

Supplementary Information for

Anion recognition by halogen bonding and hydrogen bonding bis-triazole-imidazolium [2]rotaxanes

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Materials and methods

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H₂O was de-ionized and micro filtered using a Milli-Q® Millipore machine. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Routine NMR spectra were recorded on either a Varian Mercury 300, a Bruker AVIII 400 or a Bruker AVIII 500 spectrometer with ¹H NMR titrations recorded on a Bruker AVIII 500 spectrometer. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were recorded on a Bruker μTOF spectrometer. Triethylamine was distilled from and stored over potassium hydroxide. Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA). The following compounds were prepared according to literature procedures **1**,^[1] **2** ^[2] and **9**.^[3]

Anion Exchange Protocol

The charged species was dissolved in a CH₂Cl₂ solution (ca. 50 ml), to which was added an aqueous solution of 0.1 M NH₄X (ca. 50 ml) and the mixture was shaken vigorously in a separating funnel. The organic phase was separated and the washing procedure was repeated 7 more times. After the final aqueous washing the organic phase was washed with water (50 ml), the organic phase collected, dried over MgSO₄ and the solvent was removed in vacuo.

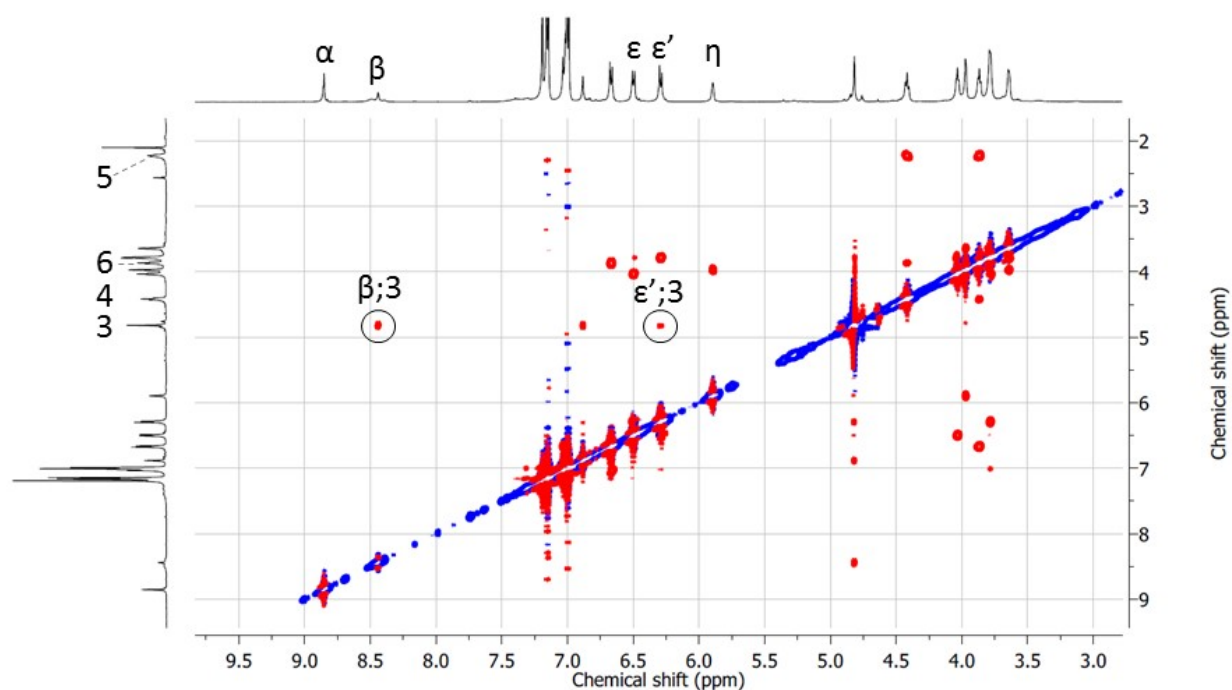
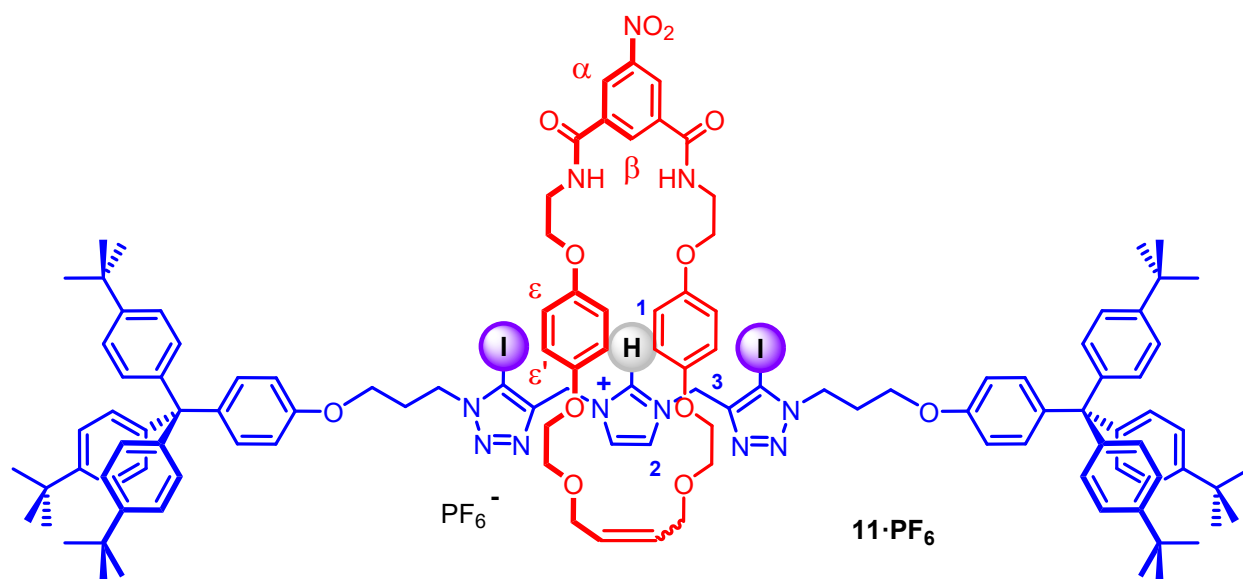
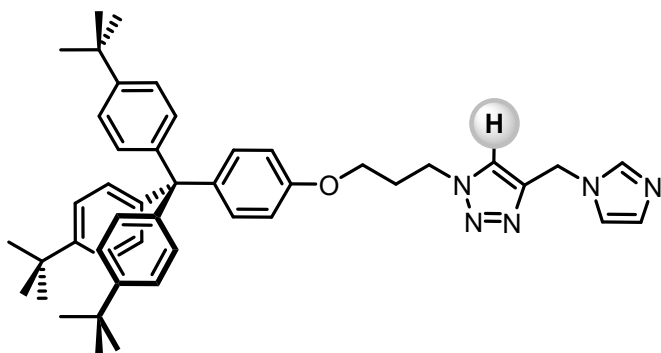


