Chloride Anion Triggered Motion in a Bis-Imidazolium Rotaxane

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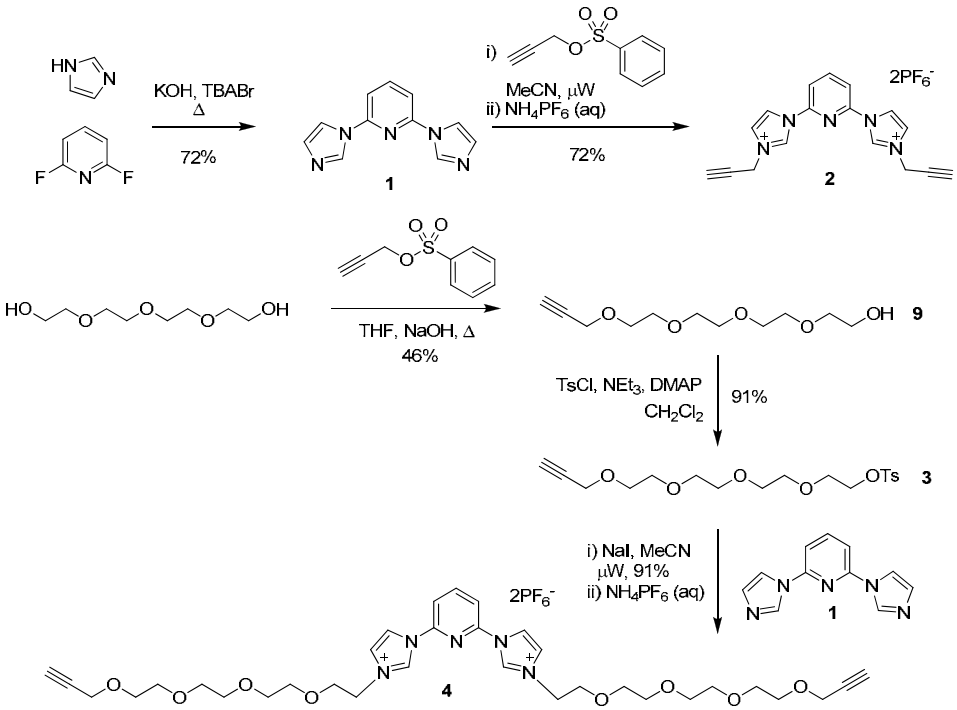
Contents

Synthesis and Characterisation

General Information:

NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^{1}H NMR operating at 300 MHz, and ^{13}C at 75.5 MHz. Mass spectra were recorded on a Bruker micrOTOF spectrometer. H_2O was de-ionised and microfiltered using a Milli-Q ® Millipore machine. All other solvents and commercial grade reagents were used without further purification.



Scheme S1 – Synthesis of threads **2** and **4**

2,6-Bis-imidazolyl-pyridine 1
KOH (5.05 g, 90 mmol), TBA Br (0.44 g, 14 mmol) and imidazole (3.06 g, 45 mmol) were stirred together for fifteen minutes in solventless conditions. 2,6-Difluoropyridine (1.9 ml, 21 mmol) was added to the reaction mixture which was then heated for two hours at 100 °C under an atmosphere of N_2. The resulting solid was left to cool and EtOH (50 ml) was added and the suspension was stirred for five minutes. The mixture was filtered under suction and the solvent removed *in vacuo*. Purification was achieved by column chromatography using silica gel eluted with ethyl acetate. The final product was afforded as a white solid in 72 % yield. ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) 8.67 (2H, s, Im*H*), 8.13 (2H, t, ^{3}J = 8.1 Hz, Py*H*), 8.00 (2H, s, Im*H*), 7.67 (2H, d, ^{3}J = 8.1 Hz, Py*H*), 7.18 (2H, s, Im*H*); ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 147.9, 142.7, 135.2, 129.3, 116.5, 110.1; HR-ESMS: *m/z* calc. for $[M]^+$ 211.0858, found 211.0858.

Short 2,6-bis-imidazoliumpyridine thread 2
2,6-Bis-imidazolyl-pyridine **1** (0.2 g, 1.0 mmol), propargyl benzenesulphonate (1.5 ml) and TBA I (0.71 g, 1.9 mmol) were dissolved in MeCN (20 ml) and heated under microwave irradiation at 160 °C for ten minutes in a sealed vial. The solvent was evaporated to afford a brown oil that was re-dissolved in H_2O (50 ml). The aqueous layer was twice extracted with CH_2Cl_2 (50 ml), and the organic layers were discarded. Addition of NH_4PF_6 (aq) to the aqueous layer resulted in the formation of a fine precipitate which was isolated by filtration, giving the product as a yellow powder in 72 % yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 10.35 (2H, s, Im*H*), 8.80 (2H, s, Im*H*), 8.60 (1H, t, ^{3}J = 8.0 Hz, Py*H*), 8.25 (2H, d, ^{3}J = 8.0 Hz, Py*H*), 8.19 (2H, s, Im*H*), 5.33 (4H, d, ^{4}J = 2.5 Hz, CH_2), 3.95 (2H, t, ^{4}J = 2.5 Hz, C≡C*H*); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 145.6, 145.3, 136.5, 124.0, 120.4, 115.3, 80.0, 76.1, 40.0 HR-ESMS: *m/z* calc. for $[M - PF_6]^+$ 434.0964, found 434.0950; Elem. Anal. Calculated for $C_{17}H_{15}F_{12}N_5P_2$ C 35.25% H 2.61% N 12.09%., found C 35.21% H 2.74% N 12.12%; mp 204 °C.

Propargyloxy-tetra-ethylene glycol 9
Tetraethyleneglycol (3.56 ml, 21 mmol), NaOH (0.99 g, 25 mmol) and propargyl benzenesulphonate (2.74 ml, 21 mmol) were added to dry THF (100 ml) and the mixture was refluxed for 3 hours. After allowing the mixture to cool, the solution was filtered and the solvent evaporated to leave a mixture of mono- and bis-substituted products. The bis-substituted product was extracted from water with toluene (2 x 50 ml) and the mono-substituted product was extracted with CH_2Cl_2 (8 x 50 ml). The organic fractions were combined and dried over $MgSO_4$, filtered and the solvent removed to afford a yellow oil in 46 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.18 (2H, d, ^{4}J = 2.4 Hz, C≡CCH_2), 3.57-3.72 (16H, m, OCH_2), 2.42 (1H, t, ^{4}J = 2.4 Hz, C≡C*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 79.6, 74.6, 72.5, 70.6, 70.5, 70.4, 70.3, 70.0, 69.1, 61.7, 58.4; HR-ESMS: *m/z* calc. for $[M+Na]^+$ 255.1208, found 255.1208.

