Cationic all-halogen bonding rotaxanes for halide anion recognition

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A family of cationic halogen bonding [2]rotaxanes have been synthesised via an active-metal template synthetic strategy. ¹H NMR spectroscopic anion titration investigations reveal these interlocked host systems recognize halides selectively over oxoanions in aqueous-organic solvent media. Furthermore, systematically modulating the rigidity and size of the rotaxanes' anion binding cavity via metal complexation, as well as by varying the number of halogen bond-donor groups in the axle component, was found to dramatically influence halide anion selectivity.

Introduction

Negatively charged species are everywhere in the natural world and play fundamental roles in many chemical, biological, anthropogenic environmental and medical processes.^{1,2} This has stimulated significant growth in the field of anion supramolecular chemistry in recent decades.^{3,4} Influenced by how biotic protein-based host systems recognize anions via intricate multiple hydrogen bond donor binding pockets, synthetic anion host design has focused mainly on exploiting hydrogen bonding as the leading non-covalent interaction to integrate into receptor structural frameworks.^{5,6} Although halogen bonding (XB), the attractive and highly-directional intermolecular interaction between electron-deficient halogen atoms and Lewis bases^{7,8}, has been extensively used in solid-state crystal engineering,⁹ its application to solution-phase anion recognition is underdeveloped.^{10–13} Notably, the relatively few halogen-bond-based receptors reported display contrasting anion selectivity and enhanced anion recognition capability compared to hydrogen bonding hosts.^{14–21} Using a discrete anion templating strategy, we have constructed a series of XB rotaxane and catenane host systems capable of binding anions in competitive protic solvent media, including pure water.^{22–24} Herein, utilising an active-metal template synthetic approach, we report the synthesis and anion binding properties of a family of unprecedented cationic all-halogen bonding [2]rotaxanes. Importantly, metal complexation and varying the number of convergent halogen bond-donor groups in the axle component, dramatically modulates the interlocked hosts' halide binding selectivities in aqueous-organic solvent media by a combination of host-guest size-complementarity and structural preorganisation.

Results and discussion

Synthesis of cationic halogen bonding rotaxanes

We recently adapted an active metal template methodology to construct a *neutral* XB rotaxane **2** using the endo/exo-conformational metal binding capability of a bis-iodotriazole-containing macrocycle component **1**.²⁵ Building on this preliminary work, a novel cationic rotaxane **3.PF₆** was synthesized via a post-rotaxane methylation reaction of **2** with excess iodomethane, in dichloromethane at room temperature, followed by preparative TLC purification and anion exchange using aqueous ammonium hexafluorophosphate (Scheme 1). Notably, electrospray ionisation mass spectrometry (ESI-MS) of the crude reaction mixture provided evidence that only mono-methylation had occurred ([m/z] = 2089.7). Comparing the ¹H NMR spectra of rotaxane **3.PF₆** with **2** revealed large upfield perturbation of methylene axle proton H_c, while proton shifts of the macrocycle component (H₃ and H₄) of **3.PF₆** were comparatively small (Figure 1), suggesting that methylation had occurred exclusively on the rotaxane's axle iodotriazole group. This was confirmed by the results of methylation control experiments where the free macrocycle **1** and iodotriazole-bearing axle were separately stirred with iodomethane under identical reaction conditions. Interestingly, while the free axle was found to be readily methylated, macrocycle **1** showed no evidence of any reaction by ESI-MS analysis. Presumably the mutual electron-withdrawing effect of the covalently linked iodotriazole motifs of the macrocycle reduces the nucleophilicity of the iodotriazole nitrogen atoms as compared to the axle's single iodotriazole group. In an effort to increase the rigidity of the rotaxane framework of **3.PF₆**, exotopic rhenium(I) metal complexation to the macrocycle component's bis-iodotriazole

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group was undertaken. An equimolar reaction of $\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2\text{Cl}$ ²⁶ and **3.PF₆** in dichloromethane solution followed by purification using preparative thin-layer silica-gel chromatography afforded the cationic Re(I)-rotaxane **4.PF₆** in 75 % yield (Scheme 1).

