Supporting Information

Superior Anion Induced Shuttling Behaviour Exhibited by a Halogen Bonding Two Station Rotaxane

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Contents

1) Part I: Synthesis S2
2) Part II: 2D ¹H NMR ROESY spectra S18
3) Part III: UV-Vis Spectroscopy S22
4) Part IV: Anion exchange molecular motion studies S23
5) Part V: X-ray Diffraction S34
Part I: Synthesis

General Information

All commercial solvents and reagents were used as purchased, unless otherwise stated. Anhydrous solvents were degassed with $N_2$ and dried by passing them through an MBraun-800 column. Triethylamine was distilled and stored over KOH pellets. Grubbs’ second generation catalyst and Cu(MeCN)$_4$·PF$_6$ were stored in a desiccator with P$_2$O$_5$. TBTA was prepared following a literature procedure.$^1$ Water was distilled and microfiltered using a Milli-Q Millipore machine. Chromatography was undertaken using silica gel (particle size: 40-63 μm) or preparative TLC plates (20 × 20 cm, 1 cm silica thickness).

Axle and rotaxane components were fully anion exchanged using a column containing an Amberlite® ion exchange resin that had been loaded with the desired anion. Amberlite® was “loaded” by washing the resin with NaOH$_{(aq)}$ (10%), H$_2$O, and either NH$_4$Cl$_{(aq)}$ (1 M), NH$_4$I$_{(aq)}$ (1 M) or NH$_4$PF$_6{(aq)}$ (0.1 M), followed by further H$_2$O, and the solvent (45:45:10 CHCl$_3$:MeOH:H$_2$O) to be used in the anion exchange. The compound was then dissolved in 5 – 10 mL of 45:45:10 CHCl$_3$:MeOH:H$_2$O and passed through the column at least three times to achieve complete anion exchange. After this the solvent was removed in vacuo, the residue redissolved in CHCl$_3$ (5 – 10 mL) and washed with H$_2$O (5 – 10 mL). After drying the organic phase over anhydrous MgSO$_4$ the solvent was removed in vacuo to give the product.$^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were recorded using Bruker AVIII400 and Bruker AVIII500 spectrometers. Mass spectra were recorded on a Waters LCT Premier (low resolution), Waters MALDI Micro MX or a Bruker μTOF instrument (high resolution).

The method for coupling amines with 1,4,5,8-naphthalenetetracarboxylic dianhydride to form NDI containing asymmetric axles $^{17, 18}$ and $^{27}$ was adapted from a literature procedure.$^2$ The compounds $^{3, 3}$ $^{9, 4}$ $^{11, 5}$ $^{16, 6}$ and $^{19, 7}$ were all synthesised according to literature procedures.
Synthesis of two-station rotaxanes 4·A and 5·A

Scheme S1. Synthetic route to two-station rotaxanes 4·Cl and 5·Cl

Biphenyl mono azide BOC-protected amine 10

Amine 9 (2.69 g, 0.01 mol, 1 eq.) was dissolved in dry CH₂Cl₂ (125 mL) and dry Et₃N (1.57 mL, 0.01 mmol, 1 eq.) was added. The solution was cooled to 0°C and Boc anhydride (4.91 g, 0.02 mmol, 2 eq.) in dry CH₂Cl₂ (125 mL) was added dropwise over five minutes. After addition, the reaction mixture was stirred at 0°C under N₂(g) for 20 minutes, and the reaction mixture left to stir overnight at room temperature under N₂(g). This solution was then diluted with CH₂Cl₂ (200 mL) and worked up by washing with a saturated NaHCO₃(aq) solution (1 × 150 mL) and H₂O (1 × 150 mL). The organic phase was dried over anhydrous MgSO₄ and the solvent removed in vacuo to give the product 10 as an off-white solid (1.62 g, 4.80 mmol, 43%).

¹H NMR (400 MHz, CDCl₃) δ = 7.59 (4H, dd, J=14.79, 8.07 Hz, ArH), 7.35 - 7.42 (4H, m, ArH), 4.40 (2H, s, CH₂), 4.38 (2H, d, J=5.75 Hz, CH₂), 1.49 (9H, s, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ = 155.9, 140.8, 139.5, 138.3, 134.3, 128.6, 127.9, 127.4, 127.2, 79.5, 54.5, 44.3, 28.4
**Proto triazole BOC-protected amine axle pre-cursor 12**

Azide 10 (19 mg, 0.06 mmol, 1 eq.) was dissolved in dry CH₂Cl₂ (2 mL). Alkyne functionalised terphenyl stopper compound 11 (30 mg, 0.06 mmol, 1 eq.), TBTA (6 mg, 0.01 mmol, 0.2 eq.), Cu(CH₂CN)₄·PF₆ (4 mg, 0.01 mmol, 0.2 eq.) and DIPEA (19 μL, 0.12 mmol, 2 eq.) were added and the resulting solution was left to stir overnight at room temperature. The reaction mixture was then washed with 25% NH₄OH (aq) (1 × 2 mL) and the organic phase was collected, dried over anhydrous MgSO₄ and the solvent removed in vacuo. The resulting residue was purified by silica gel column chromatography (99:1 CH₂Cl₂: MeOH) and compound 12 was isolated as a yellow solid (45 mg, 0.05 mmol, 85%).

**¹H NMR (400 MHz, CDCl₃)** δ = 7.66 (1H, s, triazole ArH), 7.56 - 7.60 (2H, m, biphenyl ArH), 7.53 (2H, d, J = 8.2 Hz, biphenyl ArH), 7.33 - 7.39 (4H, m, biphenyl ArH), 7.20 - 7.26 (6H, m, stopper ArH), 7.04 - 7.12 (8H, m, stopper ArH), 6.84 (2H, d, J = 8.9 Hz, stopper ArH), 5.58 (2H, s, CH₂), 5.18 (2H, s, CH₂), 1.48 (9H, s, BOC CH₃), 1.30 (27H, s, stopper CH₃).

**¹³C NMR (101 MHz, CDCl₃)** δ ppm 156.0, 148.3, 144.0, 141.3, 140.1, 139.1, 134.7, 133.4, 132.2, 130.6, 129.0, 128.6, 128.5, 127.9, 127.4, 127.2, 124.0, 123.6, 113.2, 63.0, 62.0, 54.0, 47.0, 34.2, 31.3, 30.8, 28.3.

**MS (ESI): m/z calc. for C₅₉H₆₉N₄O₃ [M+H]⁺: 881.53; found: 881.61.**

**Iodo triazole BOC-protected amine axle pre-cursor 13**

Azide 10 (100 mg, 0.3 mmol, 1 eq.) was dissolved in THF (2 mL). NaI (177 mg, 1.2 mmol, 4 eq.) and Cu(ClO₄)₂·6H₂O (219 mg, 0.6 mmol, 2 eq.) were added and the resulting suspension was left to stir for five minutes. TBTA (15.7 mg, 0.03 mmol, 0.1 eq.) and DBU (45 mg, 0.3 mmol, 1 eq.) were added to the mixture. Finally, alkyne functionalised terphenyl stopper compound 11 (160 mg, 0.3 mmol, 1 eq.), CH₃CN (2 mL) and CH₂Cl₂ (ten drops) were added and the reaction mixture was left to stir overnight in the dark. The mixture was then washed with 25% NH₄OH (aq) (1 × 3 mL) and the organic phase was collected, dried over anhydrous MgSO₄ and the solvent removed in vacuo. The resulting residue was purified by silica gel column chromatography (CH₂Cl₂). The iodo triazole containing compound 13 was isolated as an off-white solid (256 mg, 0.25 mmol, 86%).

**¹H NMR (400 MHz, CDCl₃)** δ ppm 7.54 (4H, dd, J=12.90, 8.13 Hz, biphenyl ArH), 7.33 - 7.39 (4H, m, biphenyl ArH), 7.23 (6H, d, J=8.68 Hz, stopper ArH), 7.12 (8H, s, stopper ArH), 6.91 (2H, d, J=8.93 Hz, stopper ArH), 5.65 (2H, s, CH₂), 5.11 (2H, s, CH₂), 4.36 (2H, d, J=5.50 Hz, CH₂), 1.48 (9H, s, BOC CH₃), 1.31 (27H, s, stopper CH₃).

**¹³C NMR (101 MHz, CDCl₃)** δ ppm 156.2, 148.3, 144.0, 141.3, 140.1, 139.1, 134.7, 133.4, 132.2, 130.6, 129.0, 128.6, 128.4, 127.9, 127.4, 127.2, 124.0, 123.6, 113.2, 63.0, 62.0, 54.0, 47.0, 34.2, 31.4, 30.8, 28.4, 25.6.

**MS (ESI): m/z calc. for C₅₉H₆₇N₄O₃ [M+H]⁺: 1007.43; found: 1007.43.**
Proto triazole amine axle pre-cursor 14·Cl

12 (45 mg, 0.05 mmol) was dissolved in dry Et₂O (5 mL). HCl(g) was generated in situ by the dropwise addition of concentrated H₂SO₄ to NaCl(s) and bubbled through the solution for 25 minutes. After that the solution was stirred for two hours at room temperature. The resulting precipitate was filtered and washed with Et₂O to give an off white solid 14·Cl, the hydrochloride salt of the free amine (41 mg, 0.05 mmol, 99%).

¹H NMR (400MHz, MeOD) δ = 7.94 (1H, s, triazole ArH), 7.62 (4H, dd, J = 18.2 Hz, J = 8.1 Hz, biphenyl ArH), 7.36 - 7.51 (4H, m, biphenyl ArH), 7.18 - 7.25 (6H, m, stopper ArH), 7.01 - 7.09 (8H, m, stopper ArH), 6.83 (2H, d, J = 8.9 Hz, stopper ArH), 5.58 (2H, s, CH₂), 5.13 (2H, s, CH₂), 4.06 (2H, s, CH₂), 1.23 (27H, s, stopper CH₃)

¹³C NMR (126MHz, MeOD) δ = 155.7, 148.1, 143.8, 140.4, 140.1, 133.6, 132.0, 130.4, 129.2, 128.5, 127.5, 127.4, 123.8, 112.9, 62.8, 61.4, 61.0, 54.1, 53.7, 44.6, 42.8, 33.9, 31.0, 29.4, 28.8, 18.1, 16.8


Iodo triazole amine axle pre-cursor 15·Cl

13 (298 mg, 0.30 mmol) was dissolved in dry Et₂O (25 mL). HCl(g) was generated in situ by the dropwise addition of concentrated H₂SO₄(aq) to NaCl(s) and bubbled through the solution for 25 minutes. After that the solution was stirred for two hours at room temperature. The resulting precipitate was filtered and washed with Et₂O to give the hydrochloride salt of the product as a white solid 15·Cl (280 mg, 0.30 mmol, 99%).

