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PAPER

A *meta*-xylenediamide macrocycle containing rotaxane anion host system constructed by a new synthetic clipping methodology†‡

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A novel rotaxane containing a *meta*-xylenediamide macrocycle is prepared by a new clipping methodology. Upon anion metathesis to the non-coordinating hexafluorophosphate salt, the rotaxane host system was shown to bind chloride and bromide anions more strongly than the basic oxoanions dihydrogen phosphate and acetate in the competitive solvent system 1 : 1 $CDCl_3 : CD_3OD$.

Introduction

The desire to recognise negatively charged species of biological, medical and environmental importance is a major contributory factor in the current intense research interest being shown in anion supramolecular chemistry.[1] Within this very diverse field, the use of interlocked molecules, such as rotaxanes and catenanes, to achieve anion recognition is beginning to gather pace. Possessing unique topologically constrained cavities, these molecules have the potential to demonstrate selectivity in the binding of anionic guests,[2] and a number of research groups have now reported on the anion binding properties of such species.[3–7] Our first anion binding [2]rotaxanes consisted of a *N*-methyl pyridinium axle penetrating through an isophthalamide macrocycle. Each of these rotaxanes were prepared by "clipping" a chloride anion templated orthogonal assembly of axle and bis-vinyl functionalised macrocycle precursor components using Grubbs' catalyst. Upon removal of the chloride anion template these host systems demonstrated notable selectivity for chloride over more basic oxoanions.[8]

We have since set out to adapt and improve such interlocked host systems. Chloride[9,10] and sulfate[11] selective catenanes have been constructed, as well as a ferrocene-appended redox-active rotaxane capable of electrochemical anion sensing.[12] Impressive selectivity for bromide over chloride has been demonstrated in a rotaxane containing a triazolium axle[13] and, very recently, we reported the preparation of a dicationic rotaxane able to bind chloride in solvent mixtures containing 35% water.[14] Notably, this rotaxane was prepared *via* an alternative clipping synthetic route which did not use Grubbs' catalyst.[15] The exclusion of Grubbs' catalyst is attractive for a number of reasons, for example its incompatibility with certain chemical functionalities, and its not inconsiderable expense.

In this paper we report the preparation of a novel [2]rotaxane host system, containing a *meta*-xylenediamide macrocycle, that creates a yet to be investigated interlocked hydrogen bond donating cavity. The rotaxane is synthesized *via* a new clipping condensation methodology, which does not employ Grubbs' catalyst, and has been characterized by

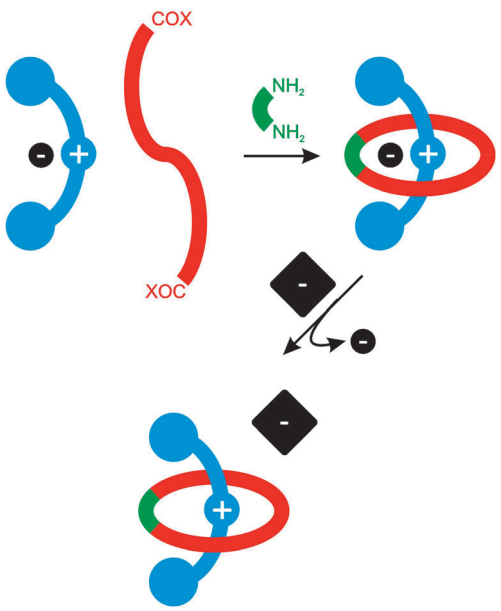

Fig. 1 Schematic representation of the preparation of the target xylene rotaxane anion host system.

