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Contrasting anion recognition behaviour exhibited by halogen and hydrogen bonding rotaxane hosts†

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A rotaxane host system containing a novel halogen bonding (XB) 5-iodo-1,2,3-triazole functionalised pyridinium motif, within its axle component, has been prepared *via* a ring closing metathesis reaction, using chloride as a template. Proton NMR titration experiments, in competitive 1 : 1 $CDCl_3$–CD_3OD solvent media, showed the XB rotaxane selectively bound halides over larger, more basic oxoanions. An all hydrogen bonding proto-triazole containing rotaxane analogue was also prepared, which in stark contrast demonstrated a reversal in the anion selectivity trend, with a preference for dihydrogen phosphate over the halides which is unprecedented for an interlocked host system.

Introduction

The exploitation of halogen bonding (XB) as a non-covalent interaction in the field of anion recognition chemistry has, until recently, been largely overlooked,[1,2] with the use of hydrogen bonding (HB), Lewis acid–base, anion–π and electrostatic interactions being much more prevalent in anion host design.[3–7] This is somewhat surprising when taking into account the halogen bond's stringent directionality and comparable bond strength to the ubiquitous hydrogen bond.[8,9] Several recent reports have demonstrated how the inclusion of XB donor groups into acyclic and macrocyclic structural frameworks has resulted in host systems that exhibit superior anion recognition behaviour when compared to HB receptor analogues.[10–16] In an effort to overcome the challenge of recognising anions in competitive protic solvent media we have constructed interlocked rotaxane and catenane host structures containing unique three dimensional cavities decorated with an array of convergent HB donors and shown such systems to be effective hosts in solvent media of this nature.[17–20] We have also recently demonstrated how the incorporation of XB donors into such interlocked structures can lead to strong anion binding and selectivity.[21–25] For example, a rotaxane containing a XB 5-iodo-1,2,3-triazolium functionalised axle component binds halides strongly in aqueous solvent media, with a preference for iodide. The HB proto-triazolium analogue was found to bind halides significantly more weakly, displaying selectivity for bromide.[26]

Herein, we report the synthesis of a XB [2]rotaxane host system containing a novel 5-iodo-1,2,3-triazole functionalised pyridinium motif within its axle component, whose anion binding properties are in stark contrast to the HB [2]rotaxane host analogue. The XB interlocked system exhibits selectivity for halides, whereas simply replacing the iodine substituent of the 5-iodo-1,2,3-triazole axle group with a proton results in the HB rotaxane host displaying a selectivity preference for dihydrogen phosphate which is unprecedented for an interlocked host.

Results and discussion

Synthesis of iodo-triazole and proto-triazole functionalised pyridinium axles

The target XB and HB rotaxanes were prepared *via* an anion templated 'clipping' rotaxanation synthetic procedure which necessitated the initial synthesis of the appropriate axle components (Scheme 1). This first involved a CuAAC reaction between propyl-azide terphenyl stopper group **1**[27] and 3-ethynylpyridine to give **2** and **3** respectively. The incorporation of iodine into compound **2** was achieved using a one-pot reaction[28] in which the iodo-triazole motif is formed in a concerted fashion. Compounds **2** and **3** were alkylated using alkyl bromide appended stopper group **4** in the presence of NaI. Following purification and anion exchange, by washing with aqueous NH_4Cl, the target axles, **5·Cl** and **6·Cl** were isolated in yields of 63% and 28%, respectively.

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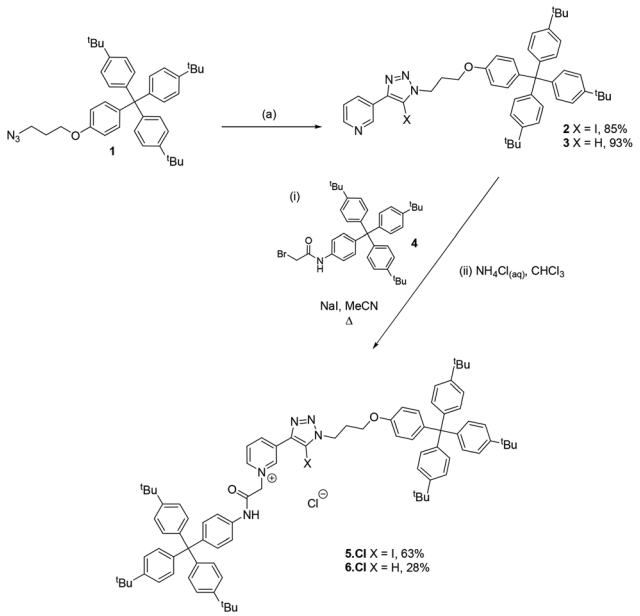