¹H NMR (400 MHz, MeOD) δ = 7.58 - 7.65 (2H, m, biphenyl ArH), 7.53 - 7.58 (2H, m, biphenyl ArH), 7.46 - 7.52 (2H, m, biphenyl ArH), 7.28 - 7.39 (2H, m, biphenyl ArH), 7.20 (6H, d, J = 8.7 Hz, stopper ArH), 7.01 - 7.12 (8H, m, stopper ArH), 6.79 - 6.91 (2H, m, stopper ArH), 5.66 (2H, s, CH₂), 5.06 (2H, s, CH₂), 4.10 (2H, s, CH₂), 1.26 (27H, s, stopper CH₃)

¹³C NMR (101MHz, MeOD) δ = 155.8, 148.1, 143.8, 140.8, 140.2, 140.1, 133.2, 132.0, 130.4, 129.2, 128.2, 127.4, 127.2, 123.8, 113.3, 62.8, 61.3, 53.7, 49.1, 48.9, 48.7, 48.5, 48.3, 48.1, 47.8, 42.7, 33.9, 31.0

MS (MALDI-TOF): m/z calc. for C₅₄H₆₁ClIN₄O [M + H]⁺: 945.36; found: 945.05.

Proto triazole NDI axle 17

The propylamine functionalised terphenyl stopper compound 16 (20 mg, 0.04 mmol, 1 eq.) and commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride (10 mg, 0.04 mmol, 1 eq.) were suspended in 1 mL of dry, degassed DMF with dry Et₃N (6 μL, 0.04 mmol, 1 eq.) in a sealed microwave vial. The suspension was sonicated for ten minutes before heating under microwave irradiation for five minutes at 140°C. The resulting yellow solution was allowed to cool and the vial opened to allow for the addition of amine 14·Cl (29 mg,
0.04 mmol, 1 eq.) and further dry Et$_3$N (6 μL, 0.04 mmol, 1 eq.). The vial was resealed and the suspension sonicated for 30 minutes before heating under microwave irradiation for a further five minutes at 140°C. Upon cooling the yellow solution was placed immediately into a round bottom flask and reduced in vacuo to give a golden yellow residue. This crude reaction mixture was purified by silica gel column chromatography (99:1 CH$_2$Cl$_2$: MeOH) to yield the desired neutral axle compound 17 (23 mg, 0.02 mmol, 41%).

$^1$H NMR (400MHz, CDCl$_3$) δ = 8.69 - 8.81 (4H, m, NDI ArH), 7.60 - 7.68 (2H, m, biphenyl ArH), 7.47 - 7.59 (5H, m, biphenyl ArH and triazole ArH), 7.33 (2H, d, J = 8.2 Hz, biphenyl ArH), 7.19 - 7.29 (12H, m, stopper ArH), 6.98 - 7.14 (16H, m, stopper ArH), 6.84 (2H, d, J = 8.9 Hz, stopper ArH), 6.64 (2H, d, J = 8.9 Hz, stopper ArH), 5.56 (2H, s, CH$_2$), 5.44 (2H, s, CH$_2$), 5.17 (2H, s, CH$_2$), 4.38 - 4.47 (2H, m, CH$_2$), 4.04 - 4.16 (2H, m, CH$_2$), 2.21 - 2.32 (2H, m, CH$_2$), 1.31 (54H, d, J = 3.4 Hz, stopper CH$_3$)

$^{13}$C NMR (101MHz, CDCl$_3$) δ = 162.9, 162.8, 156.5, 156.1, 148.3, 148.3, 144.9, 144.1, 144.0, 141.2, 140.2, 139.7, 139.6, 136.0, 133.5, 132.3, 132.1, 131.2, 131.0, 130.7, 129.7, 128.5, 127.7, 127.3, 126.7, 126.7, 126.5, 124.0, 122.5, 113.2, 112.9, 65.9, 63.0, 63.0, 62.0, 53.9, 43.7, 38.6, 34.3, 31.4, 27.9

MS (ESI): m/z calc. for C$_{108}$H$_{112}$N$_5$O$_6$ [M+H]$^+$: 1575.86; found: 1575.98.

Iodo triazole NDI axle 18

The propylamine functionalised terphenyl stopper compound 16 (40 mg, 0.07 mmol, 1 eq.) and commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride (19 mg, 0.07 mmol, 1 eq.) were suspended in 1 mL of dry, degassed DMF with dry Et$_3$N (11 μL, 0.07 mmol, 1 eq.) in a sealed microwave vial. The suspension was sonicated for ten minutes before heating under microwave irradiation for five minutes at 140°C. The resulting brown solution was allowed to cool and the vial opened to allow for the addition of amine 13·Cl (76 mg, 0.07 mmol, 1 eq.) and further dry Et$_3$N (11 μL, 0.07 mmol, 1 eq.). The vial was resealed and the suspension sonicated for 30 minutes before heating under microwave irradiation for a further five minutes at 140°C. Upon cooling the brown solution was placed immediately into a round bottom flask and the solvent removed in vacuo to give a golden brown residue. This crude reaction mixture was purified by silica gel column chromatography (99:1 CH$_2$Cl$_2$: MeOH) to yield the desired neutral axle compound 18 (59 mg, 0.03 mmol, 50%).

$^1$H NMR (400MHz, CDCl$_3$) δ = 8.76 (4H, q, J = 7.9 Hz, NDI ArH), 7.59 - 7.67 (2H, m, biphenyl ArH), 7.47 - 7.56 (4H, m, biphenyl ArH), 7.31 - 7.39 (2H, m, biphenyl ArH), 7.23 (12H, d, J = 8.4 Hz, stopper ArH), 6.98 - 7.13 (16H, m, stopper ArH), 6.85 - 6.92 (2H, m, stopper ArH), 6.64 (2H, d, J = 8.9 Hz, stopper ArH), 5.62 (2H, s, CH$_2$), 5.43 (2H, s, CH$_2$), 5.09 (2H, s, CH$_2$), 4.43 (2H, t, J = 6.6 Hz, CH$_2$), 4.10 (2H, t, J = 6.6 Hz, CH$_2$), 2.26 (2H, quin, J = 6.2 Hz, CH$_2$), 1.30 (54H, s, stopper CH$_3$)

$^{13}$C NMR (126MHz, CDCl$_3$) δ = 162.9, 162.8, 156.5, 156.2, 148.3, 148.3, 144.1, 144.0, 141.0, 140.3, 139.8, 139.6, 135.9, 133.1, 132.2, 132.1, 131.2, 131.0, 130.7, 130.7, 129.7, 128.4,
Proto triazolium NDI axle 1·Cl

Proto triazole axle 17 (23 mg, 0.02 mmol, 1 eq.) and Me3O·BF4 (9 mg, 0.06 mmol, 3 eq.) were dissolved in dry CH2Cl2 (2 mL). The solution was left to stir for two days at room temperature under N2(g). After this time the reaction was quenched with three drops of MeOH and the solvent was removed in vacuo. The resulting solid was purified by silica gel column chromatography (CH2Cl2:MeOH 95:5) and the product 1·BF4 isolated as a pale yellow solid. Subsequent anion exchange to yield 1·Cl was performed by dissolving 1·BF4 in a solvent mixture of 45:45:10 CHCl3:MeOH:H2O (10 mL) and passing the solution three times through a column of Amberlite® resin loaded with chloride (23 mg, 0.02 mmol, 97%).

1H NMR (500MHz, CDCl3) δ = 9.92 (1H, br. s, triazolium ArH), 8.76 (4H, q, J = 8.4 Hz, NDI ArH), 7.67 (2H, br. d, J = 6.6 Hz, biphenyl ArH), 7.63 (2H, d, J = 8.1 Hz, biphenyl ArH), 7.58 (2H, d, J = 7.8 Hz, biphenyl ArH), 7.50 (2H, d, J = 7.9 Hz, biphenyl ArH), 7.23 (12H, d, J = 8.2 Hz, stopper ArH), 7.14 (2H, d, J = 8.5 Hz, stopper ArH), 6.99 - 7.10 (14H, m, stopper ArH), 6.83 (2H, d, J = 8.4 Hz, stopper ArH), 6.65 (2H, d, J = 8.5 Hz, stopper ArH), 6.01 (2H, br. s., CH3), 5.43 (4H, br. s., CH2), 4.43 (2H, t, J = 6.2 Hz, CH2), 4.38 (3H, s, triazolium CH3), 4.10 (2H, br. t, J = 5.6 Hz, CH2), 2.21 - 2.30 (2H, m, CH2), 1.24 - 1.37 (54H, m, stopper CH3)

13C NMR (126MHz, CDCl3) δ = 162.9, 162.8, 148.5, 148.3, 144.1, 143.7, 142.8, 140.0, 139.6, 136.4, 132.7, 132.2, 131.2, 131.0, 130.7, 130.6, 130.0, 129.8, 128.3, 127.3, 126.8, 126.5, 124.1, 124.0, 113.1, 112.9, 63.1, 63.0, 57.7, 57.6, 38.8, 34.3, 31.9, 31.4, 31.3, 30.9, 30.0, 29.7, 29.4, 27.9, 22.7, 14.1

MS (ESI): m/z calc. for C109H111N5O6 [M+H]+: 1701.76; found: 1701.90.

Iodo triazolium NDI axle 2·Cl

Iodo triazole axle 18 (59 mg, 0.03 mmol, 1 eq.) and Me3O·BF4 (16 mg, 0.09 mmol, 3 eq.) were dissolved in dry CH2Cl2 (2 mL). The solution was left to stir for two days at room temperature under N2(g). After this time the reaction was quenched with three drops of MeOH and the solvent was subsequently removed in vacuo. The resulting solid was purified by silica gel column chromatography (CH2Cl2:MeOH 95:5) and the product 2·BF4 isolated as a pale yellow solid. Subsequent anion exchange to yield 2·Cl was performed by dissolving 2·BF4 in a solvent mixture of 45:45:10 CHCl3:MeOH:H2O (10 mL) and passing the solution three times through a column of Amberlite® resin loaded with chloride (51 mg, 0.03 mmol, 96%).