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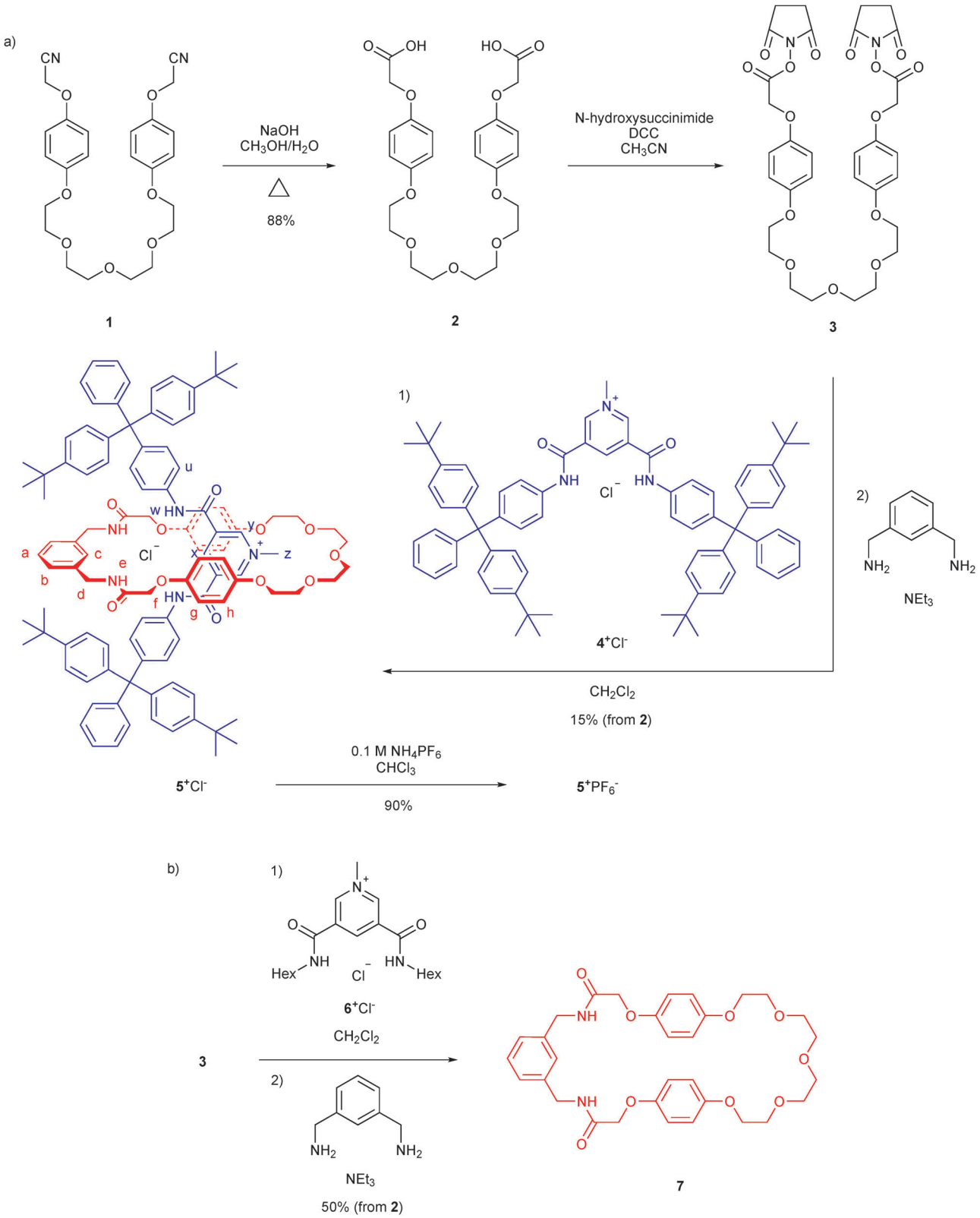
† Dedicated to Prof. Didier Astruc on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Copies of NMR and HRMS of novel compounds; crystallographic data for structure of rotaxane $\mathbf{5}^{+}Cl^{-}$, CCDC reference number 813286, and the protocol and further data from the ^{1}H NMR titrations. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20109c

NMR spectroscopy, electrospray mass spectrometry, and by the determination of a crystal structure. Anion recognition studies on the hexafluorophosphate salt of the rotaxane in the competitive 1:1 $CDCl_3:CD_3OD$ solvent system reveal the interlocked host's ability to bind chloride and bromide anions selectively in preference to basic oxoanions.



Scheme 1 Synthesis of rotaxane $\mathbf{5}^+X^-$ ($X^- = Cl^-, PF_6^-$) and xylenediamide macrocycle **7**.

Results and discussion

Design, synthesis and characterization

The target rotaxane was prepared *via* a modification of a previously reported rotaxane synthesis[15] but with the reversal of amine and activated carboxylic acid functionalities of the macrocyclic precursor components (Fig. 1).

To an equimolar mixture of an activated dicarboxylic acid macrocycle precursor and a *N*-methyl pyridinium chloride axle, an equivalent of *meta*-xylene diamine is added, which results in formation of the macrocyclic component of the rotaxane.§ Exchange of the chloride anion for a non-coordinating anion affords the anion binding host.

The actual synthesis of rotaxane $\mathbf{5}^{+}X^{-}$ (X^{-} = Cl^{-} or PF_6^{-}) is provided in Scheme 1. Dicarboxylic acid **2** was prepared by the alkaline hydrolysis of dinitrile **1**.[16] This was subsequently activated for amide formation by preparation of diester **3** utilising DCC and *N*-hydroxysuccinimide.¶ Diester **3** was then dissolved in dry CH_2Cl_2 with one equivalent of axle $\mathbf{4}^{+}Cl^{-}$. Upon complete dissolution of the two components, a slight excess of dry NEt_3 was added followed immediately by one equivalent of *meta*-xylenediamine.

The resulting crude reaction mixture was purified by thin layer preparative silica gel chromatography. Repeated running of plates was required due to the presence of the free macrocyclic component **7**, which was only marginally less polar than the rotaxane. The final isolated yield of the xylenediamide macrocycle containing rotaxane was 15% (from dicarboxylic acid **2**). Macrocycle **7** was prepared in an equivalent reaction, using unstoppered thread $\mathbf{6}^{+}Cl^{-}$ (see Scheme 1) in a yield of 50%.

Comparison of the ^{1}H NMR spectra of rotaxane $\mathbf{5}^{+}Cl^{-}$ with those of its component macrocycle **7** and axle $\mathbf{4}^{+}Cl^{-}$, indicate the interlocked nature of $\mathbf{5}^{+}Cl^{-}$ (Fig. 2). The upfield shifts of the axle cavity protons *x* and *w*, and the downfield shifts of the macrocycle cavity protons *c* and *e*, in the rotaxane compared to the free components are indicative of competitive hydrogen bonding to the chloride anion. The splitting and upfield shifts of hydroquinone protons *g* and *h* are attributed to favourable π–π stacking between the macrocycle hydroquinone motifs and the pyridinium group of the axle. In addition, hydrogen bonding of the axle's *N*-methyl pyridinium group to the polyether oxygens of the macrocycle can be inferred by the downfield shift of resonance *z*.

Further evidence to support the interlocked nature of the rotaxane was noted by the presence of intercomponent through-space peaks in the 2D ^{1}H NMR ROESY spectrum and a monocationic peak at $m/z \sim 1634.86$ in the electrospray HRMS, attributable to the organic fragment $\mathbf{5}^{+}$.