The ¹H NMR spectrum of **4.PF₆** (Figure 1) showed several notable differences compared to the precursor metal-free rotaxane **3.PF₆**. Firstly, rhenium metal complexation led to dramatically increased splitting of the macrocycle hydroquinone signals (*H*₁ and *H*₂), implying greater desymmetrisation of both hydroquinone proton environments. In addition, the downfield shift seen for *H*_a, *H*_b and *H*_c of the axle suggests that metal complexation results in conformational changes to the rotaxane framework as well. The increased splitting of the signals arising from the geminal *H*₃ protons of the macrocycle also indicates desymmetrisation, likely due to increased rigidification of the adjacent rhenium metal-complexed bis-iodotriazole moiety.

We have previously integrated the XB pyridinium-3,5-bis(iodotriazole) group into the axle component of [2]rotaxanes via an anion templation protocol.²⁷ Ambitiously, we sought to investigate whether the active metal template procedure could also be utilised for axle incorporation of this potent XB anion recognition motif. The CuAAC click reaction of macrocycle **1** with two equivalents of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$, four equivalents of 3,5-bis(iodoethynyl)pyridine **5** and eight equivalents of terphenyl stopper azide **6** afforded rotaxane **7** in 24% yield (Scheme 2). Of particular note is the observation that the stoichiometry of copper(I) catalyst significantly influenced the rotaxane yield, with a diminution in yield to 5 % observed when 1.0 equivalent of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ was used. Presumably, the various *N*-donor ligating species present in the reaction mixture were able to form coordinatively-saturated complexes with Cu^I when only one equivalent of the metal cation was present, resulting in a loss of the metal's ability to catalyse the active metal template rotaxane-forming reaction. The ¹H NMR spectrum of rotaxane **7** (Figure 2) displays diagnostic macrocycle component hydroquinone upfield shifts compared to free macrocycle **1** (Figure 2) indicative of its mechanically bonded interlocked nature.²⁸ Additional evidence was obtained in the ¹H ROESY NMR spectrum showing multiple through-space interactions between macrocycle and axle protons (see the Supporting Information). Monocationic rotaxane **8.PF₆** was produced by reacting **7** with iodomethane at room temperature in 70 % yield after anion exchange, where exclusive methylation of the most nucleophilic N atom of the axle pyridine group was observed. As seen from Figure 2, axle pyridine methylation led to increased upfield shift and splitting of the hydroquinone proton signals, indicative of enhanced aromatic donor-acceptor interactions with the electron-deficient axle pyridinium motif, as well as increased rigidity owing to hydrogen bonding interactions between the *N*-methyl pyridinium group and the polyether section of the macrocycle.²⁹ Attempts to prepare and isolate the corresponding rhenium(I)-complexed rotaxane analogue by reaction with $\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2\text{Cl}$ were unsuccessful;

numerous Re^I-complexed species were detected in the crude reaction mixture which proved inseparable. This may indicate competing complexation by the potential *N*-ligating iodotriazole units on the rotaxane axle.

Scheme 1. Synthesis of cationic rotaxanes **3.PF₆** and **4.PF₆**

Figure 1. ^1H NMR spectra of a) cationic Re^{I} -rotaxane **4.PF₆**, b) cationic rotaxane **3.PF₆** and c) neutral rotaxane **2** (CDCl_3 , 500 MHz). For atom labels see Scheme 1.

Scheme 2. Synthesis of cationic rotaxane **8.PF₆**.

Anion binding investigations

Halide and oxoanion binding studies were performed using ^1H NMR titration experiments by adding increasing quantities of anions, as their tetrabutylammonium (TBA) salt, to separate solutions of the host rotaxanes **3.PF₆**, **4.PF₆** and **8.PF₆** in 9:1 d_6 -acetone/ D_2O (v/v).

Figure 2. ^1H NMR spectra of a) cationic rotaxane **8.PF₆**, b) neutral rotaxane **7** and c) macrocycle **1** (CDCl_3 , 500 MHz). For proton labels see Scheme 2.