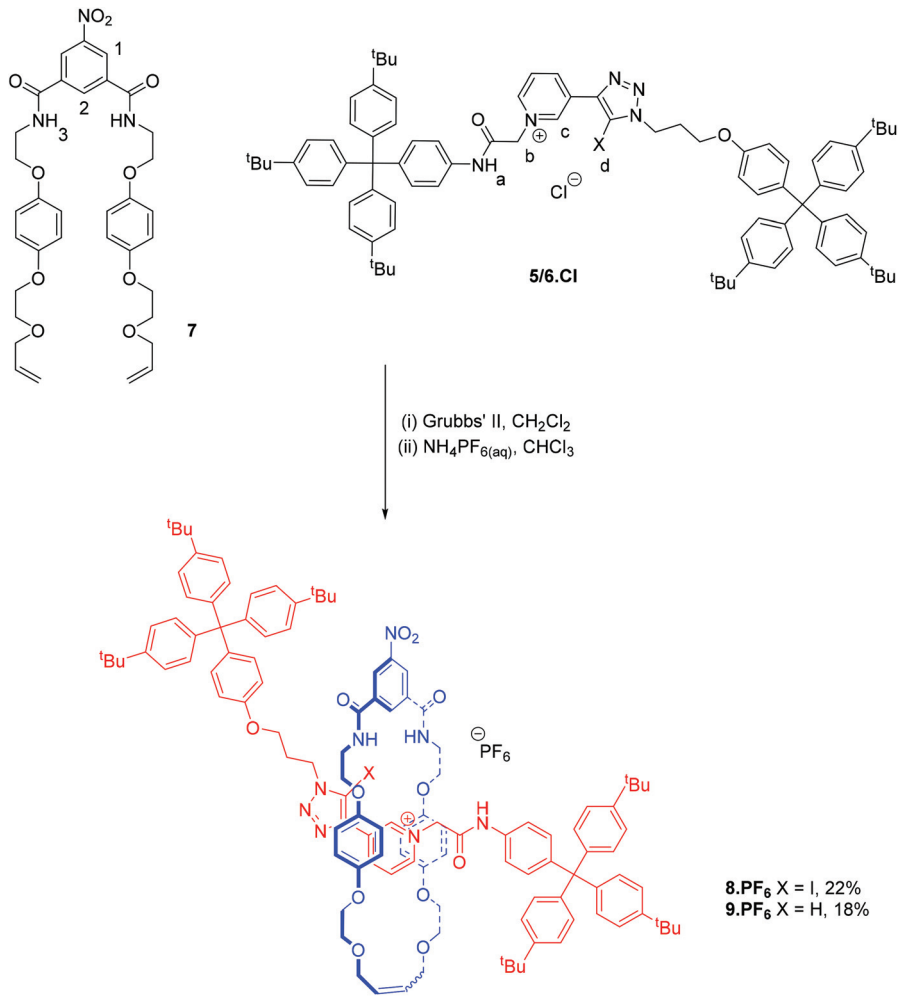
Scheme 1 Synthesis of axles **5·Cl** and **6·Cl**; (a) for X = I: 3-ethynylpyridine, $Cu(ClO_4)_2{\cdot}6H_2O$, NaI, DBU, TBTA, THF/MeCN, dark; for X = H: 3-ethynylpyridine, $Cu(MeCN)_4PF_6$, DIPEA, TBTA, CH_2Cl_2.

Synthesis of rotaxanes *via* anion templated clipping strategy

Rotaxane formation was achieved using a clipping procedure[29] in which a bis-vinyl-appended macrocycle precursor **7**[30] underwent a ring closing metathesis reaction around axle components **5·Cl** and **6·Cl** using Grubbs' second generation catalyst, with the chloride counter anion of the axles acting as a template (Scheme 2). Following purification by preparative TLC and anion exchange, by washing with aqueous NH_4PF_6, the target rotaxanes **8·PF$_6$** and **9·PF$_6$** were isolated in comparable overall yields of 22% and 18%, respectively. Both rotaxanes were characterised by ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectroscopy, and high resolution ESI mass spectrometry, with the interlocked nature of the structures confirmed by 2D ^{1}H–^{1}H ROESY NMR spectroscopy (see ESI†).