1H NMR (400MHz, CDCl3) δ = 8.66 - 8.83 (4H, m, NDI ArH), 7.54 - 7.69 (4H, m, biphenyl ArH), 7.36 - 7.54 (4H, m, biphenyl ArH), 7.23 (12H, d, J = 8.1 Hz, stopper ArH), 7.13 - 7.18 (2H, m,
Two station HB rotaxane 4-Cl

The two-station axle 1-Cl (14 mg, 8.6 μmol, 1 eq.) and bis-vinyl nitro macrocycle precursor 3 (8 mg, 12.1 μmol, 1.4 eq.) were dissolved in dry CH₂Cl₂ (2 mL) and stirred for ten minutes. Grubbs’ second generation catalyst (1 mg, 10 wt. %) was added and the solution stirred at room temperature, monitoring by TLC and ESI mass spectrometry throughout. After one day a further addition of Grubbs’ second generation catalyst (1 mg, 10 wt. %) was made and upon depletion of macrocycle precursor 3 (which occurred after two days) the solvent was removed in vacuo. The resulting crude residue was purified by preparative silica TLC (CH₂Cl₂:MeOH 95:5 and EtOAc:MeOH 95:5) to give the product two station rotaxane 1-Cl as an orange solid (16 mg, 7.1 μmol, 83%).

¹H NMR (500MHz, CDCl₃) δ = 9.62 (1H, s, internal macrocycle ArH), 9.42 (1H, s, triazolium ArH), 9.14 - 9.32 (2H, m, macrocycle NH), 8.76 (2H, s, external macrocycle ArH), 8.77 (4H, q, J = 10.5 Hz, NDI ArH), 7.66 (1H, d, J = 8.2 Hz, biphenyl ArH), 7.49 (2H, d, J = 8.2 Hz, biphenyl ArH), 7.36 (2H, d, J = 8.1 Hz, biphenyl ArH), 7.31 (2H, d, J = 8.7 Hz, biphenyl ArH), 7.21 - 7.26 (10H, m, stopper ArH), 7.16 (6H, d, J = 8.4 Hz, stopper ArH), 6.97 - 7.11 (14H, m, stopper ArH), 6.67 (2H, d, J = 8.9 Hz, stopper ArH), 6.30 - 6.45 (8H, m, hydroquinone macrocycle ArH), 5.50 - 5.55 (2H, m, alkene macrocycle CH), 5.45 (2H, s, axle CH₂), 5.24 (2H, s, axle CH₂), 4.72 (2H, s, axle CH₂), 4.60 - 4.68 (2H, m, macrocycle CH₂), 4.45 - 4.54 (2H, m, macrocycle CH₂), 4.43 (2H, t, J = 6.6 Hz, axle CH₂), 4.10 (2H, t, J = 6.6 Hz, axle CH₂), 3.91 - 3.98 (2H, m, macrocycle CH₂), 3.87 (3H, s, triazolium CH₃), 3.62 - 3.86 (12H, m, macrocycle CH₂), 3.49 - 3.58 (2H, m, macrocycle CH₂), 2.21 - 2.30 (2H, m, axle CH₂), 1.31 (54H, d, J = 3.5 Hz, stopper CH₃)

¹³C NMR (126MHz, CDCl₃) δ = 164.4, 162.9, 162.9, 156.6, 152.9, 151.9, 148.5, 148.3, 144.1, 144.0, 136.3, 132.5, 132.2, 131.2, 131.1, 130.7, 130.6, 129.9, 129.8, 129.5, 127.5, 127.3, 126.8, 126.7, 128.6, 124.3, 124.0, 114.7, 114.4, 113.5, 113.0, 70.8, 69.4, 67.7, 65.9, 63.2, 63.0, 38.6, 35.6, 35.1, 34.3, 34.3, 31.9, 31.4, 30.1, 29.7, 29.7, 29.4, 28.0, 27.0, 26.9, 26.4, 26.3, 26.2, 22.7, 14.1

MS (ESI): m/z calc. for C₁₄₁H₁₄₉N₉O₁₆ [M−Cl]⁺: 2211.1120; found: 2211.1052.
Two station XB rotaxane 5-Cl

The two-station axle 2-Cl (25 mg, 14.2 μmol, 1 eq.) and bis-vinyl nitro macrocycle precursor 3 (13 mg, 19.9 μmol, 1.4 eq.) were dissolved in dry CH₂Cl₂ (2 mL) and stirred for ten minutes. Grubbs’ second generation catalyst (1 mg, 10 wt. %) was added and the solution stirred at room temperature, monitoring by TLC and ESI mass spectrometry throughout. After one day a further addition of Grubbs’ second generation catalyst (1 mg, 10 wt. %) was made and after three days the solvent was removed in vacuo. The resulting crude residue was purified by repetitive preparative silica TLC (CH₂Cl₂:MeOH 95:5 and EtOAc:MeOH 95:5) to give the product two station rotaxane 5-Cl as an orange solid (5 mg, 2.1 μmol, 21%).

**1H NMR** (400MHz, CDCl₃) δ = 9.69 (1H, s, internal macrocycle ArH), 9.05 (2H, d, J = 1.1 Hz, external macrocycle ArH), 8.83 - 8.92 (2H, m, macrocycle NH), 8.76 (4H, q, J = 8.1 Hz, NDI ArH), 7.64 - 7.71 (2H, m, biphenyl ArH), 7.54 - 7.63 (2H, m, biphenyl ArH), 7.41 - 7.48 (2H, m, biphenyl ArH), 7.29 - 7.34 (2H, m, biphenyl ArH), 7.14 - 7.25 (14H, m, stopper ArH), 7.00 - 7.10 (14H, m, stopper ArH), 6.95 (2H, dd, J = 8.6 Hz, J = 5.6 Hz, stopper ArH), 6.67 (2H, d, J = 8.9 Hz, stopper ArH), 6.16 - 6.30 (8H, m, hydroquinone macrocycle ArH), 5.50 - 5.54 (2H, m, alkene macrocycle CH), 5.44 (2H, s, axle CH₂), 4.88 (2H, s, axle CH₂), 4.63 - 4.77 (2H, m, macrocycle CH₂), 4.41 (2H, s, axle CH₂), 4.37 - 4.46 (4H, m, CH₂ axle CH₂ macrocycle), 4.18 (3H, s, triazolium CH₃), 4.06 - 4.14 (2H, m, axle CH₂), 3.59 - 3.99 (14H, m, macrocycle CH₂), 3.41 - 3.52 (2H, m, macrocycle CH₂), 2.21 - 2.31 (2H, m, axle CH₂), 1.31 (54H, d, J = 7.3 Hz, stopper CH₃)

**13C NMR** (126MHz, CDCl₃) δ = 164.4, 162.8, 156.5, 151.9, 148.5, 148.4, 148.4, 148.3, 144.1, 143.8, 143.8, 143.7, 139.6, 136.3, 132.7, 132.5, 132.1, 131.2, 131.0, 130.7, 130.6, 130.6, 129.8, 129.7, 129.5, 129.0, 128.2, 127.9, 127.3, 127.3, 127.2, 126.7, 126.7, 124.2, 124.1, 124.0, 114.7, 114.4, 113.2, 113.2, 112.9, 70.8, 69.4, 67.7, 65.9, 63.1, 63.0, 38.6, 35.6, 34.3, 31.4, 29.7, 29.6, 27.9, 26.4, 26.3, 26.2, 22.7, 14.1

**MS (ESI):** m/z calc. for C₁₄₁H₁₄₉N₈O₁₆I₅Na [M−Cl+Na]²⁺: 1179.99891; found: 1179.99781
**Synthesis of mono station triazolium rotaxanes 6·Cl and 7·Cl**

**Scheme S2. Synthetic route to mono-station triazolium rotaxanes 6·Cl and 7·Cl**

**Chloromethyl biphenyl mono stoppered axle pre-cursor 20**

Commercially available 4,4'-bis(chloromethyl)-1,1'-biphenyl (186 mg, 0.75 mmol, 1.5 eq.) was dissolved in degassed acetone (30 mL) and to this solution was added dried K$_2$CO$_3$ (207 mg, 1.5 mmol, 3 eq.). A solution of alcohol functionalised terphenyl stopper 19 (250 mg, 0.50 mmol, 1 eq.) in acetone (10 mL) was added dropwise before heating the reaction for one day under reflux. After this time the solvent was removed *in vacuo* and the crude solid redissolved in CH$_2$Cl$_2$ (50 mL). This was washed with H$_2$O (3 × 50 mL) and the organic layer isolated and dried over anhydrous MgSO$_4$. Removal of the solvent *in vacuo* was followed by purification by silica gel column chromatography (4:1 petroleum ether:CH$_2$Cl$_2$) giving the mono stoppered axle pre-cursor 20 (182 mg, 0.25 mmol, 51%).
**1H NMR** (400MHz, CDCl₃) δ = 7.56 - 7.69 (4H, m, biphenyl ArH), 7.43 - 7.56 (4H, m, biphenyl ArH), 7.19 - 7.32 (6H, m, stopper ArH), 7.04 - 7.16 (8H, m, stopper ArH), 6.88 (2H, d, J = 7.9 Hz, stopper ArH), 5.09 (2H, s, CH₂), 4.65 (2H, s, CH₂), 1.31 (27H, s, stopper CH₃)

**13C NMR** (101MHz, CDCl₃) δ = 156.6, 148.3, 144.1, 141.0, 139.9, 136.5, 136.5, 132.3, 130.7, 128.1, 127.5, 127.3, 124.0, 113.3, 69.6, 63.1, 46.0, 34.3, 31.4

**MS (ESI):** m/z calc. for C₅₁H₅₅OClK [M+K]^+ : 758.36; found: 758.25

Biphenyl azide mono stoppered axle precursor 21

Compound 20 (114 mg, 0.16 mmol, 1 eq.) and NaN₃ (100 mg, 1.55 mmol, 10 eq.) were suspended in DMSO (40 mL) and heated at 105°C overnight. After cooling H₂O (50 mL) was added to the solution and the resulting precipitate was collected by filtration and dried under vacuum giving the desired axle pre cursor 21 (109 mg, 0.15 mmol, 94%).