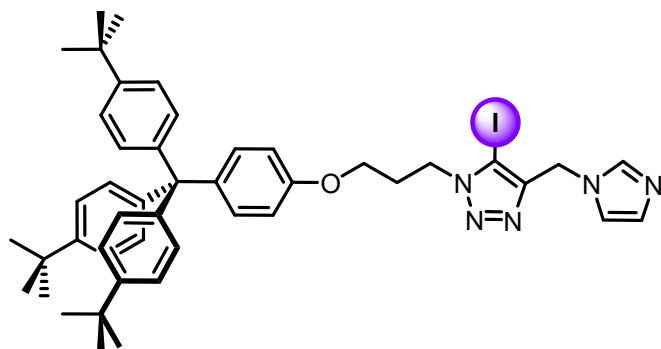
Figure S1. Truncated 2D ROESY NMR spectrum of rotaxane $\mathbf{11} \cdot \text{PF}_6$ showing selected through-space ^1H - ^1H correlations indicative of an interlocked assembly (CDCl_3 , 500 MHz, 298 K).

3

Stopper azide **2** (0.660 g, 1.12 mmol), $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (0.070 g, 0.188 mmol) and TBTA (cat. amount) were dissolved in dry degassed DCM (10 mL). Imidazole-alkyne **1** (0.100 g, 0.942 mmol) and DIPEA (cat. amount) were added. The mixture was stirred at room temperature under N_2 for 18 hours, after which, the reaction mixture was diluted with DCM (80 mL). The organics were washed with $\text{NH}_4\text{OH}_{(\text{aq})}$ (3×40 mL), H_2O (40 mL) and brine (2×40 mL) and dried over MgSO_4 . The solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (DCM/MeOH 98:2) yielded **3** as a white powder (0.600 g, 92%).