Incontrovertible proof of the interlocked nature of the chloride salt of the rotaxane was provided by elucidation of a crystal structure (Fig. 3). Crystals of the rotaxane suitable for X-ray diffraction structural determination were grown by slow diffusion of diisopropyl ether into a chloroform solution of the rotaxane, and data were collected using synchrotron radiation at Diamond Light Source beamline I19. While both axle amide protons participate in hydrogen bonding to the chloride anion (both with N(H)···Cl distances of 3.332(5) Å), only one of the macrocycle amide protons does, with an N(H)···Cl hydrogen bond length of 3.278(7) Å. The other macrocycle nitrogen resides at distance of 4.395(6) Å away, with an N–H···Cl angle of 138.9°. This is in contrast to the rotaxane's isophthalamide analogue $\mathbf{8}^{+}Cl^{-}$[14] (depicted in Fig. 4) where hydrogen bonding of both macrocyclic amide protons to the chloride anion are observed in the solid state. Comparing the ^{1}H NMR spectra of the two rotaxanes (Fig. 5a and b) reveals that while the resonances for the axle cavity

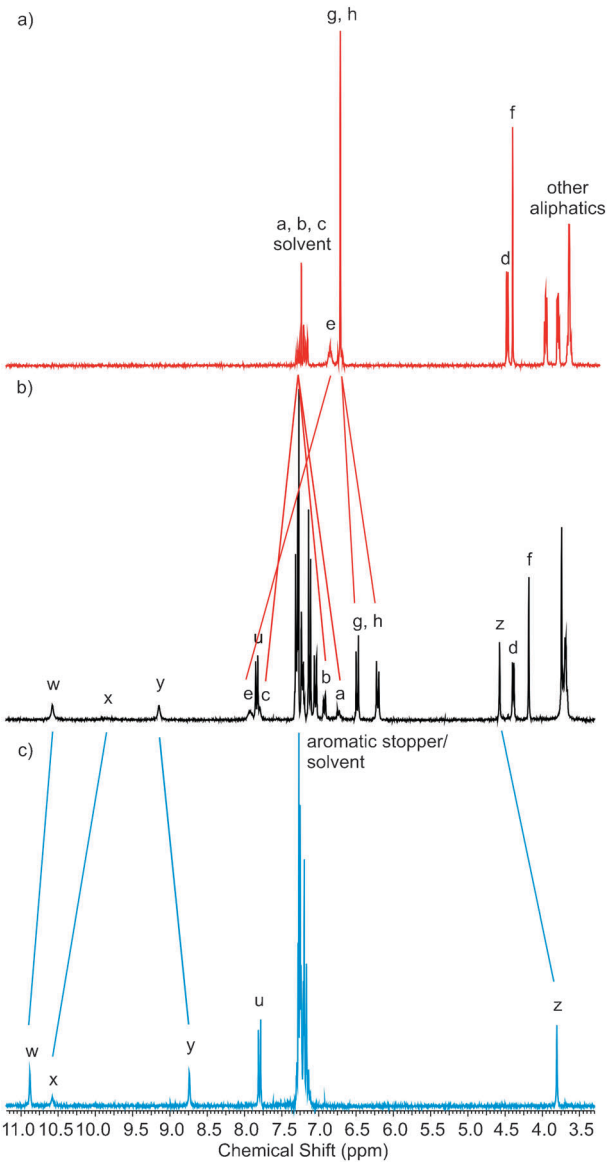


Fig. 2 Partial ^{1}H NMR spectra of (a) macrocycle **7** (b) rotaxane $\mathbf{5}^{+}Cl^{-}$ and (c) axle $\mathbf{4}^{+}Cl^{-}$. Significant peak shifts are highlighted. Solvent: $CDCl_3$, T: 293 K. For atom labels see Scheme 1.

§ It is proposed that after formation of the first amide that the chloride anion will hydrogen bond to this newly created functionality. By being also strongly bound to the positively charged axle component, the chloride anion will thus template the components, such that upon formation of the second amide, the axle is trapped within the macrocycle to produce the target rotaxane.

¶ Attempts to activate **2** to the bis-acid chloride by use of thionyl chloride often failed, suggesting the bis-acid chloride can be unstable under the experimental conditions used.