The addition of iodide to rotaxane **3.PF₆** caused upfield signal shifts of the axle triazolium methyl protons (H_d) and macrocycle methylene proton H_3 . In contrast, downfield shifts were observed for H_c on the axle immediately adjacent to the iodotriazolium group (Figure 3), as well as stopper protons H_a and H_b proximal to the interlocked anion binding cavity. This suggests that halide anion binding may be occurring slightly above the plane of the macrocycle. Analogous titrations with bromide elicited similar perturbations of the rotaxane's proton signals, although they were of smaller magnitude. In contrast, no significant shifts were observed on addition of chloride, sulphate and acetate which suggests these anions are not bound by the rotaxane, presumably because they are too strongly hydrated, and in the case of the oxoanions, too large to be encapsulated within the interlocked host cavity as well. Cationic Re^{I} -rotaxane **4.PF₆** showed similar proton signal perturbations to **3.PF₆** upon addition of bromide, however, very small shifts were noted with iodide, chloride and the oxoanions indicative of very weak association.

When rotaxane **8.PF₆** was titrated with TBAI, significant downfield shifts were seen for the internal pyridinium proton H_b , while the external proton H_a showed negligible shifts (Figure 4), implying that the iodide anion guest is bound predominantly in the space flanked by both iodotriazole

Figure 3. ^1H -NMR spectra of cationic rotaxane **3.PF₆** with a) 5.0 equivalents of TBAI present; b) 1.0 equivalent of TBAI; c) no TBAI present (500 MHz, d_6 -acetone/ D_2O = 9:1, 298 K, [host] = 1.0 mM). Proton labels follow those in Scheme 1.

groups on the axle slightly above the macrocycle plane. As seen in Figure 5, bromide and chloride elicited smaller shifts, while oxoanions acetate and sulphate showed no evidence of binding, presumably due to their inability to fit into the interlocked host cavity. WinEQNMR2³⁰ analysis of the halide titration data, monitoring iodotriazolium *N*-methyl proton H_d on the axle for rotaxanes **3.PF₆** and **4.PF₆**, and pyridinium axle proton H_b of **8.PF₆** determined 1:1 stoichiometric association constant values shown in Table 1.

Figure 4. ¹H-NMR of cationic rotaxane **8.PF₆** with a) 5.0 equivalents of TBAI present; b) 1.0 equivalent of TBAI; C) no TBAI present (500 MHz, d₆-acetone/D₂O = 9:1, 298 K, [host] = 1.0 mM). Proton labels follow those in Scheme 2.

In the aqueous solvent mixture of 9:1 d₆-acetone/D₂O, rotaxane **3.PF₆** exhibits Hofmeister bias for halide anion binding, with iodide, the least hydrated halide, showing the largest binding affinity. In stark contrast, Re^I-rotaxane **4.PF₆** exclusively recognises bromide with very weak binding of chloride and iodide; association constant values could not be determined from the titration data for these halides in this competitive aqueous solvent mixture. Importantly, this suggests exotopic rhenium (I) metal complexation of the macrocycle component of the metal-free rotaxane **3.PF₆** results in a preorganised interlocked XB host cavity of complementary size for bromide. The notable enhanced bromide association constant value of $K_a = 436 \text{ M}^{-1}$ with Re(I)-rotaxane **4.PF₆** compared to $K_a = 236 \text{ M}^{-1}$ with **3.PF₆** may also result from augmented XB donor binding strength arising from greater metal-chelated iodotriazole polarisation.^{25§}