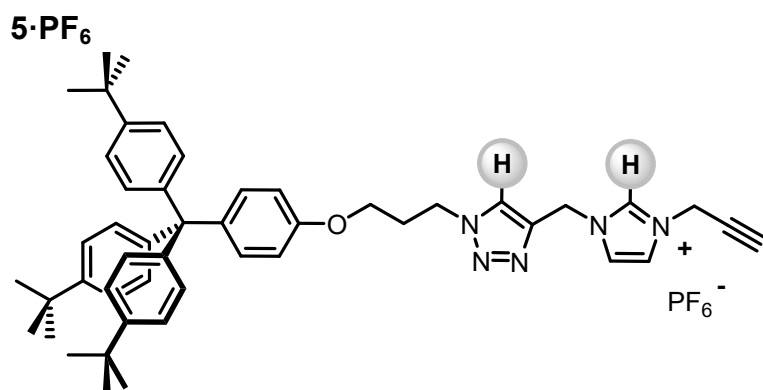
$^1\text{H NMR}$ (400 MHz; CDCl_3) δ (ppm): 7.56 (1H, s, NCHN-imidazole), 7.38 (1H, s, CH-triazole), 7.20-7.25 (6H, m, ArH), 7.06-7.14 (8H, m, ArH), 7.05 (1H, br. s, NCH-imidazole), 6.96 (1H, s, NCH-imidazole), 6.70-6.76 (2H, m, ArH), 5.21 (2H, s, NCH_2 -methylene), 4.54 (2H, t, $J = 6.9$ Hz, NCH_2), 3.91 (2H, t, $J = 5.7$ Hz, OCH_2), 2.32-2.38 (2H, m, OCH_2CH_2), 1.30 (27H, s, *tert*- CH_3); $^{13}\text{C NMR}$ (126 MHz; CDCl_3) δ (ppm): 156.24, 148.54, 144.16, 143.66, 140.42, 132.52, 130.83, 130.19, 128.36, 124.22, 122.60, 113.04, 80.71, 63.88, 63.20, 47.56, 42.50, 34.45, 31.53, 30.03; **HRESI-MS** (pos) $\text{C}_{46}\text{H}_{56}\text{ON}_5$ m/z : $[\text{M}+\text{H}]^+$ calc. 694.44794, found 694.44748.

4



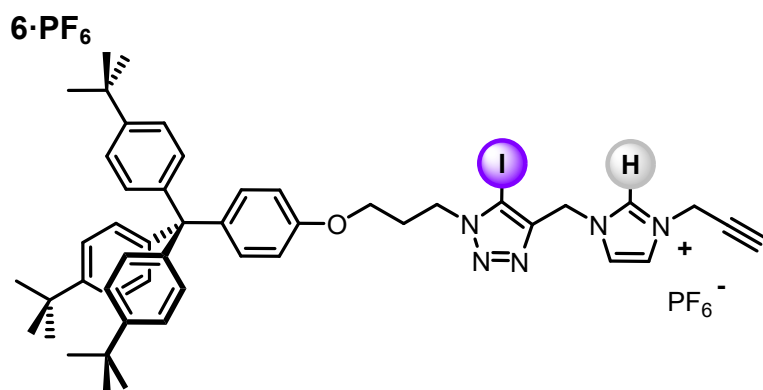
Stopper azide **2** (0.304 g, 0.517 mmol) was dissolved in dry degassed THF (2 mL) and the reaction vessel covered with foil. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.349 g, 0.940 mmol) and NaI (0.282 g, 1.88 mmol) were added and stirred under N_2 for 5 mins. TBTA (0.025 g, 0.047 mmol) was added and stirred under N_2 for 5 mins. DBU (0.071 g, 0.466 mmol) and imidazole–alkyne **1** (0.050 g, 0.466 mmol) were added in order and the mixture was stirred at room temperature for 18 hours, after which, the reaction mixture was diluted with DCM (50 mL). The organics were washed with $\text{NH}_4\text{OH}_{(\text{aq})}$ (3 × 30 mL), H_2O (30 mL) and brine (2 × 30 mL) and dried over MgSO_4 . The solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (DCM/MeOH 98:2) yielded **4** as a white powder (0.350 g, 91%).