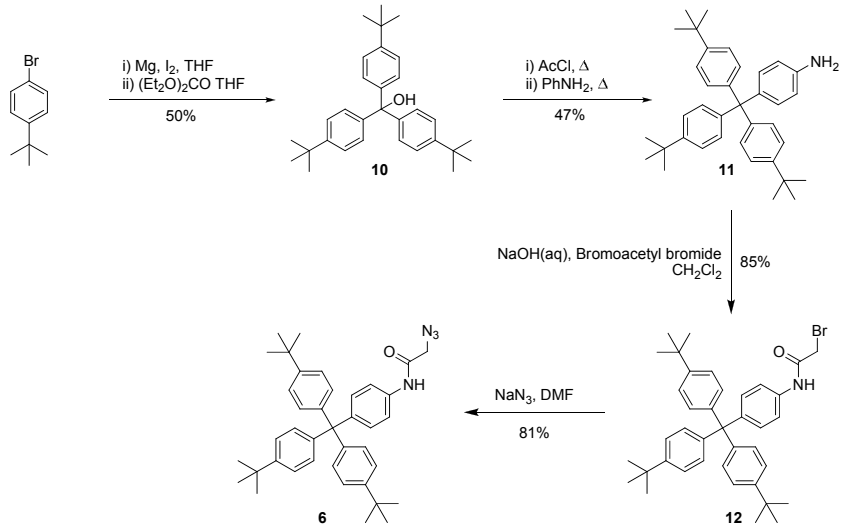
Tosyl-propargyloxy-tetra-ethylene glycol 3
To a stirring solution of propargyloxy-tetra-ethylene glycol **9** (2.75 g, 12 mmol), tosyl chloride (1.85 g, 7.9 mmol), Et_3N (10 ml) in dry CH_2Cl_2 (50 ml) DMAP (catalytic) was added and the solution was refluxed under N_2 for 16 hours. After allowing the solution to cool H_2O (50 ml) was added and the aqueous layer was neutralised with 10 % citric acid solution. The organic layers were washed with H_2O (2 x 50 ml) and brine (50 ml) before being dried with $MgSO_4$ and filtered. Evaporation of the solvent afforded a yellow oil in 91 % yield. ^{1}H NMR

(300 MHz, $CDCl_3$) δ (ppm) 7.73 (2H, d, ^3J = 8.1 Hz, Ar*H*), 7.27 (2H, d, ^3J = 8.1 Hz, Ar*H*), 4.18 (2H, d, ^4J = 2.4 Hz, C≡CCH_2), 4.09 (2H, t, ^3J = 4.7 Hz, TsOCH_2) 3.61-3.70 (14H, m, OCH_2) 2.42 (1H, t, ^4J = 2.4 Hz, C≡C*H*), 2.38 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 144.8, 132.8, 129.8, 127.9, 79.6, 74.6, 70.6, 70.5, 70.4, 70.3, 69.3, 69.2, 68.6, 61.6, 58.3, 21.6; HR-ESMS: *m/z* calc. for $[M + Na]^+$ 409.1297, found 409.1285.

Long 2,6-bis-imidazolium-pyridine thread 4

2,6-Bis-imidazolyl-pyridine **1** (0.05 g, 0.24 mmol), **3** (0.93 g, 2.4 mmol) and NaI (0.07 g, 0.48 mmol) were dissolved in MeCN (10 ml) and heated under microwave conditions for 20 minutes at 170 °C. A brown oil was produced upon evaporation of the solvent which was then subsequently dissolved H_2O (15 ml). This was washed with CH_2Cl_2 (2 x 15 ml) and the organic layers were discarded. Addition of saturated NH_4PF_6 (aq) to the aqueous layer produced a brown oil which was precipitated from hot MeOH to afford the pure product as a pale oil in 91% yield. ^{1}H NMR (500 MHz, CD_3CN) δ (ppm) 9.67 (2H, s, Im*H*), 8.46 (2H, t, ^3J = 8.2 Hz, Py*H*), 8.25 (2H, m, Im*H*), 7.98 (2H, d, ^3J = 8.2 Hz, Py*H*), 7.18 (2H, m, Im*H*), 4.48 (8H, t, ^3J = 4.7 Hz, NCH_2CH$_2$O), 4.07 (4H, d, ^4J = 2.6 Hz, C≡CCH_2) 3.93 (4H, t, ^3J = 4.7 Hz, NCH$_2$CH_2O), 3.55-3.70 (24H, m, OCH$_2$CH$_2$O), 2.68 (2H, t, ^4J = 2.6 Hz, C≡CH); ^{13}C NMR (75 MHz, CD_3CN) δ (ppm) 145.4, 136.9, 125.0, 119.7, 118.0, 115.6, 80.3, 75.3, 70.4, 69.4, 68.3, 58.2, 51.0 HR-ESMS: *m/z* calc. for $[M]^{2+}$ 320.6707, found 320.6704; Elem. Anal. calc. for $C_{33}H_{47}F_{12}N_5O_8P_2$ C 42.54 % H 5.08 % N 7.52 %, found C 41.42 % H 4.54 % N 7.87 %.

Macrocycle **5** was synthesised as previously reported.[1]



Scheme S2 – Synthesis of azide stopper **6**.

Tris(*p*-*tert*-butylphenyl)methanol 10[2]

Magnesium turnings (2.00 g, 82 mmol) were heated under an atmosphere of nitrogen at 100 ºC for 24 hours. After cooling, dry THF (5 ml) was added along with a catalytic amount of iodine. A 5 ml aliquot of a solution of 4-(*tert*-butyl)bromobenzene (14.63 g, 65.8 mmol) in dry THF (30 ml) was added to the Grignard reagent and the reaction was observed to progress through vigorous reaction and the loss of iodine colouration. The remaining solution was added slowly over 20 minutes and kept under reflux without heating. The resulting mixture was stirred for a further 2 hours. A solution of diethyl carbonate (2.7 ml, 21.9 mmol) in dry THF (3 ml) was then added drop-wise over 20 minutes and the mixture was stirred for 12 hours. The orange suspension was then acidified to pH 7 with careful addition of aqueous 1M HCl (aq) solution. H_2O (80 ml) was added and the resulting mixture extracted with CH_2Cl_2 (2 x 100 ml). The organic phases were combined, washed with H_2O (3 x 100 ml) and dried over $MgSO_4$. Filtration and solvent removal yielded a green solid, which after recrystallisation from hot hexane, produced tris(p-tert-butylphenyl)methanol **10** as a white solid in 50 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.32 (6H, d, ^3J = 7.9 Hz, Ar*H*), 7.19 (6H, d, ^3J = 7.9 Hz, Ar*H*), 2.98 (1H, s, O*H*), 1.27 (27H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 149.8, 144.2, 127.5, 124.5, 81.5, 34.3, 31.3; HR-ESMS: *m/z* calc. for $[M]^+$ 428.3079, found 428.3069; mp 168 °C.