Anion binding properties of rotaxanes 8·PF$_6$ and 9·PF$_6$

The anion binding properties of rotaxane hosts **8·PF$_6$** and **9·PF$_6$** were investigated using quantitative ^{1}H NMR titration experiments, performed in the competitive $CDCl_3$–CD_3OD (1 : 1) solvent mixture. Chemical shifts of the interlocked cavity protons were monitored upon addition of increasing equivalents of anions, added as their tetrabutylammonium (TBA) salts.



Scheme 2 Synthesis of rotaxanes **8·PF$_6$** and **9·PF$_6$** *via* clipping strategy.

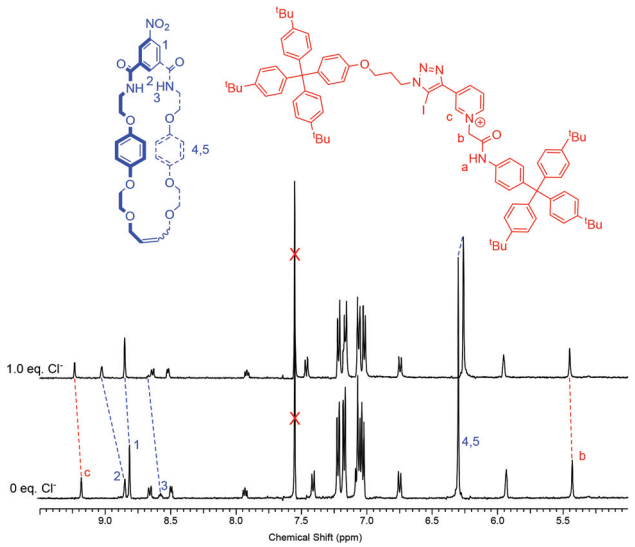


Fig. 1 Partial ^{1}H NMR spectra of **8·PF$_6$** before (bottom) and after (top) addition of one equivalent of TBA chloride (1 : 1 $CDCl_3$–CD_3OD, 298 K, 500 MHz). Peak labelled x corresponds to residual $CHCl_3$ signal.

For both rotaxanes, macrocycle proton 2 and axle proton c (see Scheme 2 for labels) moved downfield significantly upon the progressive addition of up to ten equivalents of all the anions used (Fig. 1), with the triazole proton also moving downfield in HB rotaxane **9·PF$_6$**, indicative of hydrogen bonding interactions with the anionic guest species. In XB rotaxane **8·PF$_6$**, macrocycle proton 2 underwent the greatest perturbation, with chloride causing the largest magnitude of downfield shift change (0.45 ppm) followed by bromide (0.34 ppm), iodide (0.29 ppm) and dihydrogen phosphate (0.27 ppm). A similar trend was observed for axle proton c, however the magnitude of change of chemical shift was much smaller; chloride (0.14 ppm) > bromide (0.13 ppm) > iodide (0.11 ppm) > dihydrogen phosphate (0.04 ppm).

Conversely, for HB rotaxane **9·PF$_6$** the axle proton c underwent the biggest chemical shift perturbation, with chloride again causing the largest magnitude of change (0.65 ppm) followed by bromide (0.49 ppm), dihydrogen phosphate (0.47 ppm) and iodide (0.30 ppm).

WinEQNMR2 analysis of the titration data,[31] monitoring proton 2 from the respective rotaxane's macrocycle component (Fig. 2 and 3), determined 1 : 1 stoichiometric association constants (Table 1). The XB rotaxane **8·PF$_6$** shows a preference for the halides (in the order $Br^- > I^- > Cl^-$) over the larger, more basic oxoanions, with no binding observed for acetate. This indicates the XB donor containing cavity of rotaxane **8·PF$_6$** is of complementary shape and size for halides, in particular bromide, whereas the oxoanions are too large for the interlocked binding pocket.