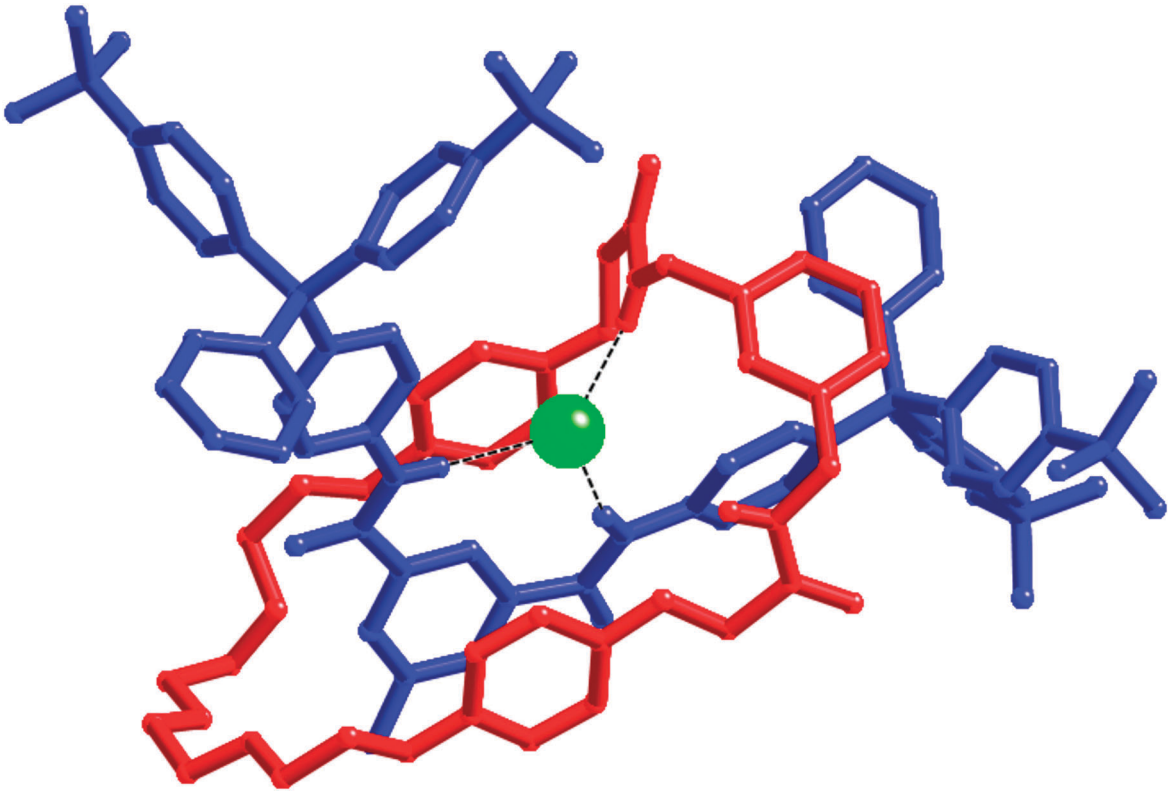


Fig. 3 X-Ray crystal structure of rotaxane $\mathbf{5}^{+}Cl^{-}$. Hydrogen bonding interactions to chloride anion are highlighted.

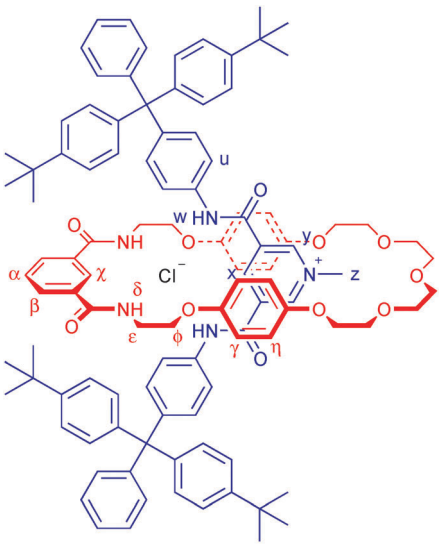


Fig. 4 Isophthalamide rotaxane analogue $\mathbf{8}^{+}Cl^{-}$.[14]

protons *w* and *x* have almost identical chemical shift in the two rotaxanes, those for the macrocycle cavity protons *c*/χ and *e*/δ are dramatically less downfield for the xylenediamide macrocycle containing rotaxane.

Washing a chloroform solution of rotaxane $\mathbf{5}^{+}Cl^{-}$ with an aqueous solution of NH_4PF_6 removed the halide anion and afforded the anion host system $\mathbf{5}^{+}PF_6^{-}$ (see Scheme 1). Inspection of the ^{1}H NMR spectrum (Fig. 5c) reveals upfield shifts of the cavity protons *c*, *e*, *w* and *x* compared to $\mathbf{5}^{+}Cl^{-}$ consistent with loss of the hydrogen-bond accepting chloride anion from the rotaxane cavity. Crucially the hydroquinone resonances *g* and *h* remain upfield and split, indicating that π–π stacking between the pyridinium and hydroquinone rings has been retained and that the rotaxane has remained interlocked upon anion exchange. Further evidence is provided by the appearance of through-space intercomponent cross-couplings in the 2D ^{1}H NMR ROESY spectrum and the molecular ion peak in HRMS (see ESI‡).

Anion binding investigations

The anion binding properties of rotaxane $\mathbf{5}^{+}PF_6^{-}$ were investigated by ^{1}H NMR titration experiments in the competitive 1 : 1 $CDCl_3$: CD_3OD solvent system. To samples of the rotaxane, aliquots of tetrabutylammonium (TBA) salts of various anions were added and NMR spectra recorded.

Table 1 1 : 1 Anion association constants, *K* (M^{-1}), of rotaxane $\mathbf{5}^{+}PF_6^{-}$[a]

Anion	K/M^{-1}
Cl^-	810
Br^-	1070
$H_2PO_4^-$	645
OAc^-	285

[a] Anions added as TBA salts. Solvent: 1 : 1 $CDCl_3$: CD_3OD. T = 293 K. Association constants, *K*, calculated using the chemical shifts of *ortho*-pyridinium proton *y* in conjunction with the computer program winEQNMR2, errors < 10%.