(*p*-Aminophenyl)tris(*p*-*tert*-butylphenyl)methane 11[2]

Tris(*p*-*tert*-butylphenyl)methanol (5.09 g, 0.012 mmol) was heated under reflux with acetyl chloride (30 ml) overnight. Once the reaction mixture had cooled to room temperature excess acetyl chloride was removed *in vacuo* to give a pale yellow solid. Aniline (30 ml) was subsequently added and the reaction mixture heated at 105 ºC for 48 hours. Upon cooling to room temperature the reaction mixture was poured onto rapidly stirring 1M HCl (aq) solution (300 ml) and stirred for a further 20 minutes. The resulting precipitate was filtered and washed with 1M K_2CO_3 (aq) solution. Recrystallisation from hot MeOH yielded the amine **11** as a white solid in 47 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.14 (6H, d, ^3J = 8.5 Hz, Ar*H*), 7.02 (6H, d, ^3J = 8.5 Hz, Ar*H*), 6.93 (2H, d, ^3J = 8.2 Hz, NH$_2$Ar*H*), 6.56 (2H, d, ^3J = 8.2 Hz, NH$_2$Ar*H*), 5.35 (2H, s, NH_2), 1.30 (27H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 148.7, 143.8, 142.8, 132.1, 130.7, 125.1, 114.5, 63.3, 34.3, 31.1; HR-ESMS: *m/z* calc. for $[M + H]^+$ 504.3625, found 504.3610; mp 268 °C.

Bromide functionalised stopper 12

Amine **11** (1.5 g, 3.41 mmol) was dissolved in a bi-phasic mixture of CH_2Cl_2 (25 ml) and NaOH (aq) (2 ml, 1.25 M) and the solution was stirred vigorously for 10 minutes. Bromoacetyl bromide (0.89 g, 4.43 mmol) was dissolved in CH_2Cl_2 (20 ml) and added dropwise into this bi-phasic mixture over 15 minutes with the solution being stirred overnight under a nitrogen atmosphere. The solution was then added to H_2O (10 ml) and the layers separated. The organic layer was washed with H_2O (2 x 10 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to leave **12** a white solid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.01 (1H, s, CON*H*), 7.41 (2H , d, ^3J = 7.9 Hz, NHAr*H*), 7.10-7.22 (10H, m, NHAr*H*, Ar*H*), 7.00 (4H, d, ^3J = 8.5Hz, Ar*H*) 3.93 (2H, s, CH_2) 1.22 (27H, s, CH_3); ^{13}C NMR (75 MHz,

$CDCl_3$) δ (ppm) 163.2, 148.4, 144.5, 143.7, 134.4 131.9, 130.9, 124.7 118.7, 63.3, 34.4, 31.2, 29.5; HR-ESMS: *m/z* calc. for $[M + Na]^+$ 646.2660, found 646.2643; mp 255 °C (decomp.).

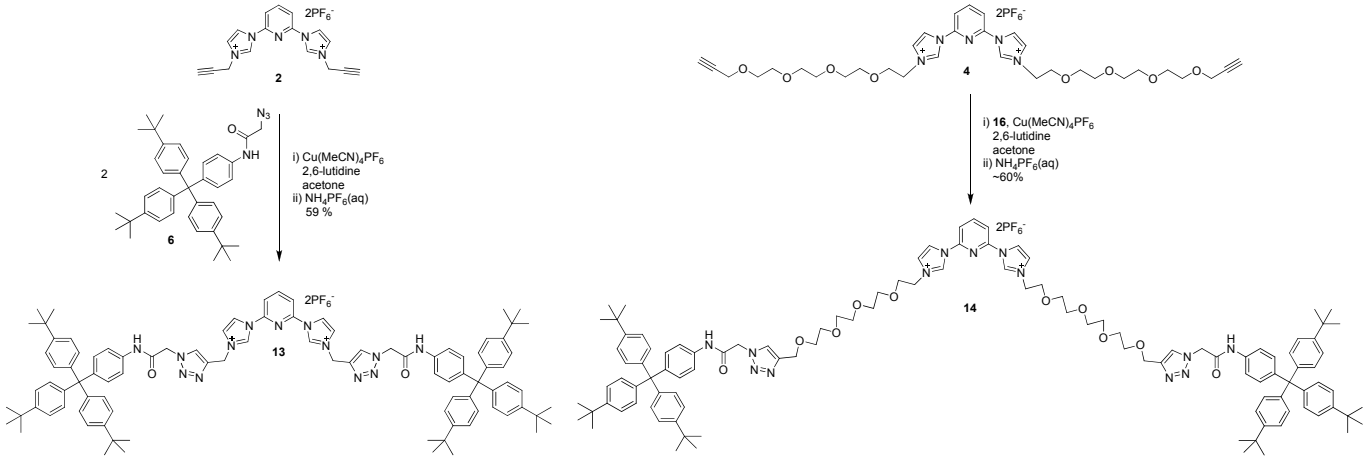
Azide functionalised stopper 6

Compound **12** (1.11 g, 1.9 mmol) and NaN_3 (1.00 g, 9.5 mmol) were dissolved in DMF (50 ml) and stirred overnight under a nitrogen atmosphere. The solvent was removed under reduced pressure and the resulting residue dissolved in Et_2O (50 ml). The solution was washed with H_2O (2 x 100 ml) and the organic layers separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed to leave the product as a pale yellow solid in 81 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.98 (1H, s, CON*H*), 7.40 (2H, d, ^{3}J = 8.8 Hz, NHAr*H*), 7.24 (6H, d, ^{3}J = 8.5 Hz, Ar*H*), 4.15 (2H, s, CH_2), 7.19 (2H, d, ^{3}J = 8.8 Hz, NHAr*H*), 7.09 (6H, d, ^{3}J = 8.5 Hz, Ar*H*), 1.26 (27H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.7, 148.4, 144.3, 143.7, 134.2 131.9, 130.7, 124.1, 118.8, 63.3, 53.0, 34.3, 31.4; HR-ESMS: *m/z* calc. for $[M + Na]^+$ 609.3569, found 609.3557; Elem. Anal. calc. for $C_{39}H_{46}N_4O$ C 79.82 % H 7.90 % N 9.55 %, found C 78.82 % H 7.91 % N 9.15 %; mp > 200 °C.

$Cu(MeCN)_4PF_6$.

Aqueous HPF_6 (113 mmol) was added in 2 ml portions to a stirred suspension of CuO (4.0 g, 28 mmol) in MeCN (125 ml). The solution was stirred for 3 minutes and then filtered to remove undissolved black solid. The pale blue filtrate was cooled to -20 °C for several hours, where upon a white precipitate of $Cu(MeCN)_4PF_6$ formed. The solid was collected by filtration and redissolved in MeCN (100 ml). A small amount of Cu^{2+} remained undissolved, which was then removed by filtration. Et_2O (100 ml) was added to the light blue filtrate and the mixture was allowed to stand for several hours at -20 °C. The required product precipitated as a white solid and was washed with Et_2O before being dried *in vacuo*. The complex was isolated in 74 % yield. Elem. Anal. Calculated for $C_8H_{12}CuF_6N_4P$ C 25.78 % H 3.25 % N 15.03 %, found C 24.37 % H 3.20 % N 13.99 %; IR (cm^{-1}) 2953, 2925, 2854, 1462, 1377, 843, 722.