**1H NMR** (400MHz, CDCl₃) δ = 7.61 (4H, dd, J = 8.3 Hz, J = 2.4 Hz, biphenyl ArH), 7.51 (2H, d, J = 7.6 Hz, biphenyl ArH), 7.39 (2H, d, J = 8.2 Hz, biphenyl ArH), 7.23 (6H, d, J = 8.6 Hz, stopper ArH), 7.04 - 7.15 (8H, m, stopper ArH), 6.87 (2H, d, J = 8.9 Hz, stopper ArH), 5.08 (2H, s, CH₂), 4.39 (2H, s, CH₂), 1.30 (27H, s, stopper CH₃)

**13C NMR** (101MHz, CDCl₃) δ = 156.6, 148.3, 144.1, 140.8, 140.1, 139.9, 136.5, 134.4, 132.3, 130.7, 128.7, 128.1, 127.5, 127.3, 124.0, 113.3, 69.6, 63.1, 54.5, 34.3, 31.4

**MS (ESI):** m/z calc. for C₅₁H₅₅O₃Na [M+Na]^+ : 749.43; found: 749.34

Proto triazole axle 22

Azide 20 (50 mg, 0.07 mmol, 1 eq.) and the alkyne functionalised terphenyl stopper compound 11 (37 mg, 0.07 mmol, 1 eq.) were dissolved in dry CH₂Cl₂ (3 mL). To this solution were added in order TBTA (7 mg, 0.01 mmol, 0.2 eq.), Cu(CH₃CN)₄·PF₆ (5 mg, 0.01 mmol, 0.2 eq.) and DIPEA (13 μL, 0.14 mmol, 2 eq.) and the reaction was left to stir overnight at room temperature. After this time the reaction mixture was washed with 25% NH₄OH (aq) (1 × 3 mL) and the organic phase was collected, dried over anhydrous MgSO₄ and the solvent removed *in vacuo*. The resulting residue was purified by silica gel column chromatography (CH₂Cl₂) and the proto triazole containing compound 22 was isolated as a white solid (58 mg, 0.05 mmol, 66%).

**1H NMR** (400MHz, CDCl₃) δ = 7.61 (1H, s, triazole ArH), 7.55 - 7.60 (4H, m, biphenyl ArH), 7.51 (2H, d, J = 7.7 Hz, biphenyl ArH), 7.36 (2H, d, J = 7.6 Hz, biphenyl ArH), 7.20 - 7.26 (12H, m, stopper ArH), 7.02 - 7.15 (16H, m, stopper ArH), 6.86 (4H, t, J = 9.1 Hz, stopper ArH), 5.59 (2H, s, CH₂), 5.19 (2H, s, CH₂), 5.08 (2H, s, CH₂), 1.31 (54H, s, stopper CH₃)

**13C NMR** (101MHz, CDCl₃) δ = 156.0, 148.3, 148.3, 144.8, 144.1, 144.0, 139.8, 136.7, 133.5, 132.3, 130.7, 129.0, 128.6, 128.6, 128.0, 127.9, 127.8, 127.2, 124.0, 123.7, 122.6, 113.2, 113.2, 69.5, 63.0, 63.0, 62.0, 54.0, 53.9, 53.4, 34.2, 31.4, 20.5
**MS (ESI):** m/z calc. for C₉₁H₁₀₂N₃O₂ [M+H]⁺: 1269.80; found: 1269.89.

**Iodo triazole axle 23**

Azide 20 (66 mg, 0.07 mmol, 1 eq.) was dissolved in THF (1 mL). NaI (54 mg, 0.28 mmol, 4 eq.) and Cu(ClO₄)₂·6H₂O (67 mg, 0.14 mmol, 2 eq.) were added and the resulting suspension was left to stir for five minutes. TBTA (5 mg, 0.01 mmol, 0.1 eq.) and DBU (15 mg, 0.07 mmol, 1 eq.) were added to the mixture. Finally, alkyne functionalised terphenyl stopper compound 11 (49 mg, 0.07 mmol, 1 eq.), and CH₃CN (1 mL) were added and the reaction mixture was left to stir overnight in the dark. The crude mixture was then washed with 25% NH₄OH (aq) (1 × 2 mL) and the organic phase was collected, dried over anhydrous MgSO₄ and the solvent removed in vacuo. The resulting residue was purified by silica gel column chromatography (CH₂Cl₂). The iodo triazole containing compound 23 was isolated as a white solid (59 mg, 0.04 mmol, 60%).

**¹H NMR** (400MHz, CDCl₃) δ = 7.57 (4H, dd, J = 8.3 Hz, J = 1.6 Hz, biphenyl ArH), 7.49 (2H, d, J = 7.8 Hz, biphenyl ArH), 7.37 (2H, d, J = 7.7 Hz, biphenyl ArH), 7.19 - 7.26 (12H, m, stopper ArH), 7.04 - 7.15 (16H, m, stopper ArH), 6.82 - 6.93 (4H, m, stopper ArH), 5.65 (2H, s, CH₂), 5.11 (2H, s, CH₂), 5.08 (2H, s, CH₂), 1.30 (54H, s, stopper CH₃)

**¹³C NMR** (101MHz, CDCl₃) δ = 148.3, 148.3, 144.1, 144.0, 144.0, 134.7, 132.3, 130.7, 130.5, 129.1, 128.6, 128.4, 128.0, 127.6, 127.5, 127.3, 124.4, 124.0, 123.7, 113.6, 113.3, 68.4, 63.1, 54.1, 53.4, 47.1, 34.3, 31.4, 30.9, 27.8, 22.2

**MS (ESI):** m/z calc. for C₉₁H₁₀₁N₃O₂I [M+H]⁺: 1395.70; found: 1395.81.

**Proto triazolium axle 24·Cl**

Proto triazole axle 22 (58 mg, 0.05 mmol, 1 eq.) and Me₃O·BF₄ (10 mg, 0.07 mmol, 1.5 eq.) were dissolved in dry CH₃Cl₂ (4 mL). The solution was left to stir for two days at room temperature under N₂(g). After this time the reaction was quenched with three drops of MeOH and the solvent was removed in vacuo. The resulting solid was purified by silica gel column chromatography (CH₂Cl₂:MeOH 95:5) and the product 24·BF₄ isolated as a pale yellow solid. Subsequent anion exchange to yield 24·Cl was performed by dissolving 24·BF₄ in a solvent mixture of 45:45:10 CHCl₃:MeOH:H₂O (10 mL) and passing the solution three times through a column of Amberlite® resin loaded with chloride (46 mg, 0.04 mmol, 69%).

**¹H NMR** (400MHz, CDCl₃) δ = 8.46 (1H, s, triazolium ArH), 7.62 - 7.66 (2H, m, biphenyl ArH), 7.47 - 7.58 (6H, m, biphenyl ArH), 7.19 - 7.26 (12H, m, stopper ArH), 7.01 - 7.17 (16H, m, stopper ArH), 6.77 - 6.89 (4H, m, stopper ArH), 5.74 (2H, s, CH₂), 5.27 (2H, s, CH₂), 5.07 (2H, s, CH₂), 4.32 (3H, s, triazolium CH₃), 1.30 (54H, s, stopper CH₃)

**¹³C NMR** (126MHz, CDCl₃) δ = 156.6, 148.4, 148.3, 148.2, 144.3, 144.1, 143.7, 140.0, 139.5, 139.4, 136.9, 132.7, 132.3, 130.7, 130.6, 130.1, 129.7, 129.2, 128.1, 128.0, 127.4, 127.3, 126.6, 124.1, 124.0, 124.0, 113.2, 113.2, 72.3, 69.5, 63.1, 63.0, 38.9, 34.3, 34.2, 31.3

S12
Iodo triazolium axle 25·Cl

Iodo triazole axle 23 (59 mg, 0.04 mmol, 1 eq.) and Me₃O·BF₄ (10 mg, 0.07 mmol, 1.5 eq.) were dissolved in dry CH₂Cl₂ (30 mL). The solution was left to stir for two days at room temperature under N₂(g). After this time the reaction was quenched with three drops of MeOH and the solvent was removed in vacuo. The resulting solid was purified by silica gel column chromatography (CH₂Cl₂:MeOH 95:5) and the product 25·BF₄ isolated as a white solid. Subsequent anion exchange to yield 25·Cl was performed by dissolving 25·BF₄ in a solvent mixture of 45:45:10 CHCl₃:MeOH:H₂O (10 mL) and passing the solution three times through a column of Amberlite® resin loaded with chloride (56 mg, 0.04 mmol, 97%).

1H NMR (400MHz, CDCl₃) δ = 7.46 - 7.56 (2H, m, biphenyl ArH), 7.31 - 7.46 (6H, m, biphenyl ArH), 7.15 - 7.25 (12H, m, stopper ArH), 6.95 - 7.15 (16H, m, stopper ArH), 6.65 - 6.86 (4H, m, stopper ArH), 5.70 (2H, s, CΗ₂), 5.36 (2H, s, CΗ₂), 4.99 (2H, s, CH₂), 4.42 (3H, s, triazolium CH₃), 1.27 (54H, s, stopper CH₃)

13C NMR (126MHz, CDCl₃) δ = 156.5, 154.5, 148.4, 148.3, 144.1, 143.8, 143.3, 142.1, 141.8, 139.9, 139.2, 136.8, 132.6, 132.3, 130.7, 130.6, 128.9, 128.0, 128.0, 127.2, 124.2, 124.1, 124.0, 113.3, 113.2, 104.6, 69.4, 63.1, 63.0, 59.5, 57.1, 39.7, 34.3, 34.3, 31.4, 29.7

MS (MALDI-TOF): m/z calc. for C₉₂H₁₀₄N₃O₂ [M – Cl]⁺: 1284.82; found: 1284.69.

HB one station rotaxane 6·Cl

The one-station axle 24·Cl (30 mg, 22.7 μmol, 1 eq.) and bis-vinyl nitro macrocycle precursor 3 (18 mg, 27.2 μmol, 1.2 eq.) were dissolved in dry CH₂Cl₂ (2 mL) and stirred for ten minutes. Grubbs’ second generation catalyst (2 mg, 10 wt. %) was added and the solution stirred at room temperature, monitoring by TLC and ESI mass spectrometry throughout. After one day a further addition of Grubbs’ second generation catalyst (2 mg, 10 wt. %) was made and upon depletion of macrocycle precursor 3 (which occurred after two days) the solvent was removed in vacuo. The resulting crude residue was purified by preparative silica TLC (EtOAc:MeOH 99:1 and CH₂Cl₂:MeOH 98:2) to give the product one station rotaxane 6·Cl as an off white solid (9 mg, 4.6 μmol, 20%).