Perturbations in the chemical shift of various cavity protons were observed, indicative of anion binding by the rotaxane (see Fig. 6). The process of anion association being fast on the NMR timescale allowed for the calculation of association constants, K, for each proton by the computer program winEQNMR2,[17] with data fitting to a 1 : 1 binding model. Values of K calculated from the chemical shift titration data of *ortho*-pyridinium proton y are provided in Table 1.‖

As observed in the isophthalamide analogue $\mathbf{8}^{+}PF_6^{-}$,[14] chloride is bound more strongly than the more basic oxoanions $H_2PO_4^{-}$ and OAc^{-} by rotaxane $\mathbf{5}^{+}PF_6^{-}$. This is attributed to only chloride being able to penetrate the interlocked cavity, whereas the larger oxoanions associate at the periphery of the rotaxane. Evidence to support this theory is provided by the lack of shift in cavity proton c and by the upfield shift in proton x for the oxoanions, in contrast to the downfield shifts of these resonances upon the addition of chloride. The binding of bromide by the rotaxane is intriguing. It is bound stronger than chloride, which may be rationalized by consideration of the crystal structure of $\mathbf{5}^{+}Cl^{-}$, which suggests that a larger monoatomic anion (such as bromide) may be able to participate in greater hydrogen bonding to the array of hydrogen bond donors in the rotaxane host's cavity. The upfield shift of cavity proton x upon addition of bromide is difficult to account for.

The association constants for Cl^{-}, $H_2PO_4^{-}$ and OAc^{-} show that these anions are bound more weakly by rotaxane $\mathbf{5}^{+}PF_6^{-}$ than by the analogous isophthalamide rotaxane $\mathbf{8}^{+}PF_6^{-}$, especially after considering that binding studies with the latter host system were carried out in the much more competitive solvent system 45 : 45 : 10 $CDCl_3$: CD_3OD : D_2O.[14] In the case of chloride—which is bound within the cavity—this may be rationalized by the consideration of the crystal structures, where greater hydrogen bonding is seen in the isophthalamide rotaxane $\mathbf{8}^{+}Cl^{-}$ than in the xylenediamide rotaxane $\mathbf{5}^{+}Cl^{-}$. More generally, the macrocyclic amides of $\mathbf{5}^{+}PF_6^{-}$ are not conjugated to the aromatic ring meaning they are less acidic and so are intrinsically poorer hydrogen bond donors than those in rotaxane $\mathbf{8}^{+}PF_6^{-}$.

Conclusions

We have successfully synthesized a novel *meta*-xylenediamide macrocycle containing rotaxane *via* a new clipping methodology. Upon exchange to the hexafluorophosphate salt, the rotaxane was shown to bind a range of anions in the competitive solvent mix 1 : 1 $CDCl_3$: CD_3OD. Chloride and bromide are bound more strongly than the more basic oxoanions dihydrogen phosphate and acetate. This is attributed to only the monoatomic halides being able to penetrate the cavity of the rotaxane, while the polyatomic oxoanions hydrogen bond peripherally. Work towards constructing further anion binding interlocked structures with alternative motifs is in progress in our laboratories.

‖ For each anion reasonable agreement was observed in the values of K calculated from the chemical shifts of protons y, x and c, provided there was a significant shift in the proton signal. See the ESI for a full set of calculated association constants.†

Experimental

General

Commerically available solvents and chemicals were used without further purification unless stated. Where dry solvents were used, they were degassed with nitrogen, dried by passing through a MBraun MPSP-800 column and then used immediately. Deionised water was used in all cases. Triethylamine was distilled from and stored over potassium hydroxide.

NMR spectra were recorded on Varian Mercury 300, Varian Unity Plus 500 and Bruker AVII 500 (with ^{13}C Cryoprobe) spectrometers. Mass spectra were carried out on Waters Micromass LCT, Waters GCT, Bruker micrOTOF and Bruker FT–IR spectrometers. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected.

Synthesis

Compounds **1**,[16] $\mathbf{4}^{+}Cl^{-}$,[8a] $\mathbf{6}^{+}Cl^{-}$[18] and $\mathbf{8}^{+}X^{-}$ (X^{-} = Cl^{-}, PF_6^{-})[14] have been reported previously. The activated diester **3** was prepared when needed and used immediately, and was not fully characterized (^1H NMR and low resolution mass spectra may be found in ESI‡).

Dicarboxylic acid 2. To dinitrile **1** (1.00 g, 2.19 mmol) suspended in CH_3OH (20 mL), was added NaOH (5.26 g, 131 mmol) in H_2O (20 mL). The reaction mixture was heated to reflux for 16 h, cooled to 0 °C, then acidified with 3 M $HCl_{(aq)}$ until pH 2. The CH_3OH was then removed *in vacuo*. The resulting white precipitate was filtered, washed with H_2O and dried on a high vacuum line to give the product as a white solid (0.95 g, 88%). Mp = 128–130 °C; δ_H(300 MHz, d_6-DMSO): 12.94 (2H, s, COO*H*), 6.80–6.87 (8H, m, Ar*H*), 4.58 (4H, s, OCH_2CO), 3.98–4.01 (4H, m, CH_2), 3.68–3.71 (4H, m, CH_2), 3.52–3.59 (8H, m, 2 × CH_2); δ_C(75 MHz, d_6-DMSO): 170.4, 152.9, 151.9, 115.3, 115.3 (sic), 69.9, 69.8, 69.0, 67.5, 65.0; m/z: (ES) 512.2134 ($[M + NH_4]^+$, $C_{24}H_{34}NO_{11}$ requires 512.2126).