In stark contrast, the HB rotaxane **9·PF$_6$** displays strong binding and selectivity for dihydrogen phosphate, followed by chloride, bromide, acetate and iodide. It is noteworthy that the selectivity for dihydrogen phosphate is unprecedented for an interlocked host system and suggests substituting iodine for a proton in the triazole axle group of the rotaxane, creates a more open mechanically bonded cavity of sufficient size for the strong association of the tetrahedral oxoanion guest species.

Furthermore, the anion association constants of HB **9·PF$_6$** are all, with the exception of iodide, of significantly greater magnitude to those exhibited by XB **8·PF$_6$**. This maybe a consequence of the large iodine halogen donor atom of the axle component of rotaxane **8·PF$_6$** imparting a degree of steric hindrance to the overall anion recognition process.

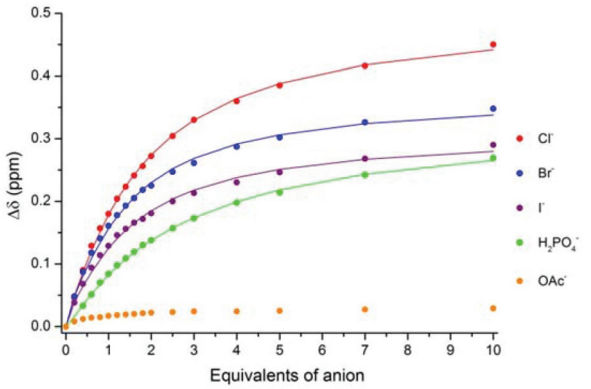


Fig. 2 Change in chemical shift of proton 2 of **8·PF$_6$** upon addition of TBA salts of various anions (1 : 1 $CDCl_3$–CD_3OD, 298 K).

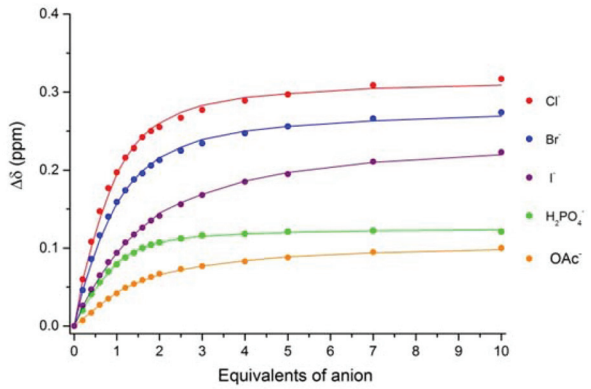


Fig. 3 Change in chemical shift of proton 2 of **9·PF$_6$** upon addition of TBA salts of various anions (1 : 1 $CDCl_3$–CD_3OD, 298 K).

Table 1 Association constants (K_a) for **8·PF$_6$** and **9·PF$_6$** with various anions[a]

Anion	K_a (**8·PF$_6$**)	K_a (**9·PF$_6$**)
Cl^-	381 (18)	1831 (29)
Br^-	532 (22)	1299 (104)
I^-	466 (48)	449 (5)
$H_2PO_4^-$	211 (12)	2399 (7)
OAc^-	—[b]	543 (26)

[a] Anions added as their tetrabutylammonium salts. Errors in parentheses. 1 : 1 $CDCl_3$–CD_3OD, 298 K. [b] Chemical shift too small to accurately determine K_a.

Conclusions

Two novel rotaxanes incorporating axle components containing a pyridinium unit functionalised with XB iodo-triazole and HB proto-triazole motifs respectively have been prepared by a clipping strategy, using the chloride anion as a template. Halogen bonding rotaxane **8·PF$_6$** was shown to selectively bind halides over the oxoanions, acetate and dihydrogen phosphate, with a preference for bromide. In startling contrast, HB rotaxane **9·PF$_6$** exhibited a preference for dihydrogen phosphate over the halides. Importantly, these observations further highlight how the integration of XB and HB donor groups into the mechanically bonded cavity can dramatically affect the anion recognition properties of the interlocked host.

