mg, 10 equiv.) was dissolved in dry DMF (2 mL) and the solution was cooled to 0 °C. NaH (60% suspension in oil, 9 mg, 10 equiv.) was added and the mixture was stirred under N₂ for 30 minutes. Vinyl sulfoxide rotaxane 16 (30 mg, 23 µmol), dissolved in 1 mL dry DMF was then added and the solution was heated to 120 °C for 16 hours. After this time, the solvent was removed in vacuo, and the resulting dark residue was purified via column chromatography (eluent: CH₂Cl₂/CH₃CN 8/2) to yield the corresponding vinyl sulfide rotaxane 14 as a colorless solid 28 mg (93 %).

Method c): 3,3-Diphenylpropane-1-thiol (88 mg, 10 equiv) was dissolved in dry DMF (2 mL) and the solution was cooled to 0 °C. NaH (60% suspension in oil, 16 mg, 10 equiv) was added and the mixture was stirred under N₂ for 30 minutes. Vinyl sulfone rotaxane 17 (50 mg, 39 µmol), dissolved in 1 mL dry DMF was then added and the solution was heated to 120 °C for 18 hours. After this time the solvent was removed in vacuo, and the resulting crude residue was subjected to column chromatography (eluent: CH₂Cl₂/CH₃CN 8/2) to yield the corresponding vinyl sulfide rotaxane 14 as a colorless solid 44 mg (90 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.24 (br s, 2H, CHC), 8.07 (dd, Jₓᵧ = 7.8 Hz, Jᵧᵧ = 1.5 Hz, 4H, CH₂B), 7.54-7.47 (m, 6H, CH₂A and NH₂D), 7.25-7.06 (m, 20H, H-Ar), 6.99 (d, J = 14.7 Hz, 1H, SCH=CH), 6.96 (s, 8H, CH₂F), 6.31 (br t, 1H, NHCO), 6.16 (br t, 1H, NHCO), 5.55 (br t, 1H, NHCO), 5.29 (d, 1H, SCH=CH), 4.43 (dd, Jₓᵧ = 14.4 Hz, Jᵧᵧ = 5.4 Hz, 4H, CH₂E), 4.38 (dd, Jₓᵧ = 5.1 Hz, 4H, CH₂E), 4.02 (t, J = 8.1 Hz, 1H, Ph₂CHCH₂NH), 3.91 (t, J = 7.8 Hz, 1H,
Ph$_2$CHCH$_2$CH$_2$S), 3.64 (dd, $J_{\text{CH2-NH}} = 5.6$ Hz, 2H, Ph$_2$CHCH$_2$NH), 3.10-3.02 (m, 2H, CH$_3$NHCOCH=CH), 2.99-2.91 (m, 2H, CH$_2$NHCOCH$_2$CH$_2$), 2.71 (t, $J = 7.5$ Hz, 2H, SCH$_2$CH$_2$), 2.30-2.21 (m, 2H, SCH$_2$CH$_2$), 1.39-1.29 (m, 4H, CH$_2$), 1.24-1.02 (m, 20H, CH$_2$ and COCH$_2$CH$_2$CO);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 172.9, 172.8, 166.5, 164.6, 143.7, 141.6, 141.2, 137.6, 133.9, 131.4, 129.2, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 127.4, 127.1, 126.6, 124.2, 116.8, 50.5, 50.0, 44.2, 44.1, 39.8, 39.6, 34.7, 30.2, 29.7, 29.5, 29.3, 29.1, 26.8 ; HRMS (FAB, NBA matrix): $m/z = 1291.6558$ (calc. for C$_{80}$H$_{89}$N$_7$O$_7$S, 1291.6544).