In spite of the presence of more XB-donor iodotriazole groups, rotaxane **8.PF₆** shows weaker bromide and iodide binding affinities compared to **3.PF₆** which may be attributed to a combination of a more spatially-restricted binding site due to greater numbers of bulky iodine atoms as well as the potentially reduced electrophilicity of the axle component's pyridinium-3,5-bis(iodotriazole) motif of **8.PF₆** compared to the isolated iodotriazolium functionalised axle moiety of **3.PF₆**.³¹ Nevertheless, the importance of host-guest geometric complementarity can be clearly seen by the contrasting halide selectivity trend of **8.PF₆** (iodide > chloride > bromide) with the Hofmeister halide selectivity preference of **3.PF₆**. In particular,

comparing the chloride binding behaviours of rotaxanes **3.PF₆** and **8.PF₆**, the former rotaxane shows no detectable binding, whereas rotaxane **8.PF₆** binds chloride with a modest preference over bromide. In spite of the tightly-bound hydration shell of chloride, the interlocked XB binding site cavity of **8.PF₆** is able to compete and bind the halide guest. It is noteworthy that Re(I)-rotaxane **4.PF₆** displays no chloride binding affinity, suggesting that binding site structural preorganisation needs to be allied to an ideal geometrically-complementary host-guest match for effective binding of highly-hydrated anions to occur.

Figure 5. Binding isotherms of anion titrations for cationic rotaxane **8.PF₆** with different halide anions. The chemical shift of the pyridinium proton *b* of the axle component is plotted as a function of equivalents of TBA salts added. (500 MHz, d₆-acetone/D₂O = 9:1, 298 K, [host] = 1.0 mM).

Table 1 Association constants, K_a (M^{-1}), for cation rotaxanes **3.PF₆**, **4.PF₆** and **8.PF₆** with various halide anions^a

Rotaxane	Anions		
	Cl ⁻	Br ⁻	I ⁻
3.PF₆	- ^b	236(16)	377(3)
4.PF₆	- ^b	436(25)	- ^b
8.PF₆	112(4)	94(4)	256(5)

^a Anions added as their TBA salts, temperature = 298 K, solvent: d₆-acetone/D₂O = 9:1, 298 K, values quoted have units of M^{-1} . The errors associated with each (< 10%) are quoted in parentheses. SO₄²⁻ and acetate did not bind to any of the rotaxanes investigated. ^b Signal shifts too small for association constant determination suggesting very weak binding.

Conclusions

A series of novel cationic all-XB [2]rotaxanes containing either three or four XB-donor groups within the binding cavity have been synthesised via an active-metal template synthetic strategy. ¹H NMR anion titration experiments revealed that the rotaxanes exhibit halide selectivity over oxoanions such as

sulphate and acetate in competitive organic-aqueous solvent media due to a combination of interlocked host–guest size complementarity and anion hydration effects. Importantly, increased rotaxane preorganisation via rhenium (I) metal complexation and varying the number and nature of the axle component XB donor groups has a dramatic effect on halide selectivity trends. For example Re(I)-rotaxane **4.PF₆** exclusively recognises bromide whereas the corresponding metal-free rotaxane **3.PF₆** displays Hofmeister bias halide selectivity. Manipulating the structure and geometry of XB donor binding sites of mechanically-interlocked hosts to further expand the repertoire of anion selectivity is continuing in our laboratories.

Experimental

General Information

All commercially available chemicals and solvents were used as received without further purification. All dry solvents were thoroughly degassed with N₂, dried through a Mbraun MPSP-800 column and used immediately. Water used was deionized and passed through a Milli-Q[®] Millipore machine for microfiltration. Amberlite[®] was prepared by washing the commercial resin beads sequentially with 10 % NaOH (aq), water, 0.1 M NH₄PF₆ (aq), further water, and finally loaded with 0.1 M NH₄PF₆ (aq) before any anion exchange to the PF₆[−] salt occurred.

NMR spectra were recorded on Bruker AVIII HD Nanobay 400 MHz, Bruker AVIII 500 MHz and Bruker AVIII 500 MHz (with ¹³C cryoprobe) spectrometers. Low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed using the Waters Micromass LCT for characterisation of compounds previously reported in the literature, and high resolution ESI-MS was recorded using Bruker microTOF spectrometer for novel compounds.