1H NMR (500MHz, CDCl₃) δ = 9.69 (1H, br. s, internal macrocycle ArH), 9.49 (1H, br. s, triazolium ArH), 9.26 - 9.42 (2H, m, macrocycle NH), 8.80 (2H, s, external macrocycle ArH), 7.55 (4H, d, J = 4.1 Hz, biphenyl ArH), 7.42 (2H, d, J = 8.1 Hz, biphenyl ArH), 7.32 (2H, d, J = 8.7 Hz, biphenyl ArH), 7.20 - 7.27 (12H, m, stopper ArH), 7.06 - 7.20 (16H, m, stopper ArH), 7.01 (2H, d, J = 8.7 Hz, stopper ArH), 6.88 (2H, d, J = 8.9 Hz, stopper ArH), 6.32 - 6.49 (8H, m, hydroquinone macrocycle ArH), 5.54 (2H, br. s., alkene macrocycle CH₂), 5.27 (2H, s, axle CH₂), 5.09 (2H, s, axle CH₂), 4.72 (2H, s, axle CH₂), 4.56 - 4.68 (2H, m, macrocycle CH₂), 4.45 - 4.56 (2H, m, macrocycle CH₂), 3.94 - 4.00 (2H, m, macrocycle CH₂), 3.88 (3H, s, triazolium...
CH₃), 3.63 - 3.92 (12H, m, macrocycle CH₂), 3.52 - 3.62 (2H, m, macrocycle CH₂), 1.31 (54H, s, stopper CH₃)

¹³C NMR (126MHz, CDCl₃) δ = 164.1, 153.0, 151.9, 148.5, 148.3, 144.1, 144.0, 132.5, 132.3, 130.9, 130.7, 130.6, 129.8, 129.6, 128.8, 128.2, 127.5, 127.2, 126.6, 124.3, 124.0, 115.0, 114.4, 113.8, 113.3, 70.8, 69.4, 68.1, 67.6, 66.5, 63.1, 39.9, 38.9, 38.7, 34.3, 34.3, 31.9, 31.4, 30.3, 29.7, 29.7, 29.4, 28.9, 23.7, 23.0, 22.7, 14.1, 14.0, 10.9


XB one station rotaxane 7·Cl

The one-station axle 25·Cl (33 mg, 22.8 μmol, 1 eq.) and bis-vinyl nitro macrocycle precursor 3 (18 mg, 27.4 μmol, 1.4 eq.) were dissolved in dry CH₂Cl₂ (2 mL) and stirred for ten minutes. Grubbs’ second generation catalyst (2 mg, 10 wt. %) was added and the solution stirred at room temperature, monitoring by TLC and ESI mass spectrometry throughout. After one day a further addition of Grubbs’ second generation catalyst (2 mg, 10 wt. %) was made and after three days the solvent was removed in vacuo. The resulting crude residue was purified by iterative preparative silica TLC (CH₂Cl₂:MeOH 97:3) to give the product one station rotaxane 7·Cl as a white solid (5 mg, 2.4 μmol, 11%).

¹H NMR (400MHz, CDCl₃) δ = 9.35 (1H, br. s, internal macrocycle ArH), 9.01 (2H, s, external macrocycle ArH), 8.38 - 8.54 (2H, m, macrocycle NH), 7.63 - 7.68 (2H, m, biphenyl ArH), 7.53 - 7.58 (2H, m, biphenyl ArH), 7.48 - 7.52 (2H, m, biphenyl ArH), 7.30 - 7.35 (2H, m, biphenyl ArH), 7.15 - 7.26 (12H, m, stopper ArH), 7.06 - 7.14 (16H, m, stopper ArH), 6.97 (2H, d, J = 2.4 Hz, stopper ArH), 6.88 (2H, d, J = 8.9 Hz, stopper ArH), 6.29 - 6.39 (8H, m, hydroquinone macrocycle ArH), 5.40 - 5.51 (2H, m, alkene macrocycle CH₂), 5.09 (2H, s, axle CH₂), 4.88 (2H, s, axle CH₂), 4.67 - 4.80 (2H, m, macrocycle CH₂), 4.51 - 4.60 (2H, m, macrocycle CH₂), 4.49 (2H, s, axle CH₂), 4.15 (3H, s, triazolium CH₃), 3.97 - 4.06 (2H, m, macrocycle CH₂), 3.85 - 3.95 (2H, m, macrocycle CH₂), 3.59 - 3.83 (10H, m, macrocycle CH₂), 3.45 - 3.56 (2H, m, macrocycle CH₂), 1.32 (54H, s, stopper CH₃)

¹³C NMR (126MHz, CDCl₃) δ = 164.4, 155.1, 153.0, 151.6, 148.5, 148.3, 144.1, 143.9, 142.8, 139.9, 135.9, 132.5, 132.3, 130.7, 130.7, 130.6, 130.2, 129.2, 128.2, 127.9, 127.4, 126.7, 124.3, 124.0, 115.8, 115.4, 114.7, 114.1, 113.2, 70.7, 69.6, 69.4, 67.6, 66.9, 63.2, 63.1, 39.8, 39.5, 37.1, 34.3, 34.3, 32.7, 31.9, 31.4, 30.0, 29.7, 29.7, 29.4, 27.1, 22.7, 19.7, 14.1

MS (ESI): m/z calc. for C₁₂₄H₁₃₉N₆O₁₂ [M − Cl]^+: 2031.9524; found: 2031.9476.
Synthesis of mono station NDI rotaxane 8

Scheme S3. Synthetic route to mono-station NDI rotaxane 8

Biphenyl amine mono stoppered axle pre-cursor 26

Azide 21 (200 mg, 0.28 mmol) was dissolved in CHCl₃ (10 mL) and Palladium on Carbon (40 mg, 20 wt. %) was added to the solution followed by MeOH (10 mL). The reaction was stirred under an atmosphere of H₂(g) for two days after which the crude mixture was filtered through a plug of Celite, which was rinsed with a further 50 mL of 1:1 CHCl₃:MeOH to give a clear solution. The solvent was then removed in vacuo and the free amine 26 isolated by silica gel column chromatography (CH₂Cl₂:MeOH 95:5) as a white solid (180 mg, 0.26 mmol, 92%).

¹H NMR (500MHz, MeOD) δ = 7.55 - 7.62 (4H, m, biphenyl ArH), 7.44 - 7.51 (2H, m, biphenyl ArH), 7.34 - 7.42 (2H, m, biphenyl ArH), 7.17 - 7.26 (6H, m, stopper ArH), 7.01 - 7.12 (8H, m, stopper ArH), 6.82 - 6.89 (2H, m, stopper ArH), 5.07 (2H, s, CH₂), 4.17 (2H, br. s, NH₂), 3.86 (2H, s, CH₃), 1.27 (27H, s, stopper CH₃)

¹³C NMR (126MHz, MeOD) δ = 156.3, 148.1, 143.9, 140.1, 139.7, 136.1, 132.0, 130.5, 127.8, 127.7, 127.1, 126.9, 123.8, 113.1, 69.5, 62.8, 44.8, 34.0, 31.0

MS (ESI): m/z calc. for C₅₁H₅₈NO [M + H]⁺: 700.45; found: 700.41.

NDI mono station axle 27

The propylamine functionalised terphenyl stopper compound 16 (40 mg, 0.07 mmol, 1 eq.) and commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride (19 mg, 0.07 mmol, 1 eq.) were suspended in 1 mL of dry, degassed DMF with dry Et₃N (6 μL, 0.07 mmol, 1 eq.) in a sealed microwave vial. The suspension was sonicated for ten minutes before heating under microwave irradiation for five minutes at 140°C. The resulting brown solution was allowed to cool and the vial opened to allow for the addition of amine 26 (50 mg, 0.07
mmol, 1 eq.) and further dry Et$_3$N (6 μL, 0.07 mmol, 1 eq.). The vial was resealed and the suspension sonicated for 30 minutes before heating under microwave irradiation for a further five minutes at 140°C. Upon cooling the brown solution was placed immediately into a round bottom flask and reduced in vacuo to give a golden brown residue. This crude reaction mixture was purified by silica gel column chromatography (CH$_2$Cl$_2$) to yield the desired one station axle compound 27 (89 mg, 0.06 mmol, 83%).

$^1$H NMR (400MHz, CDCl$_3$) δ = 8.71 - 8.83 (4H, m, NDI ArH), 7.63 (2H, s, biphenyl ArH), 7.61 - 7.68 (2H, m, biphenyl ArH), 7.52 - 7.59 (4H, m, biphenyl ArH), 7.45 - 7.50 (2H, m, biphenyl ArH), 7.19 - 7.26 (12H, m, stopper ArH), 6.96 - 7.14 (16H, m, stopper ArH), 6.80 - 6.91 (2H, m, stopper ArH), 5.45 (2H, s, C$_2$H$_2$), 5.06 (2H, s, C$_2$H$_2$), 4.44 (2H, t, J = 7.0 Hz, C$_2$H$_2$), 4.11 (2H, t, J = 6.1 Hz, C$_2$H$_2$), 2.21 - 2.33 (2H, m, C$_2$H$_2$), 1.30 (54H, s, stopper C$_3$H$_3$)

$^{13}$C NMR (126MHz, CDCl$_3$) δ = 162.9, 162.8, 162.8, 156.6, 156.5, 148.3, 144.1, 140.3, 139.9, 139.6, 136.3, 135.6, 132.3, 132.1, 131.2, 131.0, 130.7, 130.7, 129.7, 129.6, 128.0, 127.3, 127.2, 126.7, 126.7, 126.6, 124.0, 113.2, 112.9, 69.6, 65.9, 63.0, 63.0, 43.7, 38.6, 34.3, 31.4, 27.9

MS (MALDI-TOF): m/z calc. for C$_{105}$H$_{109}$N$_2$O$_6$ [M + H]$^+$: 1495.83; found: 1495.66.

NDI mono station rotaxane 8

The one-station axle 27 (45 mg, 30.1 μmol, 1 eq.) and bis-vinyl nitro macrocycle precursor 3 (30 mg, 45.2 μmol, 1.5 eq.) were dissolved in dry CH$_2$Cl$_2$ (2 mL) and stirred for ten minutes. Grubbs’ second generation catalyst (3 mg, 10 wt. %) was added and the solution stirred at room temperature, monitoring by TLC throughout. After one day a further addition of Grubbs’ second generation catalyst (3 mg, 10 wt. %) was made and upon depletion of macrocycle precursor 3 (which occurred after four days) the solvent was removed in vacuo. The resulting crude residue was purified by preparative silica TLC (CH$_2$Cl$_2$:MeOH 99:1) to give the product one station rotaxane 8 as an orange solid (1 mg, 0.47 μmol, 2%).