Rotaxane $\mathbf{5}^{+}Cl^{-}$. To a suspension of diacid **2** (113 mg, 0.228 mmol) in dry CH_3CN (10 mL) was added *N*-hydroxysuccinimide (63 mg, 0.546 mmol) and DCC (103 mg, 0.501 mmol), with the resulting reaction mixture being stirred for 16 h under N_2. The resulting DCC urea was filtered, the solvent removed *in vacuo* and the activated diester **3** taken on assuming to be quantitatively formed. The activated diester **3** (157 mg, 0.228 mmol) and axle $\mathbf{4}^{+}Cl^{-}$ (245 mg, 0.228 mmol) were added to dry CH_2Cl_2 (50 mL) and stirred for 30 min under a N_2 atmosphere. To the resulting solution NEt_3 (58 mg, 79 μL, 0.569 mmol) and *meta*-xylenediamine (31 mg, 30 μL, 0.228 mmol) were added, and the reaction stirred under N_2 for 16 h. The reaction mixture was then washed with 3 M $HCl_{(aq)}$ (2 × 50 mL) and H_2O (1 × 50 mL), the organic layer dried ($MgSO_4$) and solvent removed *in vacuo*. The crude material was purified by silica gel prep TLC plates (CH_2Cl_2 : CH_3OH 97 : 3 then repeatedly 98 : 2) to give the product as a yellow solid (56 mg, 15% from **2**). Mp = 190–200 °C (phase transition); δ_H(300 MHz, $CDCl_3$): 10.58 (2H, s, pyridinium N*H*), 9.83 (1H, br s, pyridinium ArH^4), 9.15 (2H, s, pyridinium ArH^2 & H^5),

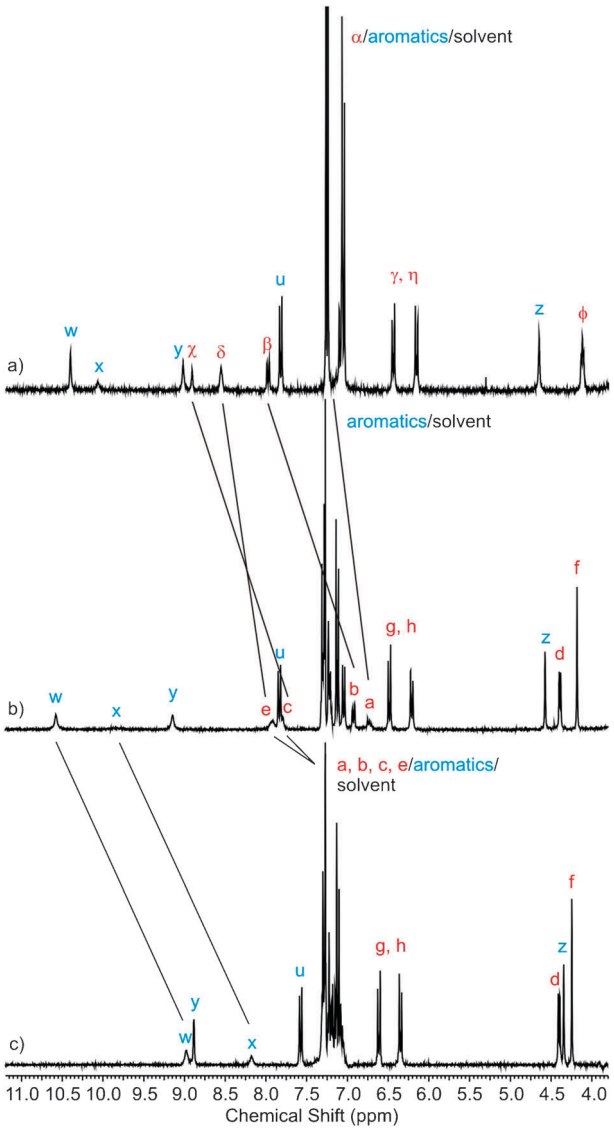


Fig. 5 Partial ^{1}H NMR spectra of (a) isophthalamide rotaxane $\mathbf{8}^{+}Cl^{-}$[14] (b) xylenediamide rotaxane $\mathbf{5}^{+}Cl^{-}$ and (c) xylenediamide rotaxane $\mathbf{5}^{+}PF_6^{-}$. Significant peak shifts are highlighted. Solvent: $CDCl_3$, T: 293 K. For atom labels see Scheme 1.