Rotaxane 3

To a solution of neutral rotaxane **2** (8 mg, 0.004 mmol) in 1 mL CHCl₃ was added CHI₃ (30 mg, 0.21 mmol) and stirred at 30°C until all the starting material was consumed. The solvent was removed and purified through preparative silica plate (5% MeOH/CH₂Cl₂). Anion exchange of the purified product to the PF₆[−] salt was achieved by washing a chloroform solution of the product with 0.1 M NH₄PF₆ (10 x 20 mL). Solvent removal then afforded the product as a white solid (6.4 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ(ppm) 7.26–7.22 (12H, m, stopper-ArH), 7.18–7.11 (16H, m, stopper-ArH), 6.77 (2H, d, ³J=8.7 Hz, stopper-ArH), 6.66 (2H, d, ³J=8.7 Hz, stopper-ArH), 6.37 (4H, d, ³J=9.2 Hz, hydroquinone ArH), 6.35 (4H, d, ³J=9.2 Hz, hydroquinone ArH), 4.89 (4H, m, CH₂), 4.47 (2H, s, CH₂), 4.26 (4H, m, CH₂), 3.95 (3H, s, CH₃), 3.82–3.40 (20H, m, CH₂), 1.80 (4H, quintet, ³J=6.8 Hz, CH₂), 1.32 (27H, s, C(CH₃)₃), 1.31 (27H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ(ppm) 156.1, 154.5, 152.7, 151.8, 148.3, 144.1, 144.0, 141.7, 140.1, 130.6, 124.2, 124.1, 115.0, 114.9, 113.2, 88.9, 78.5, 70.6, 70.0, 67.7, 67.1,

63.1, 57.9, 51.5, 50.2, 39.3, 34.3, 31.4, 29.7, 27.7; HRMS (ESI +ve) m/z=2089.6969 ([M–PF₆]⁺, C₁₀₉H₁₂₉O₉N₉I₃, calc. 2089.7075).

Rotaxane 4

Re(CO)₅Cl (1.7 mg, 0.0048 mmol) was heated at reflux in dry CH₃CN (4 mL) for 3 hrs, before the solvent was removed in vacuo and the residue redissolved in dry CH₂Cl₂ (2 mL). This solution was added to a solution of Rotaxane **2** (9 mg, 0.0043 mmol) in dry CH₂Cl₂ (2 mL) and stirred at room temperature under N₂ for 16 hrs. The solvent was removed in vacuo and the cationic Re-rotaxane product was isolated as a white solid (7 mg, 75% yield) after purification by preparative silica plate (3% MeOH/CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ(ppm) 7.26–7.20 (12H, m, stopper-ArH), 7.16–7.13 (16H, m, stopper-ArH), 6.92 (2H, d, ³J=8.3 Hz, stopper-ArH), 6.86 (2H, d, ³J=8.3 Hz, stopper-ArH), 6.69 (4H, d, ³J=8.6 Hz, hydroquinone ArH), 6.33 (4H, d, ³J=8.6 Hz, hydroquinone ArH), 5.04–4.89 (4H, m, CH₂), 4.73 (2H, s, CH₂), 4.41 (3H, s, CH₃), 4.29 (4H, m, CH₂), 3.94–3.04 (20H, m, CH₂), 2.59 (4H, m, CH₂), 1.32 (27H, s, C(CH₃)₃), 1.31 (27H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ(ppm) 195.2, 156.2, 155.0, 152.7, 152.0, 148.4, 145.2, 144.1, 142.3, 141.6, 140.9, 132.9, 132.3, 130.7, 130.6, 124.2, 115.7, 114.7, 113.3, 70.9, 70.6, 70.1, 68.5, 67.1, 63.2, 57.3, 52.0, 39.6, 34.3, 31.4, 29.7, 26.7; HRMS (ESI +ve) m/z=2395.6064 ([M–PF₆]⁺, C₁₁₂H₁₂₉O₁₂N₉Cl₃Re, calc. 2395.6169).