Stoppered axles were prepared in order to establish a working protocol for the azide-alkyne cycloaddition (Scheme S3)



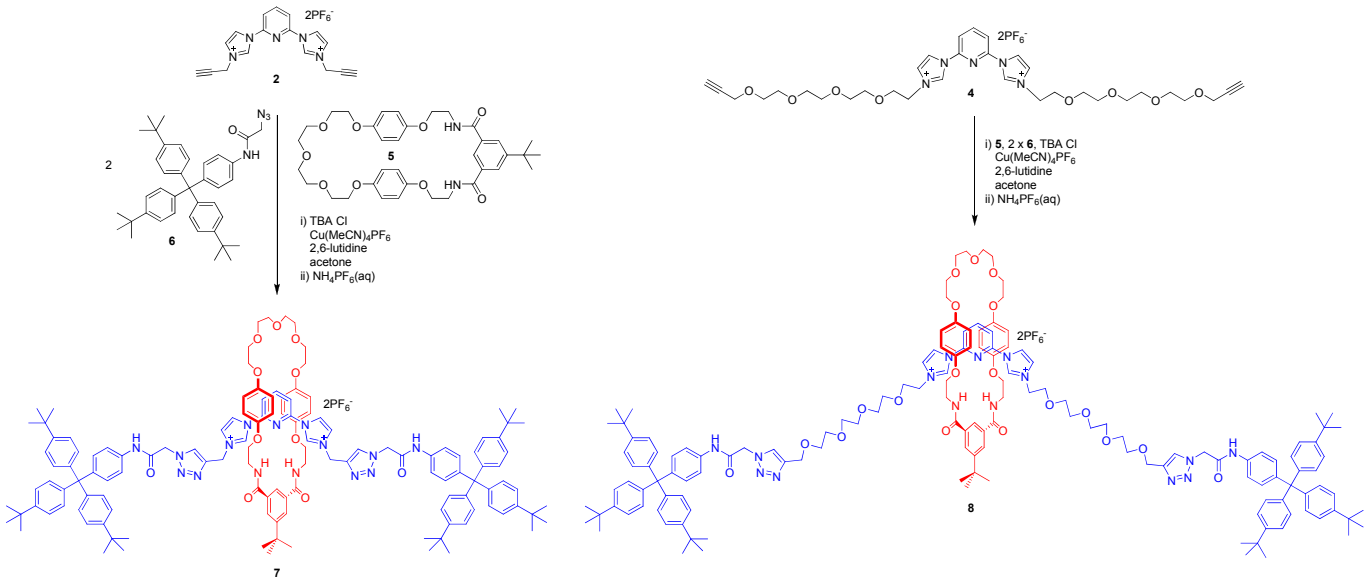
Scheme S3 – Synthesis of stoppered axles **13** and **14**.

Stoppered short 2,6-bis-imidazolium-pyridine axle 13.

Compound **2** (0.136 g, 0.235 mmol) was dissolved in dry acetone (10 ml) and sequentially $CuPF_6(MeCN)_4$ (0.018 g, 0.047 mmol), 2,6-lutidine (0.05 g, 0.47 mmol) and azide functionalised stopper **6** (0.275 g, 0.47 mmol) were added to this solution. The solution was left to stir under a N_2 atmosphere for 24 hours. Progress of the reaction was monitored by TLC in $MeCN/H_2O/KNO_3$ (aq, sat.) (17:2:1). Incomplete removal of starting materials was resolved by the addition of $CuPF_6(MeCN)_4$ (0.018 g, 0.047 mmol) and allowing a further 24 hours stirring. This procedure was repeated until all starting materials were removed. Upon evaporation of the solvent the remaining solid was washed with Et_2O (10 ml) and purified by silica gel chromatography eluted with $MeCN/H_2O/KNO_3$ (aq, sat.) (17:2:1). The solvent was reduced to a volume of *ca*. 5 ml, followed by precipitation of the product with NH_4PF_6 (aq, sat.). Isolation of the product by filtration afforded a white solid in 59 % yield. ^{1}H NMR (500MHz, acetonitrile-d_3) δ (ppm) 10.11 (2H, s, Im*H*), 8.91 (2H, s, CON*H*), 8.43 (1H, t, ^{3}J = 8.3 Hz, Py*H*), 8.22 (4H, m, Im*H*, Trz*H*), 7.95 (d, ^{3}J = 8.3 Hz, Py*H*), 7.77 (2H, s, Im*H*), 7.45 (2H, d, ^{3}J = 9.3 Hz, Ar*H*N), 7.34 (6H, d, ^{3}J = 8.8 Hz, Ar*H*), 7.24 (2H, d, ^{3}J = 9.3 Hz, Ar*H*N), 7.20 (6H, d, ^{3}J = 8.79 Hz, Ar*H*) 5.71 (4H, s, ImCH_2), 5.28 (4H, s, COCH_2), 1.27 (27H, s, CH_3); ESMS: *m/z* calc. for $[M]^{2+}$ 730.93, found 730.92.

Stoppered long 2,6-bis-imidazolium-pyridine axle 14.

Compound **4** (0.219 g, 0.235 mmol) was dissolved in dry acetone (10 ml). The remaining synthetic procedure was identical to that used in the synthesis of **13**, with the final product being isolated as an impure brown solid. MALDI-MS *m/z* calc. for $[M - PF_6^-]^+$ 1959.04, found 1958.76 calc. for $[M - H]^-$ 2103.00, found 2102.79.



Scheme S4 – Synthesis of rotaxanes **7** and **8**.

Rotaxane 7

Macrocycle **7** (0.03 g, 0.046 mmol), TBA Cl (0.013 g, 0.046 mmol) and bis-imidazolium thread **9** (0.027 g, 0.046 mmol) were dissolved in acetone (15 ml) and left to stir for 20 minutes to allow pseudorotaxane equilibriation. Sequentially $CuPF_6(MeCN)_4$ (0.004 g, 0.0092 mmol), 2,6-lutidine (11 µl, 0.092 mmol) and azide stopper **11** (0.054 g, 0.092 mmol) were added, with the reaction being left to stir overnight under a N_2 atmosphere. Reaction progress was monitored by TLC eluted with 17:2:1 $MeCN/H_2O/KNO_3$ (aq, sat.). Incomplete removal of starting materials was resolved by the addition of $CuPF_6(MeCN)_6$ (0.0035 g, 0.0092 mmol) and leaving the reaction mixture to stir overnight. This procedure was repeated until all starting materials were removed. Purification was attempted through preparatory TLC eluted with 17:2:1 $MeCN/H_2O/KNO_3$ (aq, sat.). Reduction of the solvent to *ca*. 10 ml was followed by the addition of NH_4PF_6 (aq, sat.), giving the product, albeit with significant levels of impurity. The ^{1}H NMR spectrum revealed resonances which corresponded to a downfield shift of the stopper α-CH_2 protons and the appearance of the diagnostic triazole proton at 8.2 ppm, as well as peaks corresponding to the macrocycle. However, mass spectroscopy could did not show evidence for **7**, and furthermore recollection of the ^{1}H NMR spectrum after a week revealed that decomposition was occurring.