Experimental

Iodo-triazole 2

To a solution of propyl-azide stopper **1** (273 mg, 0.47 mmol) in THF (2 mL) was added NaI (186 mg, 1.24 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (230 mg, 0.62 mmol). The mixture was stirred for 5 minutes at room temperature after which TBTA (1.6 mg, 0.031 mmol) and a THF (0.5 mL) solution of DBU (47 mg, 0.31 mmol) were added, followed by 3-ethynyl pyridine (32 mg, 0.31 mmol) and MeCN (2 mL). This was left to stir at room temperature overnight and then diluted with CH_2Cl_2 (20 mL) before being washed with $NH_4OH_{(aq.)}$ (20 mL) and $NaCl_{(sat.\ aq.)}$ (2 × 10 mL). The organics were collected dried over $MgSO_4$, filtered and the solvent removed under vacuum. The crude material was purified by silica gel column chromatography using 99 : 1 CH_2Cl_2–CH_3OH to elute the product (214 mg, 0.26 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): 9.36 (s, 1H, py-H), 8.67 (br. s, 1H, py-H), 8.37 (d, ^3J = 7.8 Hz, 1H, py-H), 7.46–7.55 (m, 1H, py-H), 7.20–7.25 (m, 6H, Ar–*H*), 7.04–7.12 (m, 8H, Ar–*H*), 6.74–6.79 (m, 2H, OAr–*H*), 4.69 (t, ^3J = 7.0 Hz, 2H, CH2–C*H*2–N), 4.05 (t, ^3J = 5.6 Hz, 2H, –CH2–C*H*2–O), 2.46 (m, 2H CH_2–CH_2–CH_2), 1.30 (s, 27H, *t*Bu). ^{13}C NMR (101 MHz, $CDCl_3$): 155.1, 147.4, 147.0, 145.7, 143.0, 139.1, 135.1, 131.3, 129.7, 123.1, 112.0, 62.8, 62.0, 47.2, 33.3, 30.4, 28.6. HRESI MS (pos.) 817.3326, calc. for $[C_{47}H_{54}N_4OI]^+$ = 817.3337.

Proto-triazole 3

To a solution of propyl-azide stopper **1** (1.00 g, 1.70 mmol), 3-ethynyl pyridine (175 mg, 1.70 mmol) and TBTA (180 mg, 0.34 mmol) in CH_2Cl_2 (150 mL) was added DIPEA (0.44 mL, 2.55 mmol) followed by $Cu(MeCN)_4PF_6$ (127 mg, 0.34 mmol). The mixture was stirred at room temperature overnight and the solvent removed under vacuum to give a yellow residue. This was purified by silica gel column chromatography using 98 : 2 CH_2Cl_2–MeOH to elute the product as an off-white solid (1.093 g, 1.58 mmol, 93%).

^{1}H NMR (300 MHz, $CDCl_3$): 9.01 (1H, s, py-*H*), 8.59 (1H, d, ^3J = 5.1 Hz, py-*H*), 8.22 (1H, d, ^3J = 7.6 Hz, py-*H*), 7.89 (1H, s, triazole C*H*), 7.37–7.41 (1H, m, py-*H*), 7.23–7.25 (6H, m, Ar–*H*), 7.07–7.13 (8H, m, Ar–*H*), 6.77 (2H, d, ^3J = 8.8 Hz, OAr–*H*), 4.68 (2H, t, ^3J = 7.0 Hz, –CH_2–N), 4.00 (2H, t, ^3J = 5.7 Hz, –CH_2–O), 2.46 (2H, m, CH_2–CH_2–CH_2), 1.31 (27H, s, ^{t}Bu). ^{13}C NMR (101 MHz, $CDCl_3$): 156.2, 149.2, 148.4, 147.1, 144.7, 144.0, 140.3, 133.0, 132.4, 130.7, 126.7, 124.1, 123.7, 120.5, 112.9, 63.8, 63.0, 47.4, 34.3, 31.4, 30.0. HRESI MS (pos.): 691.4359, calc. for $[C_{47}H_{55}ON_4]^+$ = 691.4370.

Alkyl bromide stopper 4

Stopper amine (1.00 g, 2.0 mmol) and Et_3N (0.41 g, 4.0 mmol) were dissolved in CH_2Cl_2 (150 mL) and cooled to 0 °C in an ice bath. A CH_2Cl_2 (50 mL) solution of bromoacetyl bromide (0.44 g, 2.2 mmol) was then added drop-wise, after which the solution was allowed to warm to room temperature and left to stir overnight. The mixture was then washed with 10% citric $acid_{(aq.)}$ (200 mL), saturated $NaHCO_{3(aq.)}$ (200 mL) and H_2O (200 mL). The organics were then collected, dried over $MgSO_4$, filtered and the solvent removed under vacuum to give the product as an off-white solid (1.12 g, 1.79 mmol, 91%).