$^1$H NMR (500MHz, CDCl$_3$) δ = 9.19 (1H, s, internal macrocycle ArH), 9.10 (2H, s, external macrocycle ArH), 8.50 - 8.61 (4H, m, NDI ArH), 7.53 - 7.63 (6H, m, biphenyl ArH), 7.46 - 7.51 (2H, m, biphenyl ArH), 7.18 - 7.25 (12H, m, stopper ArH), 7.03 - 7.13 (16H, m, stopper ArH), 6.83 - 6.89 (2H, m, stopper ArH), 6.71 - 6.77 (2H, m, stopper ArH), 6.24 - 6.33 (2H, m, alkene macrocycle CH), 5.63 - 5.80 (8H, m, hydroquinone macrocycle ArH), 5.27 (2H, s, axle CH$_2$), 5.05 (2H, s, CH$_2$ axle), 4.31 (2H, t, J = 7.0 Hz, CH$_2$ axle), 4.17 - 4.26 (4H, m, macrocycle CH$_2$), 3.98 - 4.17 (6H, m, macrocycle and axle CH$_2$), 3.37 - 3.81 (12H, m, macrocycle CH$_2$), 2.20 - 2.29 (2H, m, axle CH$_2$), 1.30 (54H, s, stopper CH$_3$)

$^{13}$C NMR (126MHz, CDCl$_3$) δ = 164.9, 163.5, 163.1, 156.6, 156.5, 152.4, 151.3, 149.2, 148.3, 148.3, 144.1, 144.0, 140.8, 140.1, 139.9, 136.6, 136.2, 135.3, 132.3, 131.1, 131.0, 130.7, 130.6, 130.2, 129.7, 128.6, 128.2, 128.2, 127.2, 126.7, 126.0, 125.9, 125.6, 124.0,
114.1, 114.0, 113.9, 113.2, 113.1, 71.1, 69.6, 68.8, 67.2, 66.9, 65.9, 63.0, 63.0, 44.0, 40.7, 38.5, 34.3, 31.4, 29.7, 28.1

**MS (MALDI-TOF):** $m/z$ calc. for $\text{C}_{137}\text{H}_{143}\text{N}_{5}\text{O}_{16}\text{Na} [\text{M} + \text{Na}]^+$: 2139.05; found: 2139.54
Part II: 2D $^1$H NMR ROESY spectra

2D $^1$H NMR ROESY of 4·Cl

Figure S1. Truncated $^1$H-$^1$H ROESY NMR spectrum of rotaxane 4·Cl with selected coupling interactions highlighted (CDCl$_3$, 298 K, 500 MHz).
**2D $^1$H NMR ROESY of 4·PF$_6$**

**Figure S2.** Truncated $^1$H-$^1$H ROESY NMR spectrum of rotaxane 4·PF$_6$ with selected coupling interactions highlighted (CDCl$_3$, 298 K, 500 MHz).
2D $^1$H NMR ROESY of 5-Cl

Figure S3. Truncated $^1$H-$^1$H ROESY NMR spectrum of rotaxane 5-Cl with selected coupling interactions highlighted (CDCl$_3$, 298 K, 500 MHz).

2D $^1$H NMR ROESY of 5-PF$_6$
Figure S4. Truncated $^1$H-$^1$H ROESY NMR spectrum of rotaxane 5·PF$_6$ with selected coupling interactions highlighted (CDCl$_3$, 298 K, 500 MHz).
Part III: UV-Vis Spectroscopy

Figure S5: UV-Vis spectra showing the effect of the addition of one equivalent of tetrabutylammonium chloride into a solution of rotaxane $5\cdot$PF$_6$ in CHCl$_3$ ($3.3 \times 10^{-3}$ mol L$^{-1}$). The addition of chloride leads to a decrease in intensity of the charge-transfer band at $\lambda_{\text{abs, max}} \sim 450$ nm.
Part IV: Anion molecular motion studies

Axle and rotaxane components were fully anion exchanged using a column containing an Amberlite® ion exchange resin as described in the general information and characterised by a combination of $^1$H, $^{19}$F and $^{31}$P NMR spectroscopy.

Two station HB axle 1·A

![Chemical structure of 1·A](image)

1·I

$^1$H NMR (400MHz, 4:1 CDCl$_3$:MeOD) $\delta = 8.88$ (1H, s, triazolium ArH), 8.63 - 8.79 (4H, m, NDI ArH), 7.44 - 7.62 (8H, m, biphenyl ArH), 6.91 - 7.24 (28H, m, stopper ArH), 6.81 (2H, d, $J = 9.0$ Hz, stopper ArH), 6.56 (2H, d, $J = 8.9$ Hz, stopper ArH), 5.83 (2H, s, CH$_2$), 5.39 (2H, s, CH$_2$), 5.33 (2H, s, CH$_2$), 4.35 (2H, s, CH$_2$), 4.35 (3H, s, triazolium CH$_3$), 4.07 (2H, s, CH$_2$), 2.16 - 2.28 (2H, m, CH$_2$), 1.23 (54H, s, stopper CH$_3$)

1·PF$_6$

$^1$H NMR (500MHz, CDCl$_3$) $\delta = 8.69 - 8.84$ (4H, m, NDI ArH), 8.35 (1H, s, triazolium ArH), 7.45 - 7.68 (8H, m, biphenyl ArH), 6.98 - 7.26 (28H, m, stopper ArH), 6.78 (2H, d, $J = 8.9$ Hz, stopper ArH), 6.65 (2H, d, $J = 8.7$ Hz, stopper ArH), 5.69 (2H, s, CH$_2$), 5.42 (2H, s, CH$_2$), 5.23 (2H, s, CH$_2$), 4.38 - 4.48 (2H, m, CH$_2$), 4.33 (3H, s, triazolium CH$_3$), 4.10 (2H, s, CH$_2$), 2.20 - 2.28 (2H, m, CH$_2$), 1.30 (54H, s, stopper CH$_3$)

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta = -72.5$ (d, $^1$J = 708 Hz, PF$_6$).

$^{31}$P NMR (202 MHz, CDCl$_3$) $\delta = -144.3$ (sept, $^1$J = 709 Hz, PF$_6$).

Two station XB axle 2·A
2·I

$^1$H NMR (400MHz, 4:1 CDCl$_3$:MeOD) δ = 8.63 - 8.77 (4H, m, NDI ArH), 7.42 - 7.60 (8H, m, biphenyl ArH), 6.91 - 7.25 (28H, m, stopper ArH), 6.79 - 6.86 (2H, m, stopper ArH), 6.51 - 6.59 (2H, m, stopper ArH), 5.83 (2H, s, CH$_2$), 5.38 (2H, s, CH$_2$), 5.28 (2H, s, CH$_2$), 4.38 (3H, s, triazolium CH$_3$), 4.33 - 4.42 (2H, m, CH$_2$), 4.03 - 4.11 (2H, m, CH$_2$), 2.17 - 2.28 (2H, m, CH$_2$), 1.25 (54H, s, stopper CH$_3$)

2·PF$_6$

$^1$H NMR (500MHz, CDCl$_3$) δ = 8.65 - 8.83 (4H, m, NDI ArH), 7.38 - 7.66 (8H, m, biphenyl ArH), 6.98 - 7.26 (28H, m, stopper ArH), 6.74 - 6.88 (2H, m, stopper ArH), 6.60 - 6.69 (2H, m, stopper ArH), 5.74 (2H, s, CH$_2$), 5.44 (2H, s, CH$_2$), 5.30 (2H, s, CH$_2$), 4.38 - 4.48 (2H, m, CH$_2$), 4.34 (3H, s, triazolium CH$_3$), 4.10 (2H, br. s., CH$_2$), 2.20 - 2.31 (2H, m, CH$_2$), 1.30 (54H, s, stopper CH$_3$)

$^{19}$F NMR (470 MHz, CDCl$_3$) δ = -72.5 (d, $^1J$ = 708 Hz, PF$_6$).

$^{31}$P NMR (202 MHz, CDCl$_3$) δ = -144.3 (sept, $^1J$ = 709 Hz, PF$_6$).

Two station HB rotaxane 4·A

4·I
$^1$H NMR (400MHz, 4:1 CDCl$_3$:MeOD) δ = 9.19 (1H, s, internal macrocycle ArH), 8.74 - 8.82 (3H, m, triazolium and external macrocycle ArH), 8.62 - 8.71 (4H, m, NDI ArH), 8.44 - 8.49 (2H, m, macrocycle NH), 7.39 - 7.59 (6H, m, biphenyl ArH), 7.23 - 7.28 (2H, m, biphenyl ArH), 6.96 - 7.23 (28H, m, stopper ArH), 6.88 - 6.93 (2H, m, stopper ArH), 6.59 - 6.65 (2H, m, stopper ArH), 6.03 - 6.29 (8H, m, hydroquinone macrocycle ArH), 5.78 - 5.87 (2H, m, alkene macrocycle C), 5.45 (2H, s, axle C), 5.31 (2H, s, axle CH$_2$), 4.96 (2H, s, axle CH$_2$), 4.30 - 4.42 (4H, m, axle and macrocycle CH$_2$), 4.00 (3H, s, triazolium C), 3.81 - 4.15 (14H, m, axle and macrocycle CH$_2$), 2.13 - 2.28 (2H, m, axle CH$_2$), 1.24 (54H, s, stopper C).

4·PF$_6$

$^1$H NMR (500MHz, CDCl$_3$) δ = 8.87 (2H, s, external macrocycle ArH), 8.67 - 8.78 (4H, m, NDI ArH), 8.43 (1H, br. s, internal macrocycle ArH), 8.07 (1H, br. s, triazolium), 7.54 - 7.64 (2H, m, biphenyl ArH), 7.40 - 7.52 (4H, m, biphenyl ArH), 6.97 - 7.32 (30H, m, stopper and biphenyl ArH), 6.85 - 6.94 (2H, m, stopper ArH), 6.69 (2H, d, J = 8.9 Hz, stopper ArH), 6.33 (8H, d, J = 8.4 Hz, hydroquinone macrocycle ArH), 5.77 - 5.92 (2H, m, alkene macrocycle C), 5.37 (2H, s, axle CH$_2$), 5.30 (2H, s, axle CH$_2$), 4.85 (2H, s, axle CH$_2$), 4.34 - 4.47 (2H, m, axle CH$_2$), 4.06 - 4.13 (2H, m, axle CH$_2$), 3.92 (3H, s, triazolium CH$_3$), 3.51 - 4.27 (20H, m, macrocycle CH$_2$), 2.20 - 2.32 (2H, m, axle CH$_2$), 1.29 (54H, s, stopper CH$_3$).