[3]-bis-(1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzenecyclohexacosane)--(N-(2,2-diphenyl-ethyl)-N'-{12-[E]-3-(3,3-diphenyl-propylsulfanyl)-acryloylamino]-dodecyl}-succinamide)-rotaxane (15). See the preparation of 14, Method a). $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.11 (br s, 2H, CH$_2$), 8.07 (br s, 2H, CH$_2$), 8.00 (dd, $J_{A-B} = 7.8$ Hz, $J_{B-C} = 1.0$ Hz, 4H, CH$_B$), 8.00 (d, $J_{A'-B'} = 8.3$ Hz, 4H, CH$_B$), 7.72-7.61 (m, 4H, NH$_D$), 7.46 (t, 2H, CH$_A$), 7.41 (t, 2H, CH$_A$), 7.37-7.30 (m, 4H, NH$_D$), 7.25-6.99 (m, 22H, H-Ar and 2 NHCO), 6.98 (s, 8H, CH$_F$), 6.96 (s, 8H, CH$_F$), 6.59 (br t, 1H, NHCO), 6.37 (d, $J = 15.2$ Hz, 1H, SCH=CH), 4.77 (d, 1H, SCH=CH), 4.55-4.20 (m, 16H, CH$_E$ and CH$_E$), 4.05 (t, $J = 8.0$ Hz, 1H, Ph$_2$CHCH$_2$NH), 3.69 (t, $J = 7.7$ Hz, 1H, Ph$_2$CHCH$_2$S), 3.66-3.60 (m, 2H, Ph$_2$CHCH$_2$NH), 2.91-2.83 (m, 2H, CH$_2$NHCOCH=CH), 2.53-2.44 (m, 2H, CH$_2$NHCOCH$_2$CH$_2$), 2.16-2.10 (m, 2H, SCH$_2$CH$_2$), 2.05-1.96 (m, 2H, SCH$_2$CH$_2$), 1.31-0.72 (m, 24H, CH$_2$ and COCH$_2$CH$_2$CO); LRMS (ESI+): $m/z = 1825$ [M+H]$^+$; HRMS (FAB, NBA matrix): $m/z = 1823.8721$ (calc. for C$_{112}$H$_{117}$N$_{11}$O$_{11}$S, 1823.8655).

[2]-{1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzenecyclohexacosane}--(N-(2,2-diphenyl-ethyl)-N'-{12-[E]-3-(3,3-diphenyl-propane-1-sulfanyl)-acryloylamino]-dodecyl}-succinamide)-rotaxane (16). Vinyl sulfide shuttle 14 (25 mg, 20 $\mu$mol) was dissolved in CH$_2$Cl$_2$ (1 mL), and the solution was cooled to -78 °C. MCPBA (3.5 mg, 1.0 equiv) was then added.
and the solution was allowed to warm to room temperature over 2 hours before being stirred overnight at room temperature. A saturated NaHCO₃ solution (10 mL) was then added slowly, and the aqueous layer was extracted with CH₂Cl₂ (3 x 1 mL). The combined organic layers were dried with MgSO₄, filtered and the solvent removed in vacuo. The crude residue was then purified by column chromatography (eluent: CH₂Cl₂/CH₃CN 9/1 to 9/6) to yield the corresponding vinyl sulfoxide shuttle 16 as a colorless amorphous solid 23 mg (90 %). 

\[ {^1}H \text{ NMR (400 MHz, CDCl}_3 \] δ = 8.33 (br s, 2H, CHC), 8.08 (br d, \( J_{A-B} = 7.6 \) Hz, 4H, CHB), 7.54-7.48 (m, 4H, NH_D), 7.47 (t, 2H, CH_A), 7.23-7.01 (m, 21H, H-Ar and NHCO), 6.96 (d, \( J_{F-F'} = 8.0 \) Hz, 4H, CHF), 6.91 (d, 4H, CHF'), 6.59 (d, \( J = 14.9 \) Hz, 1H, S(O)CH=CH), 6.01 (br t, 1H, NHCO), 5.93 (d, 1H, S(O)CH=CH), 5.85 (br t, 1H, NHCO), 4.43-4.34 (m, 8H, CH_E and CH_E'), 4.04 (t, \( J = 8.1 \) Hz, 1H, Ph₂CHCH₂NH), 3.82 (t, \( J = 7.8 \) Hz, 1H, Ph₂CHCH₂NH), 3.25-3.15 (m, 1H, CH₂NHCO-CH=CH), 3.13-3.05 (m, 1H, CH₂NHCOCH=CH), 3.03-2.95 (m, 2H, CH₂NHCOCH₂CH₂), 2.33-2.15 (m, 4H, S(O)CH₂CH₂), 2.08 (s, 4H, NHCOCH₂CH₂CONH), 1.51-1.31 (m, 4H, CH₂), 1.28-1.12 (m, 16H, CH₂); 

\[ {^{13}}C \text{ NMR (100 MHz, DMSO-}d\text{6) } \delta \text{ 171.9, 171.6, 165.6, 162.3, 144.5, 143.9, 143.8, 142.8, 137.5, 134.4, 134.3, 130.1, 128.6, 128.5, 128.4, 128.3, 127.8, 127.7, 127.4, 127.4, 126.3, 125.7, 50.1, 49.5, 43.2, 42.9, 40.1, 39.9, 38.5, 30.1, 30.0, 29.0, 28.8, 28.7, 28.6, 26.6; HRMS (FAB, NBA matrix): m/z = 1307.6484 (calc. for C₈₀H₈₉N₇O₈S, 1307.6493).}