$^1\text{H NMR}$ (500 MHz; CDCl_3) δ (ppm): 7.63 (1H, s, NCHN-*imidazole*), 7.20-7.26 (6H, m, ArH), 7.06-7.10 (8H, m, ArH), 7.05-6.99 (2H, m, NCH-*imidazole*), 6.70-6.76 (2H, m, ArH), 5.17 (2H, s, NCH₂-*methylene*), 4.57 (2H, t, $J = 7.0$ Hz, NCH₂), 3.99 (2H, t, $J = 5.7$ Hz, OCH₂), 2.36-2.41 (2H, m, OCH₂CH₂), 1.30 (27H, s, *tert*-CH₃); $^{13}\text{C NMR}$ (126 MHz; CDCl_3) δ (ppm): 156.19, 148.46, 146.67, 144.16, 140.25, 132.43, 130.81, 129.98, 128.10, 124.18, 119.13, 113.15, 80.30, 63.90, 63.17, 48.18, 42.35, 34.41, 31.50, 29.67; **HRESI-MS** (pos) $\text{C}_{46}\text{H}_{55}\text{ON}_5\text{I}$ m/z : $[\text{M}+\text{H}]^+$ *calc.* 820.34458, *found* 820.34387.



3 (0.350 g, 0.50 mmol) was suspended in acetone (10 mL) and propargyl bromide (0.28 mL, 2.50 mmol) added. The reaction mixture was heated under microwave irradiation at 140 °C for 75 mins and the resulting precipitate filtered to produce imidazolium–alkyne **5·Br** (0.345 g, 85%), and subjected to the anion exchange protocol.

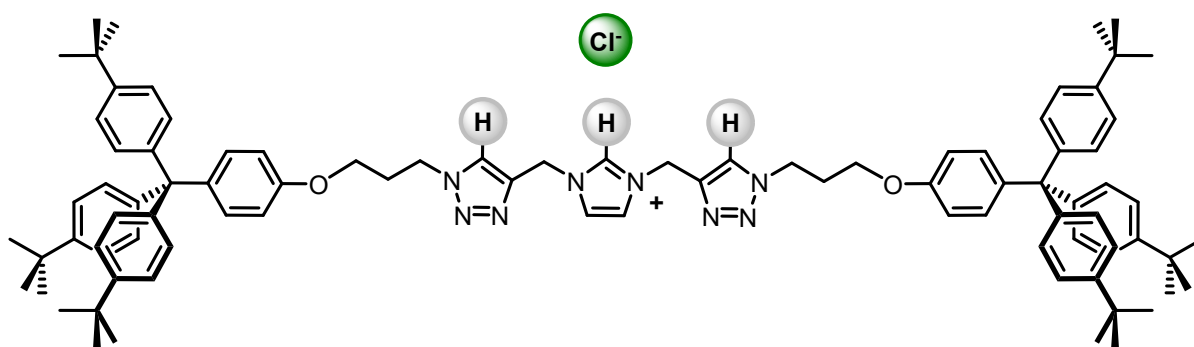
¹H NMR (400 MHz; CDCl₃) δ (ppm): 10.68 (1H, t, ⁴J = 1.7 Hz, NCHN-*imidazole*), 8.54 (1H, s, CH-*triazole*), 7.68 (1H, t, ⁴J = 1.8 Hz, NCH-*imidazole*), 7.35 (1H, t, ⁴J = 1.8 Hz, NCH-*imidazole*), 7.25-7.17 (6H, m, ArH), 7.12-6.99 (8H, m, ArH), 6.78-6.59 (2H, m, OArH), 5.84 (2H, s, *imidazolium-CH₂-triazole*) 5.16 (2H, d, ⁴J = 2.6 Hz, CH₂-*alkyne*), 4.58 (2H, t, J = 7.2 Hz, NCH₂CH₂), 3.97 (2H, t, J = 5.7 Hz, OCH₂), 2.68 (1H, t, ⁴J = 2.6 Hz, CH-*alkyne*), 2.46-2.29 (2H, m, OCH₂CH₂), 1.29 (27H, s, *tert-CH₃*); **¹³C NMR** (126 MHz; CDCl₃) δ (ppm): 156.34, 148.46, 144.19, 140.21, 139.96, 137.23, 132.42, 130.83, 125.84, 124.20, 122.88, 121.19, 113.08, 78.54, 73.42, 64.22, 63.18, 47.98, 44.78, 40.05, 34.43, 31.52, 30.10.; **HRESI-MS** (pos) C₄₉H₅₈ON₅⁺ *m/z*: [M-Br]⁺ *calc.* 732.46359, *found* 732.46270.



4 (0.200 g, 0.244 mmol) was suspended in acetone (10 mL) and propargyl bromide (0.11 mL, 1.22 mmol) added. The reaction mixture was heated under microwave irradiation at 140 °C for 75 mins and the resulting precipitate filtered to produce imidazolium–alkyne **6**·Br (0.149 g, 65%) and subjected to the anion exchange protocol.