$^{19}$F NMR (470 MHz, CDCl$_3$) δ = -72.4 (d, $^1$J = 708 Hz, PF$_6$).

$^{31}$P NMR (202 MHz, CDCl$_3$) δ = -144.3 (sept, $^1$J = 709 Hz, PF$_6$).

Two station XB rotaxane 5·A

5·I

$^1$H NMR (400MHz, 4:1 CDCl$_3$:MeOD) δ = 9.25 (1H, s, internal macrocycle ArH), 8.85 (2H, s, external macrocycle ArH), 8.63 - 8.77 (4H, m, NDI ArH), 8.38 - 8.46 (2H, m, macrocycle NH), 7.38 - 7.64 (8H, m, biphenyl ArH), 6.90 - 7.30 (30H, m, stopper ArH), 6.56 - 6.64 (2H, m, stopper ArH), 6.19 - 6.29 (8H, m, hydroquinone macrocycle ArH), 5.43 - 5.52 (2H, m, alkene macrocycle CH), 5.37 (2H, s, axle CH$_2$), 4.99 (2H, s, axle CH$_2$), 4.57 (2H, s, axle CH$_2$), 4.31 -
4.49 (6H, m, macrocycle and axle CH₂), 4.15 (3H, s, triazolium CH₃), 4.02 - 4.11 (2H, m, axle CH₂), 3.44 - 3.97 (16H, m, macrocycle CH₂), 2.16 - 2.27 (2H, m, axle CH₂), 1.25 (54H, s, stopper CH₃)

5·PF₆

¹H NMR (500MHz, CDCl₃) δ = 8.97 (3H, br. s, external and internal macrocycle ArH), 8.57 - 8.74 (4H, m, NDI ArH), 7.43 - 7.62 (8H, m, biphenyl ArH), 7.01 - 7.32 (28H, m, stopper ArH), 6.84 - 6.94 (2H, m, stopper ArH), 6.72 (2H, d, J = 8.9 Hz, stopper ArH), 5.98 (10H, br. s., hydroquinone macrocycle ArH and alkene macrocycle CH), 5.43 (2H, br. s, axle CH₂), 5.30 (2H, br. s, axle CH₂), 5.00 (2H, br. s, axle CH₂), 4.34 - 4.43 (2H, m, axle CH₂), 4.31 (3H, s, triazolium CH₃), 3.57 - 4.13 (22H, m, axle and macrocycle CH₂), 2.21 - 2.29 (2H, m, axle CH₂), 1.29 (54H, s, stopper CH₃)

¹⁹F NMR (470 MHz, CDCl₃) δ = -72.5 (d, ¹J = 707 Hz, PF₆).

³¹P NMR (202 MHz, CDCl₃) δ = -144.3 (sept, ¹J = 709 Hz, PF₆).

One station HB rotaxane 6·A

6·I

¹H NMR (400MHz, 4:1 CDCl₃:MeOD) δ = 9.22 (1H, s, internal macrocycle ArH), 8.73 (3H, s, triazolium and external macrocycle ArH), 8.62 - 8.70 (2H, m, macrocycle NH), 7.36 - 7.53 (8H, m, biphenyl ArH), 6.94 - 7.29 (30H, m, stopper ArH), 6.84 (2H, d, J = 8.9 Hz, stopper ArH), 6.24 - 6.60 (8H, m, hydroquinone macrocycle ArH), 5.60 - 5.70 (2H, m, alkene macrocycle CH), 5.31 (2H, s, axle CH₂), 5.04 (2H, s, axle CH₂), 4.80 (2H, s, axle CH₂), 4.67 - 4.78 (2H, m, macrocycle CH₂), 4.29 - 4.39 (2H, m, macrocycle CH₂), 3.85 (3H, s, triazolium CH₃), 3.54 - 4.07 (16H, m, macrocycle CH₂), 1.24 (54H, s, stopper CH₃)
6·PF$_6$

$^1$H NMR (500MHz, CDCl$_3$) $\delta$ = 8.87 (2H, s, external macrocycle ArH), 8.50 (1H, br. s, internal macrocycle ArH), 8.25 (1H, br. s, triazolium ArH), 7.43 - 7.60 (8H, m, biphenyl ArH), 7.03 - 7.29 (28H, m, stopper ArH), 6.95 (2H, d, $J$ = 8.5 Hz, stopper ArH), 6.88 (2H, d, $J$ = 8.7 Hz, stopper ArH), 6.26 - 6.58 (8H, m, hydroquinone macrocycle ArH), 5.64 - 5.73 (2H, m, alkene macrocycle CH), 5.21 (2H, s, axle CH$_2$), 5.07 (2H, s, axle CH$_2$), 4.73 (2H, s, axle CH$_2$), 4.33 - 4.51 (4H, m, macrocycle CH$_2$), 3.79 (3H, s, triazolium CH$_3$), 3.52 - 4.15 (16H, m, macrocycle CH$_2$), 1.31 (54H, s, stopper CH$_3$)

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ = -72.7 (d, $^1J$ = 706 Hz, PF$_6$).

$^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ = -144.3 (sept, $^1J$ = 709 Hz, PF$_6$).

One station XB rotaxane 7·A

7·I

$^1$H NMR (400MHz, 4:1 CDCl$_3$;MeOD) $\delta$ = 9.28 (1H, s, internal macrocycle ArH), 8.88 (2H, d, $J$ = 1.3 Hz, external macrocycle ArH), 7.42 - 7.66 (8H, m, biphenyl ArH), 6.90 - 7.32 (30H, m, stopper ArH), 6.80 - 6.87 (2H, m, stopper ArH), 6.29 - 6.43 (8H, m, hydroquinone macrocycle ArH), 5.34 - 5.42 (2H, m, alkene macrocycle CH), 5.06 (2H, s, axle CH$_2$), 4.92 (2H, s, axle CH$_2$), 4.50 (2H, s, axle CH$_2$), 4.43 - 4.62 (4H, m, macrocycle CH$_2$), 4.13 (3H, s, triazolium CH$_3$), 3.94 - 4.16 (4H, m, macrocycle CH$_2$), 3.45 - 3.90 (12H, m, macrocycle CH$_2$), 1.25 (54H, s, stopper CH$_3$)
7-PF<sub>6</sub>

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) \( \delta = 8.83 - 8.92 \) (3H, m, internal and external macrocycle ArH), 7.38 - 7.59 (8H, m, biphenyl ArH), 7.01 - 7.32 (28H, m, stopper ArH), 6.90 - 6.98 (2H, m, stopper ArH), 6.80 - 6.90 (2H, m, stopper ArH), 6.31 - 6.56 (8H, m, hydroquinone macrocycle ArH), 5.49 - 5.58 (2H, m, alkene macrocycle CH), 5.03 (4H, s, axle CH<sub>2</sub>), 4.72 (2H, br. s, axle CH<sub>2</sub>), 4.34 - 4.52 (2H, m, macrocycle CH<sub>2</sub>), 4.18 - 4.32 (2H, m, macrocycle CH<sub>2</sub>), 4.15 (3H, s, triazolium CH<sub>3</sub>), 3.52 - 4.12 (16H, m, macrocycle CH<sub>2</sub>), 1.30 (54H, s, stopper CH<sub>3</sub>)

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) \( \delta = -72.5 \) (d, \( ^1J = 706 \) Hz, PF<sub>6</sub>).

<sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) \( \delta = -144.3 \) (sept, \( ^1J = 709 \) Hz, PF<sub>6</sub>)

**Method for Estimation of Percentage Occupancies**

A \( \Delta \delta \) scale in each anionic state of the system (counter anion) for each station (NDI and triazolium) was constructed using the \( \delta \) values of the station’s diagnostic protons, H<sub>e,e’</sub> and H<sub>i</sub> respectively, obtained from their \(^1\)H NMR spectra. The following equation was then used to estimate the occupancy of a station:

\[
\text{Occ.(station)} = \frac{\Delta \delta(\text{rotaxane})}{\Delta \delta(\text{model})}
\]

Where,

\[
\Delta \delta(\text{rotaxane}) = \delta(0\% \text{ occ.}) - \delta(\text{rotaxane})
\]

\[
\Delta \delta(\text{model}) = \delta(0\% \text{ occ.}) - \delta(100\% \text{ occ.})
\]

And,

\[
\delta(100\% \text{ occ.}) = \delta \text{ of the station’s diagnostic protons in the model one station rotaxane}
\]

\[
\delta(0\% \text{ occ.}) = \delta \text{ of the station’s diagnostic protons in the two station axle}
\]

\[
\delta(\text{rotaxane}) = \delta \text{ of the station’s diagnostic protons in the two station rotaxane}
\]

The estimation of the percentage occupancies of each station in the XB two station rotaxane 5-PF<sub>6</sub> in CDCl<sub>3</sub> is used as an example to demonstrate this.

For the triazolium station (Figures S6 to S9):

\[
\delta(0\% \text{ occ.}) = \delta(H_i) (2-PF_6) = 4.41 \text{ ppm}
\]
Figure S6. Truncated $^1$H NMR spectrum of two station axle $2 \cdot PF_6(CDCl_3, 298 K, 400 MHz)$

$\delta(100\% \text{ occ.}) = \delta(H_i) \ (7 \cdot PF_6) = 4.15 \text{ ppm}$

Figure S7. Truncated $^1$H NMR spectrum of one station rotaxane $7 \cdot PF_6(CDCl_3, 298 K, 400 MHz)$

$\delta(\text{rotaxane}) = \delta(H_i) \ (5 \cdot PF_6) = 4.31 \text{ ppm}$

Figure S8. Truncated $^1$H NMR spectrum of two station rotaxane $5 \cdot PF_6(CDCl_3, 298 K, 400 MHz)$

Therefore: Occ.(triazolium) = $(4.41 - 4.31) / (4.41 - 4.15) = 0.38 = 38%$

And this implies: Occ.(NDI) = $1 - 0.38 = 0.62 = 62%$
Figure S9. $\Delta\delta$ scale for the triazolium station as the hexafluorphosphate salt in CDCl$_3$

For the NDI station (Figures S10 to S13):

$\delta(0\% \text{ occ.}) =\delta(\text{H}_{e,e'}) (2\cdot \text{PF}_6) = 8.76$ ppm

\[ \Delta\delta = \delta(100\% \text{ occ.}) - \delta(0\% \text{ occ.}) \]

$\delta(100\% \text{ occ.}) =\delta(\text{H}_{e,e'}) (8) = 8.56$ ppm
δ(rotate) = δ(H_{e,e'}) (5·PF₆) = 8.65 ppm

\[ \Delta \delta(\text{rotate}) = 0.11 \]
\[ \delta(\text{rotate}) = 8.65 \]
\[ \delta(0\% \text{ occ.}) = 8.76 \]
\[ \delta(100\% \text{ occ.}) = 8.56 \]
\[ \Delta \delta(\text{model}) = 0.2 \]

\( \text{Occ.}(\text{NDI}) = (8.76 - 8.65) / (8.76 - 8.56) = 0.55 = 55\% \)

And this implies: Occ.(triazolium) = 1 – 0.55 = 0.45 = 45\%

\( \Delta \delta(\text{model}) \) for NDI was always found to be smaller than \( \Delta \delta(\text{model}) \) for the triazolium station.