[2]-(1,4,7,14,17,20,-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexaco-sane)-(N-(2,2-diphenyl-ethyl)-N'-{12-[(E)-3-(3,3-diphenyl-propylsulfonyl)-acryloylamino]-dodecyl}-succinamide)-rotaxane (17). Method a): Vinyl sulfoxide shuttle 16 (25 mg, 20 µmol) was dissolved in CH₂Cl₂ (1 mL), and the solution was cooled to -78 °C. MCPBA (7.0 mg, 2.0 equiv) was then added and the solution was allowed to warm to room temperature over 2 hours before being stirred overnight at room temperature. A saturated NaHSO₃ solution (0.5 mL) was then added slowly to quench the reaction, and the aqueous layer was then extracted with CH₂Cl₂ (3 x 1 mL). The
combined organic layers were washed with saturated NaHCO₃(aq) (3 x 1 mL), water (1 mL) and brine (1 mL), before being dried with MgSO₄, filtered, and the solvent evaporated. The crude residue was purified using flash column chromatography on silica gel (eluent: CH₂Cl₂/CH₃CN 9/1 to 7/3) to yield the corresponding vinyl sulfone shuttle 17 as a colorless amorphous solid 23 mg (92 %).

Method b): Identical as Method a) However starting from vinyl sulfide shuttle 14 and using a larger excess of MCPBA (3.0 equiv) to give 23 mg of product (88 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.28 (br s, 2H, CHC), 8.07 (br d, Jₐ₋ₐ = 7.8 Hz, 4H, CHB), 7.54 (br t, 4H, NHD), 7.47 (t, Jₐ₋ₐ = 7.8 Hz, 2H, CHₐ), 7.26-7.16 (m, 21H, H-Ar and NHCO), 7.02 (d, J = 14.7 Hz, 1H, SO₂CH=CH), 6.94 (s, 8H, CHF), 6.67 (d, 1H, SO₂CH=CH), 6.31 (br t, 1H, NHCO), 6.02 (br t, 1H, NHCO), 4.45-4.35 (m, 8H, CHₑ and CHₑ'), 4.02 (t, J = 8.1 Hz, 1H, Ph₂CHCH₂NH), 3.88 (t, J = 7.8 Hz, 1H, Ph₂CHCH₂CH₂S), 3.70-3.63 (m, 2H, Ph₂CHCH₂NH), 3.29-3.20 (m, 2H, CH₂NHCOCH=CH), 3.02-2.94 (m, 2H, CH₂NHCOCH₂CH₂), 2.73-2.68 (m, 2H, SO₂CH₂CH₂), 2.38-2.27 (m, 2H, SO₂CH₂CH₂), 1.51-1.31 (m, 4H, CH₂), 1.29-1.01 (m, 20H, CH₂ and COCH₂CH₂CO); ¹³C NMR (100 MHz, CDCl₃) δ = 172.9, 172.8, 166.6, 162.6, 142.6, 141.5, 137.6, 137.1, 136.4, 133.9, 131.5, 129.2, 129.1, 128.9, 128.7, 128.0, 127.9, 127.6, 127.2, 126.9, 124.3, 53.2, 50.5, 49.8, 44.2, 44.0, 40.2, 29.7, 29.2, 29.0, 28.9, 27.6, 26.8, 22.7; HRMS (FAB, NBA matrix): m/z = 1323.6458 (calc. for C₈₀H₈₉N₇O₉S, 1323.6442).
Scheme 6. Synthesis of Threads 18 and 19.\textsuperscript{a}

\textsuperscript{a} Reagents and conditions: (i) MCPBA, CH$_2$Cl$_2$, -78 °C to RT, 2 h, 90\% (18); (vii) MCPBA, CH$_2$Cl$_2$, RT, 18 h, 94\% (19).