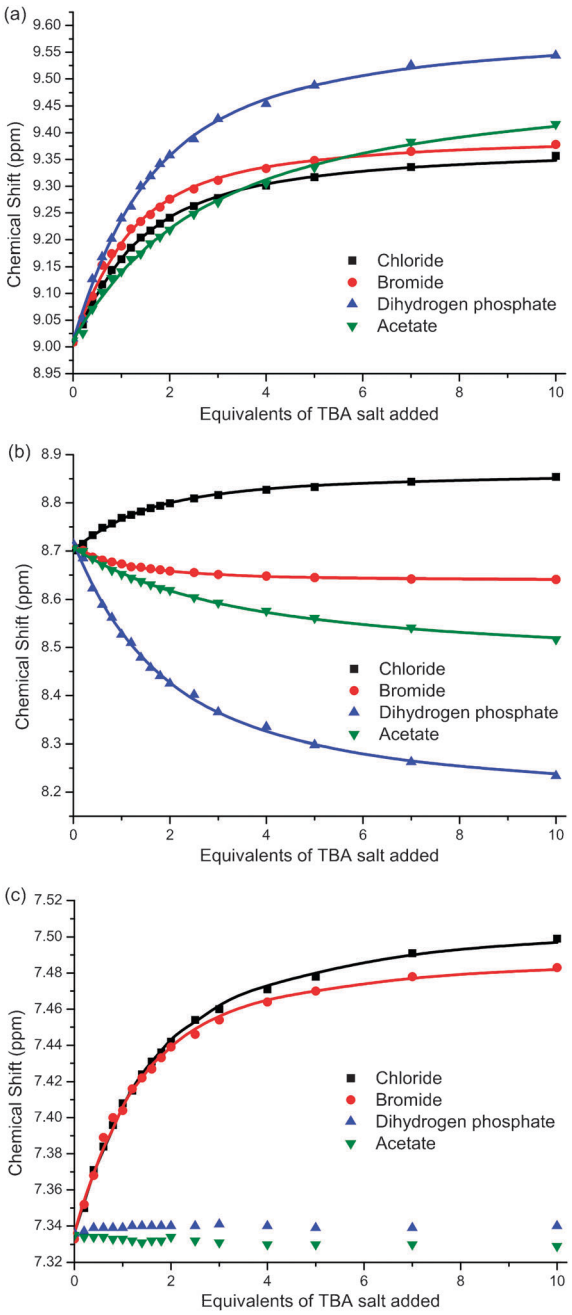


Fig. 6 Plots of chemical shift of (a) *ortho*-pyridinium proton *y* and (b) *para*-pyridinium proton *x* and (c) internal xylyl cavity proton *c* of rotaxane $\mathbf{5}^{+}PF_6^{-}$ *versus* equivalents of TBA salt added. Solvent: 1 : 1 $CDCl_3$: CD_3OD, T: 293 K.

7.92 (2H, app s, xylyl NH), 7.84 (4H, d, ^{3}J = 8.5 Hz, stopper ArH), 7.79 (1H, s, xylyl ArH^{2}), 7.03–7.32 (30H, m, stopper ArH), 6.92 (2H, d, ^{3}J = 7.9 Hz, xylyl ArH^{4} & H^{6}), 6.73 (1H, t, ^{3}J = 7.9 Hz, xylyl H^{2}), 6.48 (4H, d, ^{3}J = 8.8 Hz, hydroquinone ArH), 6.21 (4H, d, ^{3}J = 8.8 Hz, hydroquinone ArH), 4.57 (3H, s, $N^{+}CH_3$), 4.39 (4H, d, ^{3}J = 5.9 Hz, CH_2NH), 4.18 (4H, s, $C(O)CH_2$), 3.67–3.74 (16H, m, 4 × OCH_2), 1.34 (36H, s, $(CH_3)_3$); δ_C(125.8 MHz, $CDCl_3$): 167.8, 158.4, 152.6, 152.3, 148.4, 147.0, 145.3, 144.3, 143.6, 137.9, 135.4, 133.5, 131.8, 131.2, 130.8, 128.4, 127.7, 127.4, 125.8, 124.3, 119.5, 116.0, 114.6, 70.7, 70.7 (sic), 70.1, 68.7, 68.0, 63.9, 49.0, 43.0, 34.3, 31.4 (1 ArC missing); *m*/*z*: (ES) 1634.8687 ($[M–Cl]^{+}$, $C_{106}H_{116}N_5O_{11}$ requires 1634.8666).

Rotaxane $\mathbf{5}^{+}PF_6^{-}$. A solution of rotaxane $\mathbf{5}^{+}Cl^{-}$ (56 mg, 0.0335 mmol) in $CHCl_3$ (15 mL) was washed with 0.1 M $NH_4PF_{6(aq)}$ (10 × 10 mL), then H_2O (3 × 10 mL). The organic layer was dried ($MgSO_4$) and then the solvent removed to give the product as a yellow solid. (54 mg, 90%). Mp = 120–140 °C (phase transition), at 240 °C decomposition); δ_H(300 MHz, $CDCl_3$): 8.98 (2H, br s, pyridinium NH), 8.89 (2H, s, pyridinium ArH^{2} & H^{5}), 8.18 (1H, s, pyridinium ArH^{4}), 7.57 (4H, d, ^{3}J = 8.8 Hz, stopper ArH), 7.05–7.32 (34H, m, xylyl ArH^{2}, H^{4}, H^{5} & H^{6} xylyl NH & stopper ArH), 6.61 (4H, d, ^{3}J = 8.8 Hz, hydroq ArH), 6.34 (4H, d, ^{3}J = 8.8 Hz, hydroquione ArH), 4.40 (4H, d, ^{3}J = 5.9 Hz, CH_2NH), 4.35 (3H, s, $N^{+}CH_3$), 4.25 (4H, s, $C(O)CH_2$), 3.70–3.73 (12H, m, 3 × OCH_2), 3.49–3.51 (4H, m, OCH_2), 1.33 (36H, s, $(CH_3)_3$);

δ_C(125.8 MHz, $CDCl_3$): 168.2, 158.6, 152.3, 152.3 (sic), 148.6, 146.9, 144.7, 144.5, 143.5, 138.6, 134.9, 134.1, 132.0, 131.1, 130.7, 128.9, 127.7, 127.4, 126.6, 125.9, 124.3, 119.0, 116.5, 114.7, 70.8, 70.5, 70.2, 68.6, 67.3, 63.8, 48.9, 42.8, 34.3, 31.4. δ_F (282.4 MHz, $CDCl_3$): −70.6 (d, ^1J = 713 Hz, PF_6^-); δ_P(121.5 MHz, $CDCl_3$) δ: −144.1 (septet, ^1J = 713 Hz, PF_6^-). m/z: (ES) 1634.8726 ($[M–PF_6]^+$, $C_{106}H_{116}N_5O_{11}$ requires 1634.8666).