¹H NMR (400 MHz; CDCl₃) δ (ppm): 10.78 (1H, s, NCHN-*imidazolium*), 7.48 (1H, t, *J* = 1.8 Hz, NCH-*imidazole*), 7.43 (1H, t, *J* = 1.8 Hz, NCH-*imidazole*), 7.19-7.25 (6H, m, ArH), 7.05-7.10 (8H, m, ArH), 6.70-6.73 (2H, m, OArH), 5.65 (2H, s, *imidazolium-CH₂-triazole*), 5.38 (2H, d, ⁴*J* = 2.6 Hz, CH₂-*alkyne*), 4.59 (2H, t, *J* = 7.0 Hz, NCH₂), 3.98 (2H, t, *J* = 5.6 Hz, OCH₂), 2.65 (1H, t, ⁴*J* = 2.6 Hz, CH-*alkyne*), 2.42-2.36 (2H, m, OCH₂CH₂), 1.29 (27H, s, CH₃); ¹³C NMR (126 MHz; CDCl₃) δ (ppm): 156.16, 148.36, 144.05, 143.59, 140.14, 137.28, 132.31, 130.69, 124.08, 122.21, 121.73, 113.01, 85.62, 78.16, 73.73, 63.99, 63.05, 48.40, 45.47, 40.18, 34.31, 31.39, 29.52; HRESI-MS (pos.) C₄₉H₅₇ON₅I⁺ *m/z*: [M-Br]⁺ *calc.* 858.36023, *found* 858.35943.

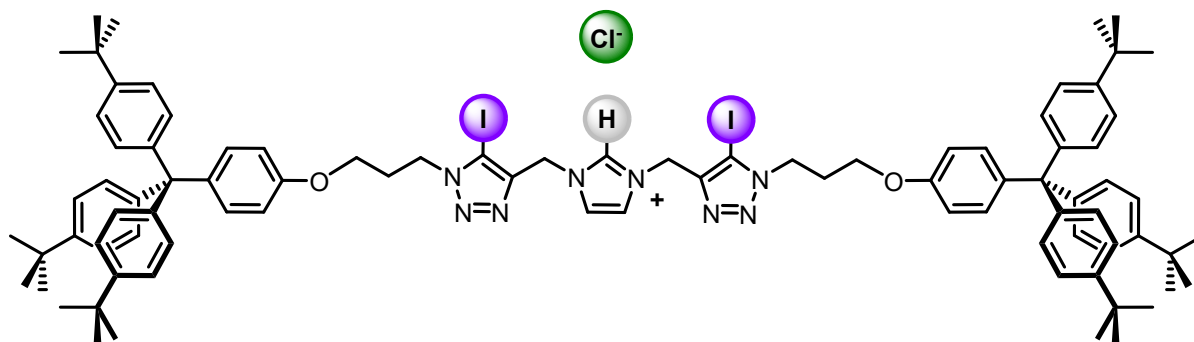
7·Cl



5-PF6 (0.100 g, 0.14 mmol) and stopper azide **2** (0.096 g, 0.16 mmol) were dissolved in dry DCM (4 mL). TBTA (0.014 g, 0.027 mmol) followed by $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (0.011 g, 0.027 mmol) and DIPEA (0.026 g, 0.20 mmol) were added and the reaction mixture was stirred at room temperature for 18 hours. The reaction was diluted with DCM (20 mL) and washed with $\text{NH}_4\text{OH}_{(\text{aq})}$ (3×20 mL) and brine (2×15 mL) and dried over anhydrous MgSO_4 and filtered. To the crude reaction mixture TFA (0.5 mL) was added and stirred for 30 mins. The solvent and excess TFA were removed *in vacuo* and the reaction mixture was purified *via* silica gel column chromatography (DCM/MeOH 95:5) and subjected to the anion exchange protocol. The solvent was removed *in vacuo* to afford HB imidazolium–bis(triazole) axle **7·Cl** (0.086 g, 42%).