^{1}H NMR (300 MHz, $CDCl_3$): 8.09 (1H, br. s, –C(O)N*H*–), 7.40 (2H, d, ^3J = 8.4 Hz, NH–Ar–*H*), 7.19–7.26 (8H, m, Ar–*H*), 7.08–7.11 (6H, m, Ar–*H*), 4.02 (2H, s, –CH_2–Br), 1.31 (27H, s, ^{t}Bu). ^{13}C NMR (101 MHz, $CDCl_3$): 163.2, 148.5, 144.5, 143.7, 134.4, 131.9, 130.7, 124.2, 118.7, 63.4, 34.3, 31.4, 29.5. HRESI MS (neg.) 622.2694, calc. for $[C_{39}H_{45}ONBr]^-$ = 622.2690.

Iodo-triazole pyridinium axle 5·Cl

To a suspension of iodo-triazole **2** (100 mg, 0.12 mmol) and alkyl bromide stopper **4** (92 mg, 0.15 mmol) in MeCN (20 mL) was added NaI (55 mg, 0.37 mmol). The mixture was heated at reflux for 48 h after which it was cooled to room temperature and the solvent removed under vacuum. The crude material was purified by silica gel column chromatography using 98 : 2 CH_2Cl_2–MeOH to elute the product. This was subsequently dissolved in CH_2Cl_2 (30 mL) and washed with 1 M $NH_4Cl_{(aq.)}$ (8 × 30 mL) and H_2O (2 × 30 mL). The organics were dried over $MgSO_4$ and the solvent removed under vacuum to give the chloride salt of the product as an off-white solid (107 mg, 0.077 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): 11.55 (s, 1H, N*H*), 9.76 (s, 1H, py-*H*), 9.27 (d, ^3J = 5.0 Hz, 1H, py-*H*), 8.84 (d, ^3J = 8.0 Hz, 1H, py-*H*), 7.79 (app. t, ^3J = 7.0 Hz, 1H, py-*H*), 7.53 (d, ^3J = 8.7 Hz, 2H, NAr–*H*), 7.16–7.25 (m, 28H, Ar–*H*), 6.71 (d, ^3J = 8.9 Hz, 2H, OAr–*H*), 6.16 (br. s, 2H, N^+–C*H*2), 4.60 (t, ^3J = 7.0 Hz, 2H, –CH_2–N), 3.96 (t, ^3J = 5.4 Hz, 2H, –CH_2–O), 2.30–2.40 (m, 2H CH_2–CH_2–CH_2), 1.30 (s, 27H, ^{t}Bu), 1.27 (s, 27H, ^{t}Bu). ^{13}C NMR (101 MHz, $CDCl_3$): 160.2, 155.2, 147.3, 143.4, 143.2, 143.0, 142.8, 141.5, 141.3, 139.2, 133.9, 131.3, 130.8, 130.6, 129.7, 126.6, 123.1, 118.0, 112.0, 81.3, 62.8, 62.2, 62.0, 47.5, 33.3, 30.4, 28.7, 28.5. HRESI MS (pos.) 1360.6823, calc. for $[C_{86}H_{99}N_5O_2I]^+$ = 1360.6838.

Proto-triazole pyridinium axle 6·Cl

To a suspension of proto-triazole **3** (250 mg, 0.36 mmol) and alkyl bromide stopper **4** (269 mg, 0.43 mmol) in MeCN (50 mL) was added NaI (5 mg, 0.04 mmol). The mixture was

heated at reflux for 72 h after which it was cooled to room temperature and the solvent removed under vacuum. The crude material was purified by silica gel column chromatography using 95 : 5 CH_2Cl_2–MeOH to elute the product. This was subsequently dissolved in $CHCl_3$ (30 mL) and washed with 1 M $NH_4Cl_{(aq.)}$ (8 × 30 mL) and H_2O (2 × 30 mL). The organics were dried over $MgSO_4$, filtered and the solvent removed under vacuum to yield the chloride salt of the product as an off-white solid (127 mg, 0.10 mmol, 28%).