Rotaxane 5

To a solution of macrocycle **1** (20 mg, 0.024 mmol) in dry DCM (2.4 mL) under N₂ was added Cu(CH₃CN)₄PF₆ (18 mg, 0.048 mmol) and stirred for 5 minutes. Stopper azide (112 mg, 0.192 mmol) and 3,5-bisiodoalkyne pyridine (36 mg, 0.096 mmol) were added and the solution stirred at room temperature for 96 hours. The reaction mixture was dilute with CHCl₃ (20 mL) and washed with EDTA (0.02 M in 1 M NH₄OH aq, 10 mL x 2), water (5 mL) and then dried with MgSO₄. After preparative silica plate (3% MeOH/DCM), the rotaxane was gained as a white solid (14 mg, 24% yield). ¹H NMR (500 MHz, CDCl₃) δ(ppm) 9.23 (2H, s, pyridine-ArH), 8.77 (1H, s, pyridine-ArH), 7.26–7.24 (12H, d, ³J=9.0 Hz, stopper-ArH), 7.13–7.11 (16H, d, ³J=9.0, stopper-ArH), 6.68 (4H, d, ³J=8.7 Hz, stopper-ArH), 6.37 (4H, d, ³J=9.0 Hz, hydroquinone ArH), 6.33 (4H, d, ³J=9.0 Hz, hydroquinone ArH), 4.86 (4H, t, ³J=4.2 Hz, CH₂), 4.24 (4H, t, ³J=4.2 Hz, CH₂), 4.17 (4H, t, ³J=5.9 Hz, CH₂), 3.78–3.63 (20H, m, CH₂), 2.02 (4H, quintet, ³J=5.9 Hz, CH₂), 1.32 (54H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ(ppm) (ppm) 156.3, 153.0, 151.8, 148.3, 144.2, 141.9, 139.8, 132.3, 132.2, 130.7, 124.1, 114.9, 114.9, 113.1, 79.3, 70.7, 70.6, 69.5, 67.6 67.3, 64.0, 63.1, 50.2, 47.9, 34.3, 31.4, 29.7, 29.4, 22.7, 14.1; HRMS (ESI +ve) m/z=2373.6608 ([M+H]⁺, C₁₁₇H₁₃₄O₉N₁₃I₄, calc. 2373.6634).

Rotaxane 6

To a solution of rotaxane **5** (10 mg, 0.004 mmol) in dry DCM (1 mL) was added CH₃I (3 mg, 0.02 mmol). The reaction mixture was stirred overnight. The solvent was removed to afford the rotaxane I[−] salt. Anion exchange of the product to the PF₆[−] salt was achieved by washing a chloroform solution of the product with 0.1 M NH₄PF₆ (10 x 20 mL). Solvent removal then afforded the product as a white solid. (7 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ(ppm) 9.35 (2H, s, pyridine-ArH), 8.29 (1H, s, pyridine-ArH), 7.21 (12H, d, ³J=8.7, stopper-ArH), 7.15 (4H, d, ³J=8.7, stopper-ArH), 7.08 (12H, d, ³J=8.7, stopper-ArH), 6.88 (4H, d, ³J=8.7 Hz, stopper-ArH), 6.26 (4H, d, ³J=9.0 Hz, hydroquinone ArH), 5.95 (4H, d, ³J=9.0 Hz, hydroquinone ArH), 4.77 (4H, t, ³J=4.4 Hz, CH₂), 4.65 (3H, s, CH₃), 4.61 (4H, t, ³J=7.1 Hz, CH₂), 4.11 (8H, m, CH₂), 3.73–3.45 (16H, m, CH₂), 2.49 (4H, quintet, ³J=6.2 Hz, CH₂), 1.31 (54H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ(ppm) 156.4, 152.6, 152.0, 148.4, 144.1, 142.3, 142.2, 141.7, 140.2, 133.5, 132.4, 130.7, 130.5, 124.1, 116.2, 115.2, 114.4, 113.2, 81.3, 79.9, 70.9, 69.9, 67.6, 67.4, 64.1, 63.1, 50.3, 49.0, 48.3, 41.0, 34.3, 31.9, 31.4, 29.7, 22.7, 14.1; HRMS (ESI +ve) m/z 2387.6802 ([M-PF₆]⁺, C₁₁₈H₁₃₆O₉N₁₃I₄, calc. 2387.6790).

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Notes and references

§ Rotaxane **4**.PF₆ is not luminescent so anion sensing studies could not be undertaken.

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