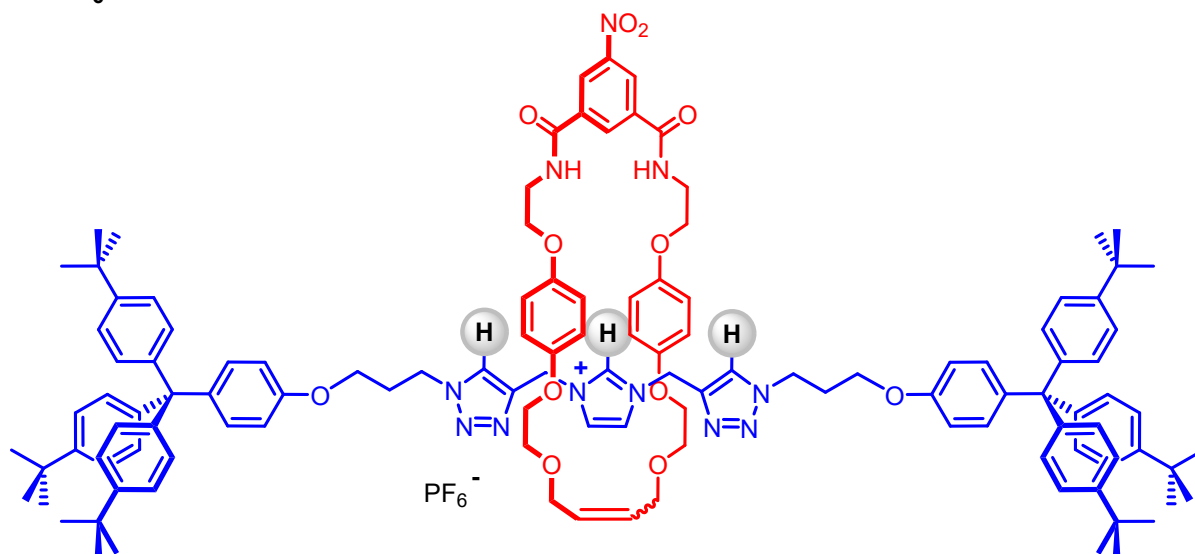
$^1\text{H NMR}$ (400 MHz; $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1) δ (ppm): 8.95 (1H, s, NCHN-imidazolium), 8.02 (2H, s, NCH-imidazolium), 7.50 (2H, s, CH-triazole), 7.27-7.12 (12H, m, ArH), 7.03 (16H, m, ArH), 6.70-6.65 (4H, m, OArH), 5.43 (4H, s, NCH₂-methylene), 4.56 (2H, t, $J = 7.2$ Hz, NCH₂CH₂), 3.93 (4H, t, $J = 5.7$ Hz, OCH₂), 2.41-2.27 (4H, m, OCH₂CH₂), 1.25 (54H, s, tert-CH₃); $^{13}\text{C NMR}$ (126 MHz; CDCl_3) δ (ppm): 156.29, 148.89, 148.46, 144.18, 140.32, 140.22, 132.48, 130.84, 124.21, 113.06, 110.90, 104.79, 64.06, 63.19, 47.71, 34.44, 31.52, 30.03, 29.85; **HRESI-MS** (pos) $\text{C}_{89}\text{H}_{107}\text{O}_2\text{N}_8^+$ m/z : $[\text{M}-\text{Cl}]^+$ *calc.* 1320.85451, *found* 1320.85507.

8·Cl



Stopper azide **2** (0.069 g, 0.117 mmol) was dissolved in dry degassed THF (2 mL) and the reaction vessel covered with foil. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.079 g, 0.107 mmol) and NaI (0.064 g, 0.426 mmol) were added and stirred under N_2 for 5 mins. TBTA (0.006 g, 0.011 mmol) was added and stirred under N_2 for 5 mins. DBU (0.016 g, 0.107 mmol) and imidazolium–alkyne **6·PF₆** (0.100 g, 0.107 mmol) were added in order and the mixture was stirred at room temperature for 18 hours, after which, the reaction mixture was diluted with DCM (50 mL). The organics were washed with $\text{NH}_4\text{OH}_{(\text{aq})}$ (3 × 30 mL), H_2O (30 mL) and brine (2 × 30 mL) and dried over MgSO_4 and filtered. To the crude reaction mixture TFA (0.5 mL) was added and stirred for 30 mins. The solvent and excess TFA were removed *in vacuo* and the reaction mixture was purified *via* silica gel column chromatography (DCM/MeOH 95:5). and subjected to the anion exchange protocol. The solvent was removed *in vacuo* to afford XB imidazolium–bis(iodotriazole) axle **8·Cl** (0.059 g, 35%).