^{1}H NMR (300 MHz, $CDCl_3$): 11.58 (1H, s, N*H*), 10.91 (1H, s, py-*H*), 9.03 (1H, d, ^3J = 7.7 Hz, py-*H*), 8.84 (1H, s, triazole C*H*), 8.76 (1H, d, ^3J = 5.9 Hz, py-*H*), 7.84–7.89 (1H, m, py-*H*), 7.60 (2H, d, ^3J = 8.8 Hz, NAr–*H*), 7.19–7.25 (12H, m, Ar–*H*), 7.05–7.13 (16H, m, Ar–*H*), 6.74 (2H, d, ^3J = 8.8 Hz, OAr–*H*), 5.87 (2H, br s, N^+–C*H*2), 4.66 (2H, t, ^3J = 7.0 Hz, –CH_2–N), 4.00 (2H, t, ^3J = 5.2 Hz, –CH_2–O), 2.44 (2H, m, CH_2–CH_2–CH_2), 1.28–1.30 (54H, m, ^{t}Bu). ^{13}C NMR (126 MHz, 1 : 1 $CDCl_3$–CD_3OD): 157.2, 149.3, 149.2, 145.2, 145.0, 144.7, 135.8, 133.1, 132.6, 131.5, 131.5, 125.1, 124.9, 124.8, 119.6, 113.8, 64.9, 64.2, 63.9, 34.9, 34.9, 31.7, 29.9. HRESI MS (pos.): 1234.7865, calc. for $[C_{86}H_{100}N_5O_2]^+$ = 1234.7872.

XB rotaxane 8·PF_6

Iodo-triazole pyridinium axle **5·Cl** (45 mg, 0.032 mmol) and bis-vinyl macrocycle precursor **7** (21 mg, 0.032 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature for 1 h. Grubbs' second generation catalyst (2.1 mg, 10% by weight) was added and the mixture stirred for 48 h, after which another portion of the catalyst was added (2.1 mg) followed by stirring for a further 48 h. The solvent was then removed under vacuum and the crude material purified by preparative thin layer chromatography (CH_2Cl_2–MeOH 98 : 2; followed by EtOAc–MeOH 98 : 2). The product was then dissolved in $CHCl_3$ (15 mL) and washed with 0.1 M $NH_4PF_{6(aq.)}$ (8 × 20 mL) and H_2O (2 × 20 mL). The organics were dried over $MgSO_4$, filtered and the solvent removed under vacuum to yield **8·PF_6** as a light brown solid (15 mg, 0.007 mmol, 22%).

^{1}H NMR (500 MHz, 1 : 1 $CDCl_3$–MeOD): 10.27 (s, 1H, axle N*H*), 9.21 (s, 1H, py-*H*), 8.91 (s, 1H, int. macro. Ar–*H*), 8.82 (br s, 2H, ext. macro. Ar–*H*), 8.66 (d, ^3J = 8.2 Hz, 1H, py-*H*), 8.58–8.63 (m, 2H, macro. N*H*), 8.53 (d, ^3J = 5.2 Hz, 1H, py-*H*), 7.91–7.98 (m, 1H, py-*H*), 7.42 (d, ^3J = 8.2 Hz, 2H, axle NAr–*H*), 7.22 (d, ^3J = 8.4 Hz, 6H, stopper Ar–*H*), 7.17 (d, ^3J = 8.4 Hz, 8H, stopper Ar–*H*), 7.04–7.09 (m, 8H, stopper Ar–*H*), 7.00–7.04 (d, ^3J = 8.4 Hz, 6H, stopper Ar–*H*), 6.74 (d, ^3J = 8.9 Hz, 2H, OAr–*H*), 6.29 (br s, 8H, hydroquinone Ar–*H*), 5.94 (s, 2H, alkene C*H*), 5.47 (s, 2H, N^+–CH_2), 4.30 (t, ^3J = 6.6 Hz, 2H, axle –CH_2–N), 3.99–4.07 (m, 4H, macro. CH_2), 3.57–3.92 (m, 18H, macro. CH_2, axle –CH_2–O), 2.16 (m, 2H, axle CH_2–CH_2–CH_2), 1.25–1.27 (m, 54H, ^{t}Bu). ^{13}C NMR (126 MHz, 1 : 1 $CDCl_3$–CD_3OD): 165.5, 156.2, 152.4, 152.4, 148.5, 148.4, 148.2, 144.4, 144.1, 143.7, 143.0, 141.5, 140.2, 136.2, 134.8, 132.2, 131.7, 131.6, 131.0, 124.1, 124.0, 118.8, 114.9, 114.6, 113.0, 82.0, 70.9, 69.2, 67.5, 66.6, 63.6, 63.3, 63.0, 39.8, 34.1, 34.0, 30.9, 29.5, 28.8, 26.6, 26.5, 26.0, 26.0, 25.9. ^{19}F NMR (470 MHz, 1 : 1 $CDCl_3$–CD_3OD): −71.4 (d, $^1J_{F,P}$ = 714 Hz). ^{31}P NMR (202 MHz, 1 : 1 $CDCl_3$–CD_3OD): −144.2 (septet, $^1J_{P,F}$ = 714 Hz). HRESI MS (pos.) 1982.9169, calc. for $[C_{118}H_{134}N_8O_{12}I]^+$ = 1982.9193.