(+/-)-N-(2,2-Diphenyl-ethyl)-N'-[12-[(E)-3-(3,3-diphenyl-propane-1-sulfinyl)-acryloylamino]-do-decyl]-succinamide (18). Vinyl sulfide thread 13 (200 mg, 0.26 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL), and the solution was cooled to -78 °C. MCPBA (45 mg, 1.0 equiv) was then added and the solution was allowed to warm to room temperature over 2 hours before being stirred at room temperature overnight. A saturated NaHCO$_3$ solution (3 mL) was then slowly added and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 3 mL). The combined organic layers were dried with MgSO$_4$, filtered and the solvent evaporated. The crude residue was purified using flash column chromatography on silica gel (eluent: petroleum ether/EtOAc 6/4 to EtOAc) to yield the corresponding vinyl sulfoxide as a colorless amorphous solid 182 mg (90 \%). $^1$H NMR (400 MHz, CDCl$_3$, 50 ºC) $\delta$ = 7.32 (d, $J$ = 14.4 Hz, 1H, SCH=CH), 7.27-7.09 (m, 20H, H-Ar), 6.87 (br t, 1H,
N-(2,2-Diphenyl-ethyl)-N’-{12-[(E)-3-(3,3-diphenyl-propane-1-sulfonyl)-acryloylamino]-dodecyl}-succinamide (19). Vinyl sulfoxide 18 (80 mg, 0.10 mmol) was dissolved in CH₂Cl₂ (2 mL). MCPBA (26 mg, 1.5 equiv) was then added and the solution was allowed to stir at room temperature for 18 hours. A saturated NaHSO₃ solution (1 mL) was then added slowly, and the resulting biphasic mixture was vigorously stirred at room temperature for 15 minutes. The aqueous layer was then extracted with CH₂Cl₂ (3 x 2 mL). Combined organic layers were washed with a saturated sodium bicarbonate solution (3 x 1 mL), water (1 mL) and brine (1 mL), dried with magnesium sulfate, filtered and the solvent evaporated. The resulting white solid was purified using flash column chromatography on silica gel (eluent: petroleum ether/EtOAc 1/1 to pure EtOAc) to yield the corresponding vinyl sulfone 19 as a colorless amorphous solid 77 mg (94%). ¹H NMR (400 MHz, CDCl₃) δ = 7.25-7.08 (m, 21H, SCH=CH and H-Ar), 7.02 (br t, 1H, NHCO), 6.90 (d, J = 14.7 Hz, 1H, SCH=CH), 6.11 (br t, 2H, NHCO), 4.09 (t, J = 7.8 Hz, 1H, Ph₂CHCH₂NH), 3.92 (t, J = 8.0 Hz, 1H, Ph₂CHCH₂S), 3.77 (dd, J = 5.7 Hz, 2H, Ph₂CHCH₂NH), 3.26-3.18 (m, 2H, CH₂NHCOCH=CH), 3.12-3.04 (m, 2H, CH₂NHOCH₂CH₂), 2.92-2.84 (m, 2H, SO₂CH₂CH₂), 2.48-2.39 (m, 2H, SO₂CH₂CH₂), 2.32 (s, 4H, COCH₃CH₃CO), 1.49-1.32 (m, 4H, CH₂), 1.29-1.12 (m, 16H,
CH_2); ^13^C NMR (100 MHz, CDCl_3) δ = 172.3, 172.1, 161.6, 157.9, 142.6, 141.8, 137.0, 130.1, 129.7, 128.9, 128.7, 128.5, 128.3, 128.2, 128.0, 127.6, 126.9, 126.8, 53.2, 50.5, 43.9, 40.2, 39.6, 31.9, 31.8, 29.7, 29.4, 29.1, 29.0, 28.9, 27.8, 26.7; LRMS (ESI+): m/z = 808.5 [M+H]^+.

4. X-ray Data

The structure of rotaxane 7 in the solid state was determined by X-ray crystallography. Suitable single crystals were obtained by slow diffusion of diethyl ether into a solution of the rotaxane 7 in dichloromethane. X-ray data for each of the rotaxanes is shown below.

7: C_{65}H_{61}N_{5}O_{12}SCl_{2}, M=1207.16, crystal size 0.06×0.06×0.01mm, monoclinic P2_1/n, a=18.838(1), b=17.343(2), c=19.035(4) Å, α=97.085(1), β=90.41(10), γ=98.695(1)°, V=6219.33(11) Å^3, Z=4, ρ_{calc}=1.289 Mg m^{-3}; MoKα radiation (graphite monochromator, λ=0.71073 Å), μ=0.080 mm^{-1}, T=180(2)K. 10380 data (3580 unique, R_{int}=0.0792, 2.18<θ<22.61°), 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 0.58-1.00). 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={Σ[w(F_o^2−F_c^2)^2]/Σ[w(F_o^2)^2]}^{1/2}=0.067, conventional R=0.067. Amide hydrogen atoms were refined isotropically subject to a distance constraint N-H = 0.98 Å, with the remainder constrained; anisotropic displacement parameters were used for all non-hydrogen atoms.

Crystallographic data for 6, 4, 7 and 8 (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-160649 (6), CCDC-829630 (7) and CCDC-161353 (8). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).
5. References