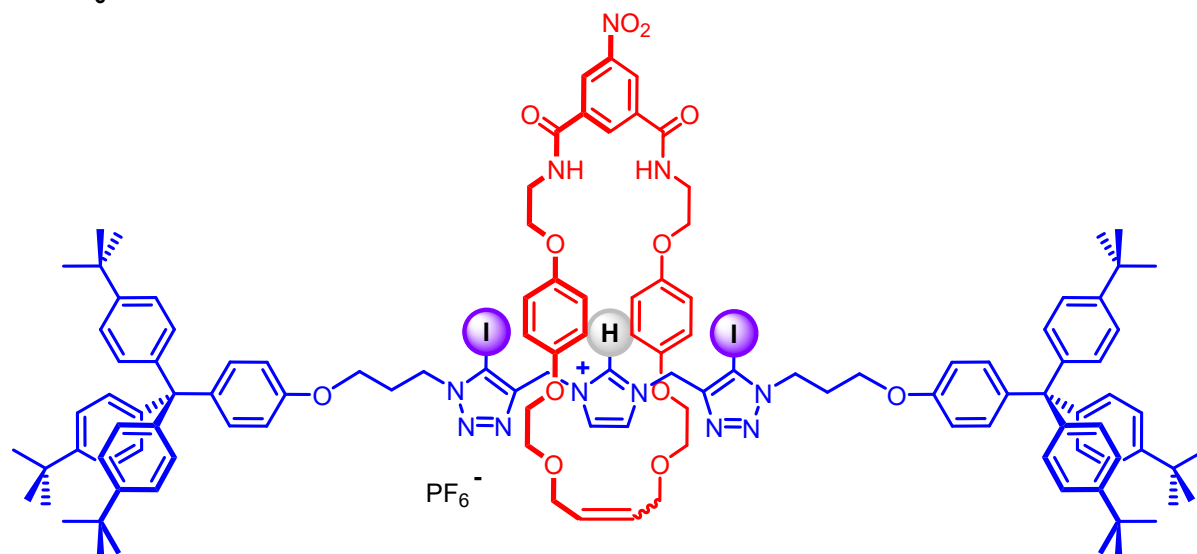
¹H NMR (400 MHz; CDCl_3) δ (ppm): 11.02 (1H, s, NCHN-imidazolium), 7.25-7.19 (12H, m, ArH), 7.18 (2H, s, NCH-imidazolium), 7.09-7.03 (16H, m, ArH), 6.74-6.68 (4H, m, OArH), 5.68 (4H, s, NCH₂-methylene), 4.54 (4H, t, $J = 7.3$ Hz, NCH₂CH₂), 3.96 (4H, t, $J = 5.6$ Hz, OCH₂), 2.49-2.22 (4H, m, OCH₂CH₂), 1.29 (54H, s, *tert*-CH₃); **¹³C NMR** (126 MHz; $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1) δ (ppm): 155.82, 147.94, 143.76, 143.66, 139.70, 131.82, 130.28, 123.63, 122.57, 112.60, 83.73, 77.35, 63.57, 62.64, 47.96, 44.49, 33.73, 30.67, 29.00; **HRESI-MS** (pos) $\text{C}_{89}\text{H}_{105}\text{O}_2\text{N}_8\text{I}_2^+$ [M-Cl]⁺ *calc.* 1571.6444, *found* 1571.64021.

10·PF₆

Imidazolium–bis(triazole) axle **7·Cl** (0.015 g, 0.011 mmol) and bis-vinyl macrocycle precursor **9** (0.011 g, 0.016 mmol) were dissolved in anhydrous DCM (6 mL) and stirred at room temperature for 30 mins. Grubbs' second generation catalyst (1.1 mg, 10% by weight) was added and the mixture was stirred for 48 hours, after which another portion of catalyst was added (1.1 mg) followed by stirring for a further 48 hours. The solvent was removed *in vacuo* and the crude reaction mixture purified *via* preparative TLC (EtOAc/MeOH 95:5 followed by DCM/MeOH 97:3) and subjected to the anion exchange protocol. The organics were dried over MgSO₄, filtered and the solvent removed *in vacuo* to yield HB rotaxane **10·PF₆** as an off white solid (0.008 g, 35%).