HB rotaxane 9·PF_6

Proto-triazole pyridinium axle **6·Cl** (60 mg, 0.047 mmol) and bis-vinyl macrocycle precursor **7** (31 mg, 0.047 mmol) were dissolved in CH_2Cl_2 (~10 mL) and stirred at room temperature for 30 min. Grubbs' 2nd generation catalyst (3.1 mg, 10% by weight) was added and the mixture stirred for a further 72 h, after which the solvent was removed under vacuum. The crude brown residue was purified using preparative plate thin layer chromatography (98 : 2 EtOAc–MeOH). The product was then dissolved in $CHCl_3$ (15 mL) and washed with 0.1 M $NH_4PF_{6(aq.)}$ (8 × 15 mL) and H_2O (2 × 15 mL). The organics were dried over $MgSO_4$, filtered and the solvent removed under vacuum to yield the **9·PF_6** as an off-white solid (17 mg, 0.008 mmol, 18%).

^{1}H NMR (500 MHz, 1 : 1 $CDCl_3$–CD_3OD) 8.85 (1H, s, int. macro. Ar–*H*), 8.79 (2H, s, ext. macro. Ar–*H*), 8.77 (1H, s, py-*H*), 8.53 (2H, br. s, macro. N*H*), 8.38 (1H, d, ^3J = 8.1 Hz, py-*H*), 8.32 (1H, d, ^3J = 5.6 Hz, py-*H*), 8.14 (1H, s, triazole C*H*), 7.83 (1H, m, py-*H*), 7.39 (2H, d, ^3J = 8.9 Hz, NAr–*H*), 7.17–7.23 (14H, m, stopper Ar–*H*), 7.02–7.08 (14H, m, stopper Ar–*H*), 6.74 (2H, d, ^3J = 8.9 Hz, OAr–*H*), 6.31–6.37 (8H, m, hydroquinone Ar–*H*), 5.94 (2H, br. s, alkene C*H*), 5.24 (2H, s, N^+–CH_2), 4.44 (2H, t, ^3J = 7.3 Hz, axle –CH_2–N), 4.00–4.03 (4H, m, macro. CH_2), 3.67–3.88 (18H, m, macro CH_2, axle –CH_2–O), 2.26 (2H, m, axle CH_2–CH_2–CH_2), 1.27 (27H, s, ^{t}Bu), 1.25 (27H, s, ^{t}Bu). ^{13}C NMR (126 MHz, 1 : 1 $CDCl_3$–CD_3OD) 166.3, 156.9, 153.2, 153.2, 149.2, 149.0, 144.8, 144.5, 144.0, 141.0, 140.9, 136.9, 135.4, 132.9, 132.5, 131.9, 131.3, 131.3, 130.3, 128.4, 125.9, 124.9, 124.7, 119.4, 115.7, 115.4, 113.7, 71.6, 69.9, 68.3, 67.1, 64.5, 64.1, 63.7, 63.0, 40.7, 34.8, 34.8, 31.8, 30.0. ^{19}F NMR (470 MHz, 1 : 1 $CDCl_3$–CD_3OD): −73.0 (d, $^1J_{F,P}$ = 711 Hz). ^{31}P NMR (202 MHz, 1 : 1 $CDCl_3$–CD_3OD): −144.4 (septet, $^1J_{P,F}$ = 711 Hz). HRESI MS (pos.) 1857.0165, calc. for $[C_{118}H_{135}N_8O_{12}]^+$ = 1857.0226.

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