Rotaxane 8

The procedure adopted was analogous to that for the synthesis of **19** (chloride templated), using acetone (15 ml), macrocycle **7** (0.03 g, 0.046 mmol), TBA Cl (0.013g, 0.046mmol), bis-imidazolium thread **12** (0.043 g, 0.046 mmol), $CuPF_6(MeCN)_4$ (0.0035 g, 0.0092 mmol), 2,6-lutidine (11 µl, 0.092 mmol) and azide stopper **16** (0.054 g, 0.092 mmol). The product was isolated as a brown solid in 12 % yield. ^{1}H NMR (500 MHz, CD_3CN) δ (ppm) 9.81 (s, 2H, Im*H*), 9.14-9.12 (s, 4H, N*H* stopper, N*H* macrocycle), 8.26 (t, ^{3}J = 8.1 Hz, 2H, Py*H*), 8.17 (s, 2H, Trz*H*), 8.07 (2H, s, Ar*H* macrocycle), 7.93 (1H, s, Ar*H* macrocycle), 7.85 (2H, d, ^{3}J = 8.1 Hz, Py*H*), 7.78 (2H, s, Im*H*), 7.70 (2H, s, Im*H*), 7.42 (4H, d, ^{3}J = 8.8 Hz, NHAr*H* *s*topper), 7.35 (4H, d, J = 8.8 Hz, NHAr*H* *s*topper), 7.32 (12H, d, ^{3}J = 8.6 Hz, Ar*H* stopper), 7.19 (12H, d, ^{3}J = 8.6 Hz, Ar*H* stopper), 6.86 (4H, d, ^{3}J = 9.2 Hz, HQ*H*), 6.83 (4H, d, ^{3}J = 9.2 Hz, HQ*H*), 5.18 (s, 4H, $COCH_2$, stopper) 4.48 (s, 4H, OCH_2Trz), 4.39 (4H, t, ^{3}J = 4.4 Hz, ImCH_2), 4.10 (4H, t, ^{3}J = 5.2 Hz, NHCH_2 macrocycle), 4.00 (4H, t, ^{3}J = 4.4 Hz, OCH_2 macrocycle), 3.86 (4H, t, ^{3}J = 4.8 Hz, OCH_2 thread), 3.75 (8H, m, OCH_2 macrocycle), 3.65-3.52 (16H, m, OCH_2CH_2O), 1.26 (63H, s, CH_3); ^{13}C NMR (125 MHz, CD_3CN) δ (ppm) 166.9, 164.3, 153.1, 152.3, 148.6, 145.5, 145.4, 144.8, 144.3, 143.6, 135.7, 135.7, 135.6, 134.6, 131.1, 127.5, 125.3, 125.2, 124.6, 124.6, 124.4, 122.1, 119.1, 119.0, 118.9, 118.8, 70.3, 70.3, 70.1, 70.0, 69.9, 69.8, 69.6, 69.4, 67.9, 67.0, 63.6, 63.4, 52.4, 50.4, 39.5, 34.7, 34.0, 30.6, 30.4; ESMS: *m/z* calc. for $[M]^{2+}$ 1232.20, found 1232.18.

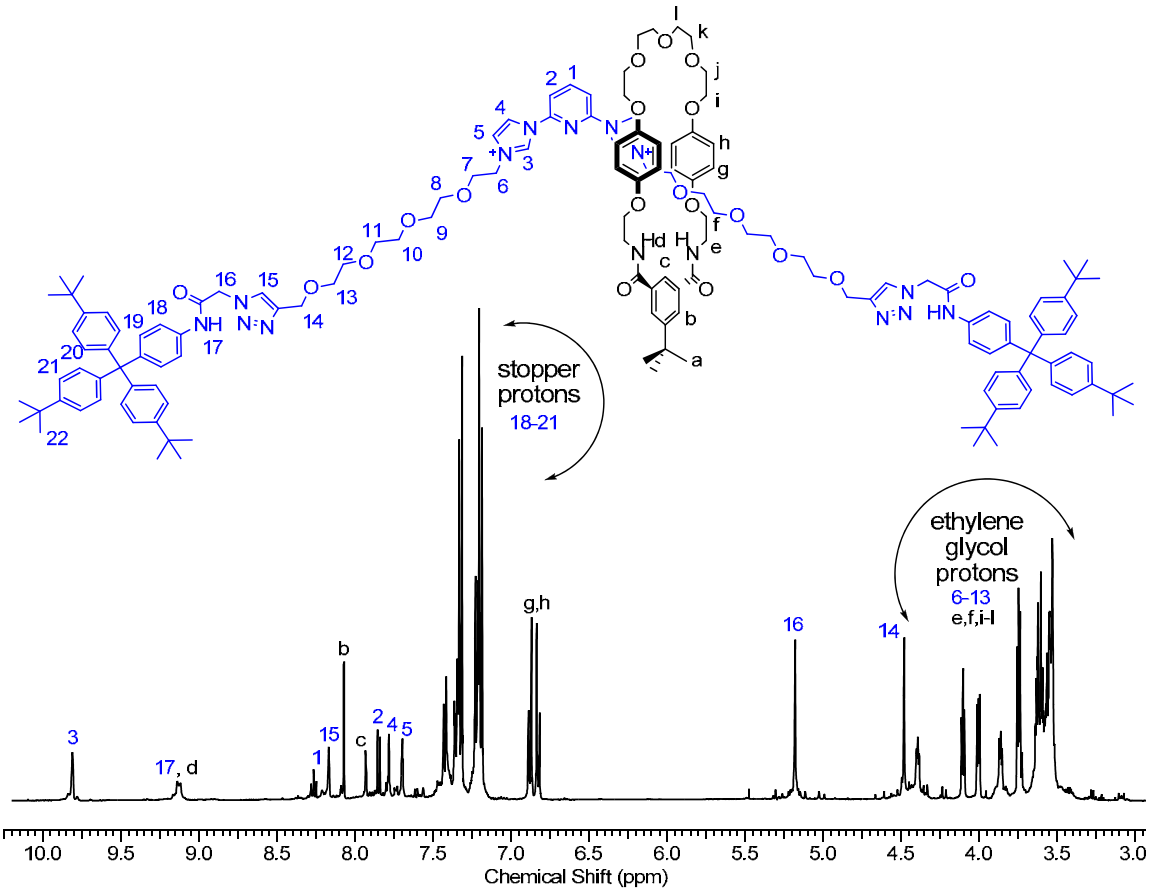


Figure S1 – Assigned 1H NMR spectrum of rotaxane **8** (acetonitrile-d_3, 293K).