\( ^1\text{H} \text{ NMR spectra of the compounds 1·Cl, 1·I, 1·PF₆, 2·Cl, 2·I, 2·PF₆, 4·Cl, 4·I, 4·PF₆, 5·Cl, 5·I, 5·PF₆, 6·Cl, 6·I, 6·PF₆, 7·Cl, 7·I, 7·PF₆ and 8 in CDCl₃ gave the following } \delta(H_i) \text{ and } \delta(H_{e,e'}) \text{ values that were then used to estimate the percentage occupancies of the two station rotaxanes 4·A and 5·A shown in Figure 7 in the main article (Tables S1 and S2).} \)
Table S1. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station HB rotaxane 4·A in CDCl$_3$

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ.(triazolium)</th>
<th>% Occ.(NDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triazolium</td>
<td>Cl$^-$</td>
<td>3.88</td>
<td>4.38</td>
<td>3.88</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>3.87</td>
<td>4.41</td>
<td>3.87</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>3.92</td>
<td>4.33</td>
<td>3.79</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>NDI</td>
<td>Cl$^-$</td>
<td>8.76</td>
<td>8.76</td>
<td>8.56</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>8.76</td>
<td>8.76</td>
<td>8.56</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>8.73</td>
<td>8.73</td>
<td>8.56</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

Table S2. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station XB rotaxane 5·A in CDCl$_3$

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ. (triazolium)</th>
<th>% Occ. (NDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triazolium</td>
<td>Cl$^-$</td>
<td>4.18</td>
<td>4.40</td>
<td>4.16</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>4.16</td>
<td>4.37</td>
<td>4.15</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>4.31</td>
<td>4.41</td>
<td>4.15</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>NDI</td>
<td>Cl$^-$</td>
<td>8.76</td>
<td>8.76</td>
<td>8.56</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>8.76</td>
<td>8.76</td>
<td>8.56</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>8.65</td>
<td>8.65</td>
<td>8.56</td>
<td>45</td>
<td>55</td>
</tr>
</tbody>
</table>

$^1$H NMR spectra of the compounds 1·Cl, 1·I, 1·PF$_6$, 2·Cl, 2·I, 2·PF$_6$, 4·Cl, 4·I, 4·PF$_6$, 5·Cl, 5·I, 5·PF$_6$, 6·Cl, 6·I, 6·PF$_6$, 7·Cl, 7·I, 7·PF$_6$ and 8 in 4:1 CDCl$_3$:MeOD gave the following $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were then used to estimate the percentage occupancies of the two station rotaxanes 4·A and 5·A shown in Figure 8 in the main article (Tables S3 and S4).

Table S3. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station HB rotaxane 4·A in 4:1 CDCl$_3$:CD$_3$OD

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ.(triazolium)</th>
<th>% Occ.(NDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triazolium</td>
<td>Cl$^-$</td>
<td>3.92</td>
<td>4.33</td>
<td>3.86</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>4.00</td>
<td>4.35</td>
<td>3.85</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>4.01</td>
<td>4.31</td>
<td>3.86</td>
<td>67</td>
<td>33</td>
</tr>
<tr>
<td>NDI</td>
<td>Cl$^-$</td>
<td>8.69</td>
<td>8.69</td>
<td>8.51</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>8.67</td>
<td>8.70</td>
<td>8.51</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>PF$_6^-$</td>
<td>8.65</td>
<td>8.65</td>
<td>8.51</td>
<td>74</td>
<td>26</td>
</tr>
</tbody>
</table>
Table S4. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station XB rotaxane 5·A in 4:1 CDCl$_3$:CD$_3$OD

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ.(triazolium)</th>
<th>% Occ.(NDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triazolium</td>
<td>Cl$^-$</td>
<td>4.17</td>
<td>4.42</td>
<td>4.17</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Triazolium</td>
<td>I$^-$</td>
<td>4.15</td>
<td>4.39</td>
<td>4.13</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>Triazolium</td>
<td>PF$_6^-$</td>
<td>4.25</td>
<td>4.37</td>
<td>4.14</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>NDI</td>
<td>Cl$^-$</td>
<td>8.70</td>
<td>100</td>
<td>0</td>
<td></td>
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<tr>
<td>NDI</td>
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<td>8.70</td>
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<td>NDI</td>
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<td>8.63</td>
<td>63</td>
<td>37</td>
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</tr>
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</table>

$^1$H NMR spectra of the compounds 1·Cl, 1·I, 1·PF$_6$, 2·Cl, 2·I, 2·PF$_6$, 4·Cl, 4·I, 4·PF$_6$, 5·Cl, 5·I, 5·PF$_6$, 6·Cl, 6·I, 6·PF$_6$, 7·Cl, 7·I, 7·PF$_6$ and 8 in 1:1 CDCl$_3$:MeOD gave the following $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were then used to estimate the percentage occupancies of the two station rotaxanes 4·A and 5·A shown in Figure 9 in the main article (Tables S5 and S6).

Table S5. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station HB rotaxane 4·A in 1:1 CDCl$_3$:CD$_3$OD

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ.(triazolium)</th>
<th>% Occ.(NDI)</th>
</tr>
</thead>
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<tr>
<td>Triazolium</td>
<td>I$^-$</td>
<td>4.21</td>
<td>4.36</td>
<td>3.94</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>Triazolium</td>
<td>PF$_6^-$</td>
<td>4.21</td>
<td>4.34</td>
<td>3.95</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>Triazolium</td>
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<td>4.35</td>
<td>3.98</td>
<td>49</td>
<td>51</td>
</tr>
<tr>
<td>NDI</td>
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<td>8.63</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NDI</td>
<td>PF$_6^-$</td>
<td>8.61</td>
<td>8.71</td>
<td>8.55</td>
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<td>NDI</td>
<td>Cl$^-$</td>
<td>8.61</td>
<td>37</td>
<td>63</td>
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<td></td>
</tr>
</tbody>
</table>

Table S6. Tabulated $\delta(H_l)$ and $\delta(H_{e,e'})$ values that were used to estimate the percentage occupancies of the two station XB rotaxane 5·A in 1:1 CDCl$_3$:CD$_3$OD

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>$\delta$(rotaxane)</th>
<th>$\delta$(0% occ.)</th>
<th>$\delta$(100% occ.)</th>
<th>% Occ.(triazolium)</th>
<th>% Occ.(NDI)</th>
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<tr>
<td>Triazolium</td>
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<td>4.40</td>
<td>4.19</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>Triazolium</td>
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<td>4.30</td>
<td>4.40</td>
<td>4.19</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
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<td>8.65</td>
<td>8.71</td>
<td>8.55</td>
<td>60</td>
<td>40</td>
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<tr>
<td>NDI</td>
<td>PF$_6^-$</td>
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<td>37</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NDI</td>
<td>Cl$^-$</td>
<td>8.63</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Part V: X-ray Diffraction

Single crystal X-ray diffraction data for 5·Cl were collected using synchrotron radiation on Beamline I19 at Diamond Lightsource. The diffractometer was equipped with a Cryostream N2 open-flow cooling device, and the data were collected at 100(2) K. Cell parameters and intensity data (including inter-frame scaling) were processed using CrysAlis Pro.

All structures were solved by charge-flipping methods using SUPERFLIP. All structures were refined using full-matrix least-squares on $F^2$ within the CRYSTALS suite. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally visible in the difference map and their positions and displacement parameters were refined using restraints prior to inclusion into the model using riding constraints.

Discussion of Structures

Crystals suitable for X-ray diffraction structural analysis were obtained for the chloride salt of the XB rotaxane 5·Cl by slow evaporation of a solution of the rotaxane in 1:1 CDCl$_3$:CD$_3$OD. All crystals were small and very weakly diffracting; despite the use of synchrotron radiation, diffraction was relatively weak and data were of relatively low quality. Despite this, the structure of the rotaxane, the location of the macrocycle along the two station axle, and the locations of the anion, chloroform and water molecules can be determined unambiguously. The macrocycle can be clearly seen, situated at the iodonitriazolium station with the coordinating chloride anion encapsulated within the rotaxane’s three-dimensional binding cavity. Short contacts between the I···Cl$^-$ (2.987(6) Å) and N–H···Cl$^-$ (2.626(14) Å) indicate strong halogen and hydrogen bonds, respectively, with distances shorter than the sum of the van der Waals’ radii (XB: 80%, HB: 93%), which contribute to the stabilisation of the rotaxane–anion complex.

Areas of diffuse electron density, which appear to result from disordered solvent molecules was present. While one molecule of chloroform and one molecule of water were apparent from the difference map, the remaining diffuse electron density could not be modelled sensibly. Therefore PLATON-SQUEEZE was used to include this electron density in the refinement.

Thermal motion of the stopper-‘Bu groups and the macrocycle polyether part are evident. It was possible to model this motion as positional disorder over two sites. However in some cases, the ellipsoids for the stopper-‘Bu groups are quite large as a result of relatively low quality data. It was necessary to apply restraints to bond lengths and angles, as well as thermal and vibrational ellipsoid parameters of the affected atoms to ensure a chemically sensible refinement.

Accommodating the chloride anion within the rotaxane cavity appears to be quite sterically demanding, causing the polyether-alkene part of the macrocycle to adopt a relatively strained geometry. This appears to force a hydrogen atom from the alkene group and a hydrogen atom from the iodonitriazolium-methyl group close together.

Hydrogen atoms were located from the difference map but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry and $U_{iso}(H)$, after which the positions were refined with riding constraints. Water treatment: the H atoms were located in the difference map near the oxygen atom and refined with soft restraints, whereafter the positions were refined with riding constraints.
References