Supplementary Information for

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

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Synthesis – General Remarks

All commercial solvents and reagents were used as purchased, unless otherwise stated. Anhydrous solvents were degassed with N₂ and dried by passing them through an MBraun-800 column. Triethylamine was distilled and stored over KOH pellets. Tetrabutylammonium (TBA) salts, Grubbs’ second generation catalyst and Cu(MeCN)₄PF₆ were stored in a desiccator with P₂O₅. TBTA was prepared following a literature procedure. 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 x 20 cm, 1 cm silica thickness).

¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded using Varian Mercury 300, Bruker AVIII400 and Bruker AVIII500 spectrometers. Mass spectra were recorded on a Waters LCT Premier instrument (low resolution) or a Bruker μTOF instrument (high resolution).
Characterisation of rotaxanes 8.PF$_6$ and 9.PF$_6$

XB Rotaxane 8.PF$_6$

Figure S1: $^1$H NMR spectrum of rotaxane 8.PF$_6$ (1:1 CDCl$_3$/CD$_3$OD, 298 K, 500 MHz)

Figure S2: $^{13}$C NMR spectrum of rotaxane 8.PF$_6$ (1:1 CDCl$_3$/CD$_3$OD, 298 K, 126 MHz)
HB Rotaxane 9.PF$_6$

Figure S3: $^1$H NMR spectrum of rotaxane 9.PF$_6$ (1:1 CDCl$_3$/CD$_3$OD, 298 K, 500 MHz)

Figure S4: $^{13}$C NMR spectrum of rotaxane 9.PF$_6$ (1:1 CDCl$_3$/CD$_3$OD, 298 K, 126 MHz)
Figure S5: High resolution mass spectrum of rotaxane 9.PF₆

ROESY NMR Spectra

XB Rotaxane 8.PF₆

Figure S6: Truncated ¹H-¹H ROESY NMR spectrum of rotaxane 8.PF₆ with coupling interactions highlighted (1:1 CDCl₃/CD₃OD, 298 K, 500 MHz).
HB Rotaxane 9.PF₆

Figure S7: Truncated ¹H-¹H ROESY NMR spectrum of rotaxane 9.PF₆ with coupling interactions highlighted (1:1 CDCl₃/CD₃OD, 298 K, 500 MHz).
\(^1\)H NMR Titration Protocol

Titration experiments were performed on a Bruker AVIII500 spectrometer operating at 500 MHz for \(^1\)H NMR and at a temperature of 298 K. An initial volume of host rotaxane of 0.5 mL was used at a concentration of 2 mM. Solutions of the respective anions (50 mM) as their TBA salts were added in aliquots, with spectra recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 10.0 equivalents. Association constants were calculated form the data obtained using the software package WinEQNMR\(^2\), following the macrocycle proton 2. An estimate of the association constant and the observed chemical shifts of proton 2 from each of the spectra recorded were added to the programs input file. Refinement of the data using a non-linear least-squares regression analysis gave an optimised fit between the observed and calculated data. Comparison of the experimental and calculated binding isotherms confirmed that a 1:1 binding model was appropriate.

References