¹H NMR (500 MHz; CDCl₃/CD₃OD/D₂O 45:45:10) δ (ppm): 8.80 (2H, s, ArH-ext. macro.), 8.60 (1H, s, ArH-int. macro.), 7.78 (2H, s, CH-triazole axle), 7.29 (2H, s, NCH-imidazolium axle), 7.26-7.19 (12H, m, ArH-axle), 7.12-7.06 (16H, m, ArH-axle), 6.68-6.65 (4H, m, OArH-axle), 6.50 (4H, d, *J* = 9.0 Hz, ArH-macro.), 6.36 (4H, d, *J* = 9.0 Hz, ArH-macro), 5.78-5.73 (2H, m, CH-alkene macro.), 5.20 (4H, s, NCH₂-methylene axle), 4.32 (4H, t, *J* = 6.9 Hz, NCH₂CH₂-axle), 3.99 (4H, t, *J* = 4.9 Hz, CH₂-macro.), 3.93-3.91 (4H, m, CH₂-macro.), 3.83-3.80 (4H, m, CH₂-macro.), 3.79-3.73 (8H, m, CH₂-macro., OCH₂-axle), 3.67-3.64 (4H, m, CH₂-macro.), 2.13-2.09 (4H, m, OCH₂CH₂-axle), 1.29 (54H, s, tert-CH₃); ¹³C NMR (126 MHz; CDCl₃) δ (ppm): 164.73, 156.30, 152.94, 152.21, 149.07, 148.48, 144.17, 140.35, 135.95, 132.46, 130.84, 130.81, 129.62, 126.51, 125.13, 124.21, 121.96, 114.96, 114.48, 113.04, 71.12, 69.52, 67.83, 66.24, 63.97, 63.18, 47.83, 40.64, 34.44, 31.52, 30.08, 29.85, 22.85 (one peak missing, presumed overlapped); HRESI-MS (pos) C₁₂₁H₁₄₂O₁₂N₁₁ *m/z*: [M-A]⁺ calc. 1941.08340, found 1941.08375.

11·PF₆



Imidazolium–bis(triazole) axle **7·Cl** (0.040 g, 0.025 mmol) and bis-vinyl macrocycle precursor **9** (0.024 g, 0.037 mmol) were dissolved in anhydrous DCM (15 mL) and stirred at room temperature for 30 mins. Grubbs' second generation catalyst (2.4 mg, 10% by weight) was added and the mixture was stirred for 48 hours, after which another portion of catalyst was added (2.4 mg) followed by stirring for a further 48 hours. The solvent was removed *in vacuo* and the crude reaction mixture purified *via* preparative TLC (EtOAc/MeOH 95:5 followed by DCM/MeOH 97:3). The product was dissolved in DCM (10 mL) and subjected to the anion exchange protocol. The organics were dried over MgSO₄, filtered and the solvent removed *in vacuo* to yield XB rotaxane **11·PF₆** as an off white solid (0.014 g, 24%).

¹H NMR (500 MHz; CDCl₃/CD₃OD/D₂O 45:45:10) δ (ppm): 8.82 (2H, s, ArH-ext. macro.), 8.75 (1H, s, ArH-int. macro.), 7.43 (2H, s, NCH-imidazolium axle), 7.30-7.18 (12H, m, ArH-axle), 7.11-7.05 (16H, m, ArH-axle), 6.69-6.64 (4H, m, OArH-axle), 6.43 (4H, d, *J* = 9.1 Hz, ArH-macro), 6.35 (4H, d, *J* = 9.0 Hz, ArH-macro), 5.87-5.82 (2H, m, CH-alkene macro.), 5.17 (4H, s, NCH₂-methylene axle), 4.26 (4H, t, *J* = 6.9 Hz, NCH₂CH₂-axle), 4.03-3.94 (8H, m, CH₂-macro.), 3.88-3.82 (4H, m, CH₂-macro.), 3.80-3.72 (8H, m, CH₂-macro., OCH₂-axle), 3.71-3.66 (4H, m, CH₂-macro.), 2.09 (4H, t, *J* = 6.7 Hz, OCH₂CH₂-axle), 1.29 (54H, s, tert-CH₃); ¹³C NMR (126 MHz; CDCl₃) δ (ppm): 164.98, 156.26, 153.12, 152.35, 148.87, 148.51, 144.17, 143.82, 140.36, 136.67, 135.56, 132.46, 130.82, 129.99, 126.21, 124.22, 122.60, 115.61, 114.66, 113.12, 71.27, 69.66, 67.67, 66.56, 63.85, 63.19, 48.82, 44.60, 40.23, 34.45, 31.53, 22.85 (two peaks missing, presumed overlapped); HRESI-MS (pos) C₁₂₁H₁₄₀O₁₂N₁₁I₂ *m/z*: [M-A]⁺ *calc.* 2192.87668, *found* 2192.87577.

References

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- [2] V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby, D. B. Walker, *J. Am. Chem. Soc.* 2006, 128, 2186–2187.
- [3] M. R. Sambrook, P. D. Beer, M. D. Lankshear, R. F. Ludlow, J. A. Wisner, *Org. Biomol. Chem.* 2006, 4, 1529–1538.