Crystallography

Single crystals of thread **2** were grown by slow diffusion of diisopropyl ether into an acetonitrile solution of **2**. Single crystal X-ray diffraction data were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer, equipped with a Cryostream N_2 open-flow cooling device,[3] and the data were collected at 150(2) K or 100(2) K. A series of ω-scans were performed in such a way as to collect every independent reflection to a maximum resolution of 0.77 Å, aiming for 99.5 % completeness. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.[4]
The structures were solved by direct methods using the SIR92 software.[5] The structure was refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters, unless specified otherwise. Disordered hexafluorophosphate anions were modelled using refined partial occupancies. The H atoms were located in 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 (C-H in the range 0.93-0.98 Å and isotropic displacement factors in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions constrained using rides. Selected crystallographic data are presented in Table S1. Full details can be found in the .cif online.

Figure S2 – Crystal structure of 2, showing thermal ellipsoids at 50% probability.

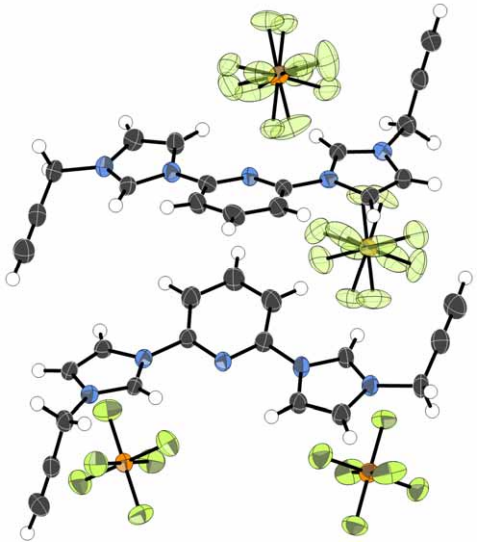


Table S1 Selected crystallographic data for thread **2**.

Compound reference	5782
Chemical formula	$C_{17}H_{15}N_5$•2(F_6P)
Formula Mass	579.27
Crystal system	Triclinic
a/Å	8.1846(2)
b/Å	15.6823(4)
c/Å	18.6804(6)
α/°	106.1594(12)
β/°	101.0415(11)
γ/°	91.8678(13)
Unit cell volume/Å^3	2250.93(11)
Temperature/K	150
Space group	$P\bar{1}$
No. of formula units per unit cell, *Z*	4
No. of reflections measured	34026
No. of independent reflections	10185
R_{int}	0.068
Final R_1 values ($I > 2\sigma(I)$)	0.0495
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1145
Final R_1 values (all data)	0.0797
Final $wR(F^2)$ values (all data)	0.1288

NMR Studies

^{1}H NMR titrations were performed using a Varian Unity Plus 500 spectrometer. A solution of the intended guest species (10^{-5} mol in 0.10 ml solvent) was added in a stepwise fashion to a solution of macrocycle **5** (10^{-6} mol in 0.50 ml solvent) at 293 K. Spectra were measured and chemical shifts recorded at 22 titration points (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents of guest to host). Data from the titrations was used in Job plot-type analyses.[7] These plot χ_H against $\chi_H.\Delta\delta$, where $\Delta\delta$ is the difference between the observed chemical shift of a specific proton and the chemical shift of the pure host, and χ_H is the mole fraction. The binding stoichiometry can then be inferred from the position of the maximum. The resulting titration data, along with the binding stoichiometry and estimates of binding constants and final chemical shifts, were entered into the WinEQNMR2[8] programme to obtain stability constants. Iterations were then performed to provide the most accurate result.

Firstly, TBA chloride was titrated into macrocycle **5** in order to gauge its anion coordination ability in the absence of threading components. The spectra and analysis are given in Fig. S3 and an equilibrium constant of 2369 (28) mol^{-1} dm^3 was obtained.

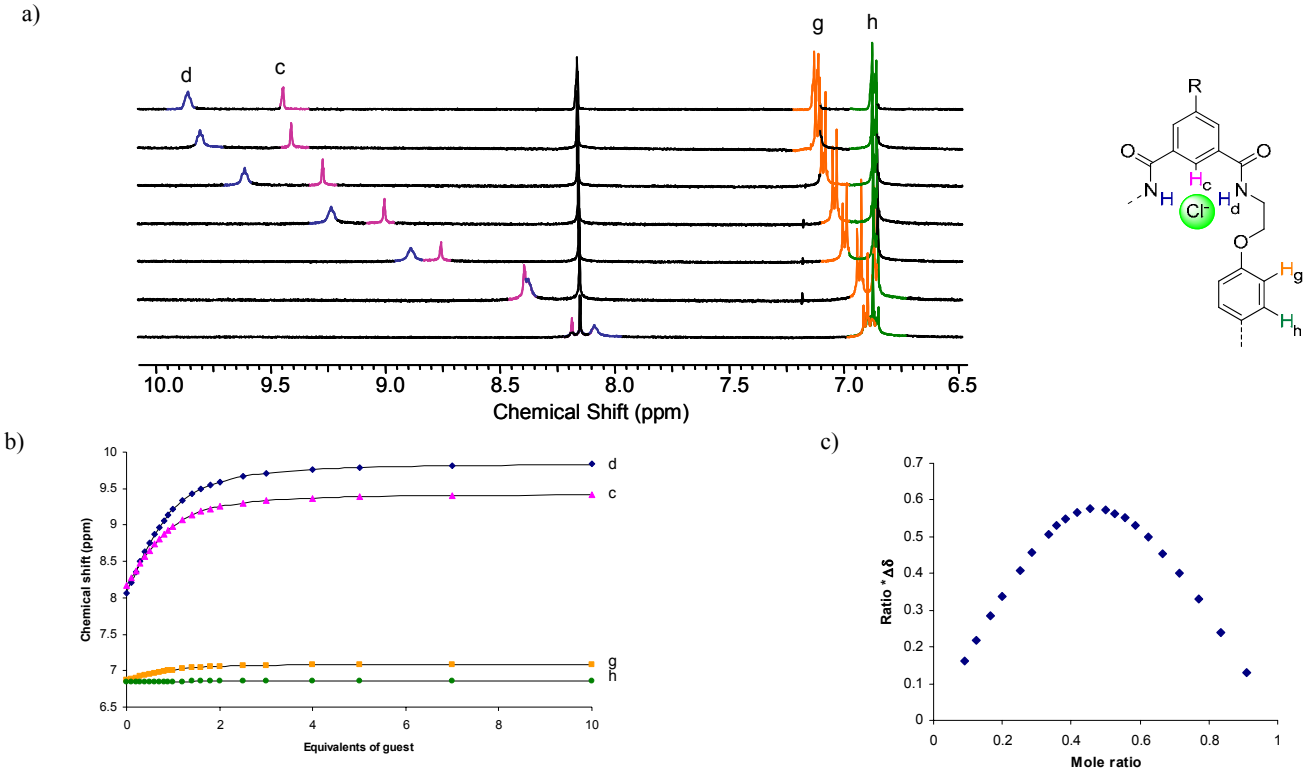


Figure S3 – ^{1}H NMR peak perturbations of macrocycle **5** for the addition of TBA chloride in acetone-d_6. Coloured points designate the proton resonances as indicated. Black lines, where present, represent the binding curves fitted using WinEQNMR2.

Subsequently, hexafluorophosphate threading components 2 and 4 were added to a 1:1 solution of **5** and TBA Cl, resulting in upfield shifts of the hydroquinone (H_g and H_h) and amide (H_d) proton peaks (Fig. S4).

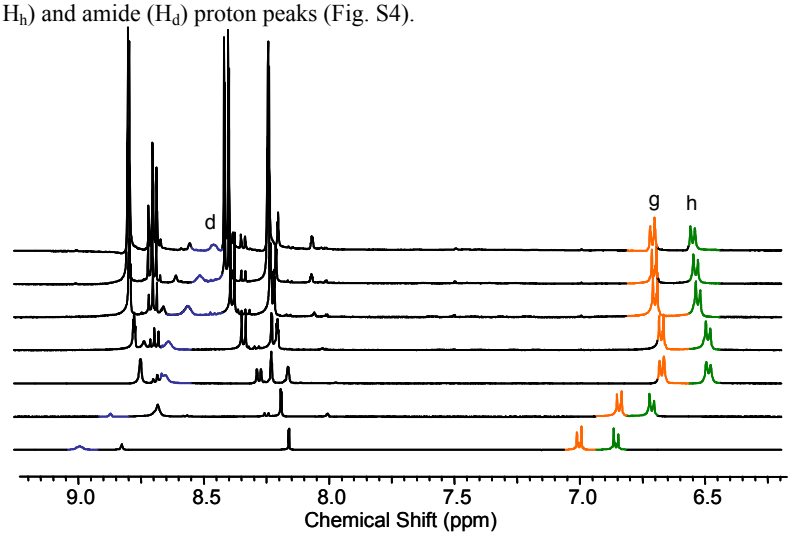


Figure S4 –^{1}H NMR titration of **2** into **5**.Cl$^-$ in acetone-d_6, 293 K. Spectra shown at (bottom to top) 0, 0.2, 0.6, 1.0, 2.0, 5.0 and 10.0 equivalents of **2**.

Although apparently association constants of > 10^4 mol^{-1} dm^3 were obtained, the total peak shift relative to **5** is informative (Table S2).

	5.Cl^-	**5.2**.Cl^-	**5.4**.Cl^-
Acetone-d_6	+0.103, -0.004	-0.224, -0.371	-0.272, -0.399
Acetonitrile-d_3	+0.008, -0.008	-0.200, -0.323	-0.302, -0.421

Table S2 – $\delta\Delta_{1eqv}$ of the hydroquinone protons H_g and H_h of macrocycle **5**-based assemblies

^{1}H ROESY spectroscopy (using the Varian Unity Plus 500 spectrometer) was used to examine through-space interactions in a 1:1:1 mixture of **2**, **5**, and TBA Cl in acetone-d_6. Strong dipolar through-space interactions were observed between the hydroquinone protons on **5** and all three imidazolium protons and the 3,5 pyridine protons of **2** (Fig. S5). This is highly indicative of interpenetration of **2** through **5**.

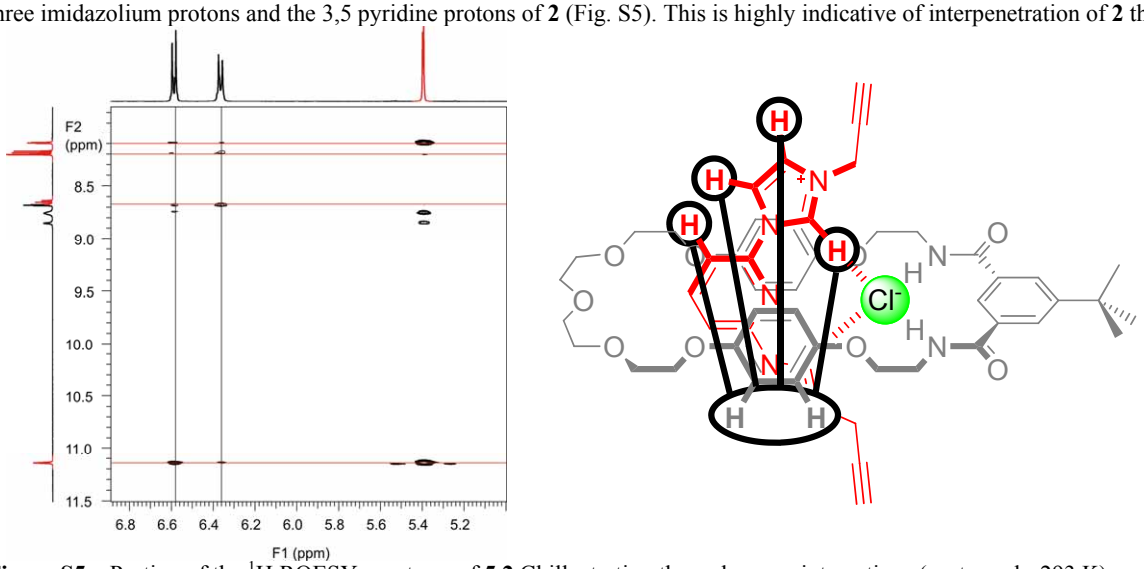


Figure S5 – Portion of the ^{1}H ROESY spectrum of **5.2**.Cl illustrating through-space interactions (acetone-d_6, 293 K)

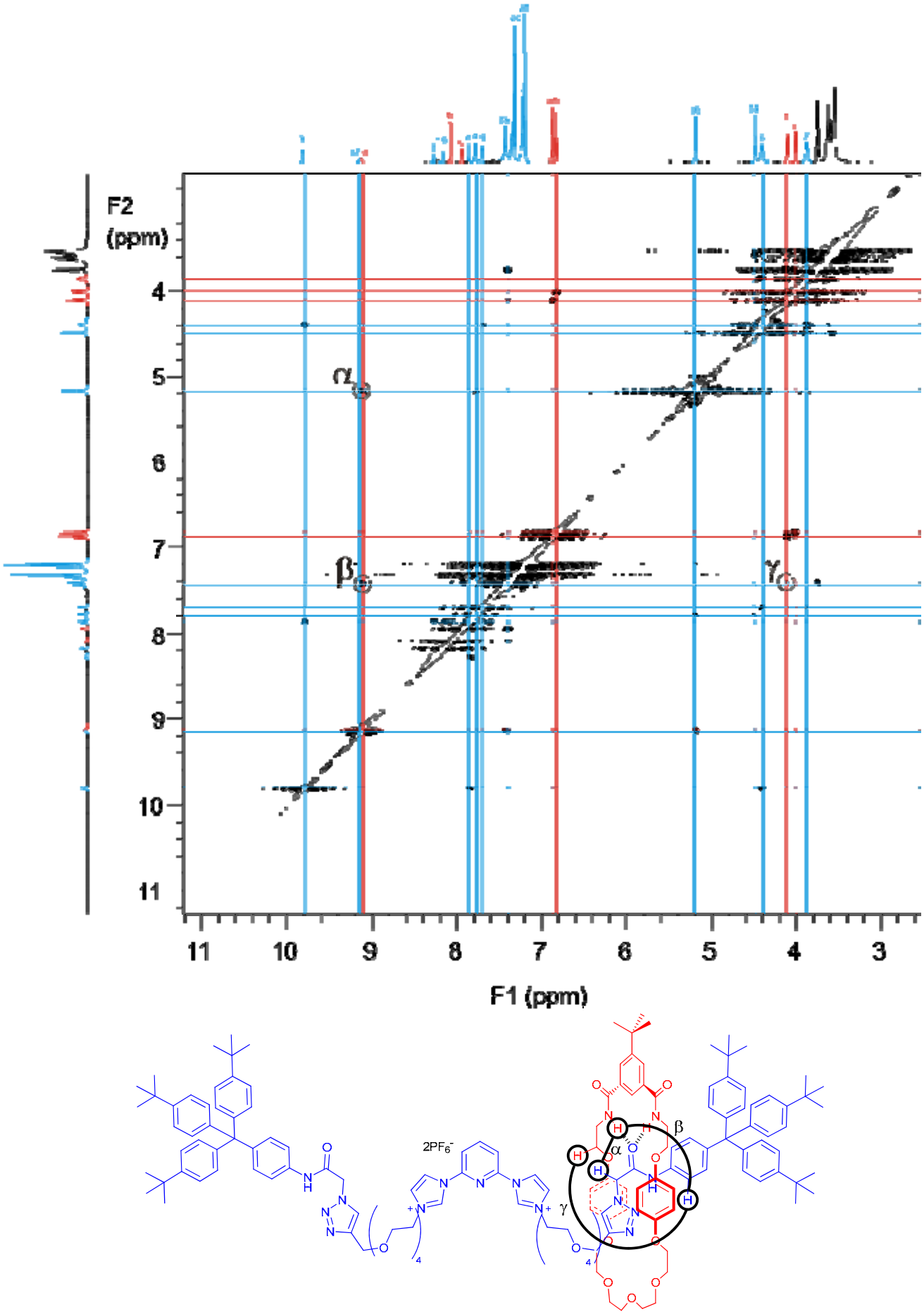


Figure S6 – ^{1}H ROESY spectrum of **8** illustrating relevant through-space interactions (acetone-d_6, 293 K). The area below 3 ppm is swamped by the methyl, solvent, and water peaks.

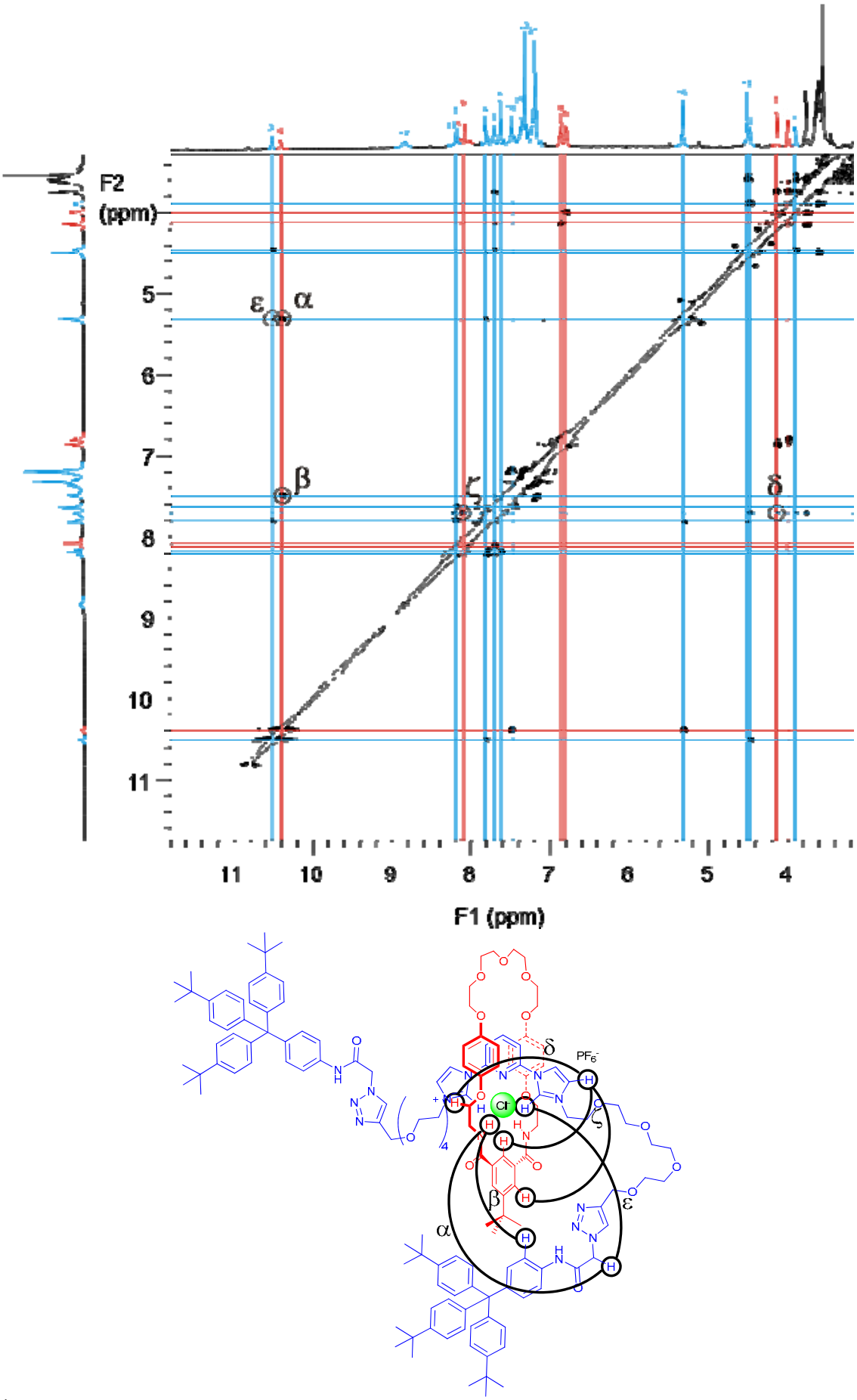


Figure S7 – ^{1}H ROESY spectrum of **8** + TBACl illustrating relevant through-space interactions (acetone-d_6, 293 K). The area below 3 ppm is swamped by the methyl, solvent, and water peaks.

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