Macrocycle 7. To a suspension of diacid **2** (54 mg, 0.101 mmol) in dry CH_3CN (5 mL) was added *N*-hydroxysuccinimide (30 mg, 0.243 mmol) and DCC (50 mg, 0.222 mmol), with the resulting reaction mixture being stirred for 16 h under N_2. The resulting DCC urea was filtered, the solvent removed *in vacuo* and the activated diester **3** taken on assuming to be quantitatively formed. A solution of activated diester **3** (70 mg, 0.101 mmol) and template $\mathbf{7}^+Cl^-$ (39 mg, 0.110 mmol) were added to dry CH_2Cl_2 (20 mL) and stirred for 30 min under a N_2 atmosphere. To this solution, NEt_3 (26 mg, 35 μL, 0.253 mmol) and *meta*-xylenediamine (14 mg, 13 μL, 0.101 mmol) were added, and the reaction stirred under N_2 for 16 h. The reaction mixture was then washed with 3 M $HCl_{(aq)}$ (2 × 20 mL), $NaHCO_{3(aq)}$ (2 × 20 mL) and H_2O (1 × 20 mL), the organic layer dried ($MgSO_4$) and solvent removed *in vacuo*. The crude material was purified by silica gel column chromatography ($CHCl_3$: CH_3OH 98 : 2 to 97 : 3) to give the product as a white solid (30 mg, 50% from **2**). Mp = 176–178 °C; δ_H(300 MHz, $CDCl_3$): 7.19–7.34 (4H, m, xylyl Ar*H*), 6.91 (2H, br s, N*H*), 6.72–6.78 (8H, m, hydroquinone Ar*H*), 4.53 (4H, d, ^3J = 5.9 Hz, $NHCH_2$), 4.46 (4H, s, $C(O)CH_2$), 4.00–4.04 (4H, m, $ArOCH_2CH_2O$), 3.84–3.87 (4H, m, $ArOCH_2CH_2O$), 3.68–3.73 (8H, m, 2 × OCH_2); δ_C(75 MHz, $CDCl_3$): 168.2, 153.9, 151.2, 138.5, 129.0, 127.4, 125.9, 115.7, 115.4, 70.8, 70.6, 69.7, 68.1, 67.8, 42.7; m/z: (ES) 617.2485 ($[M + Na]^+$, $C_{32}H_{38}N_2NaO_9$ requires 617.2470).

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Notes and references

1 See the special themed issue on *Supramolecular Chemistry of Anionic Species* in *Chem. Soc. Rev.*, 2010, **39**, 3581–4008.
2 M. J. Chmielewski, J. J. Davis and P. D. Beer, *Org. Biomol. Chem.*, 2009, **7**, 415–424.
3 A. Andrievsky, F. Ahuis, J. L. Sessler, F. Vögtle, D. Gudat and M. Moini, *J. Am. Chem. Soc.*, 1998, **120**, 9712–9713.
4 M. J. Gunter, S. M. Farquhar and K. M. Mullen, *New J. Chem.*, 2004, **28**, 1443–1449.
5 J. J. Gassensmith, S. Matthys, J. J. Lee, A. Wojcik, P. V. Kamat and B. D. Smith, *Chem.- Eur. J.*, 2010, **16**, 2916–2921.
6 M. K. Chae, J.-M. Suk and K.-S. Jeong, *Tetrahedron Lett.*, 2010, **51**, 4240–4242.
7 Y. J. Zhao, Y. L. Li, Y. J. Li, H. Y. Zheng, X. D. Yin and H. B. Liu, *Chem. Commun.*, 2010, **46**, 5698–5700.
8 (*a*) J. A. Wisner, P. D. Beer, M. G. B. Drew and M. R. Sambrook, *J. Am. Chem. Soc.*, 2002, **124**, 12469–12476; (*b*) M. R. Sambrook, P. D. Beer, M. D. Lankshear, R. F. Ludlow and J. A. Wisner, *Org. Biomol. Chem.*, 2006, **4**, 1529–1538; (*c*) P. D. Beer, M. R. Sambrook and D. Curiel, *Chem. Commun.*, 2006, 2105–2117; (*d*) M. D. Lankshear and P. D. Beer, *Acc. Chem. Res.*, 2007, **40**, 657–668.
9 M. R. Sambrook, P. D. Beer, J. A. Wisner, R. L. Paul and A. R. Cowley, *J. Am. Chem. Soc.*, 2004, **126**, 15364–15365.
10 K.-Y. Ng, A. R. Cowley and P. D. Beer, *Chem. Commun.*, 2006, 3676–3678.
11 B. Huang, S. M. Santos, V. Felix and P. D. Beer, *Chem. Commun.*, 2008, 4610–4612.
12 N. H. Evans and P. D. Beer, *Org. Biomol. Chem.*, 2011, **9**, 92–100.
13 K. M. Mullen, J. Mercurio, C. J. Serpell and P. D. Beer, *Angew. Chem. Int. Ed.*, 2009, **48**, 4781–4784.
14 L. M. Hancock, L. C. Gilday, S. Carvalho, P. J. Costa, V. Félix, C. J. Serpell, N. L. Kilah and P. D. Beer, *Chem.-Eur. J.*, 2010, **16**, 13082–13094.
15 L. M. Hancock and P. D. Beer, *Chem.-Eur. J.*, 2009, **15**, 42–44.
16 K.-Y. Ng, V. Felix, S. M. Santos, N. H. Rees and P. D. Beer, *Chem. Commun.*, 2008, 1281–1283.
17 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311–312.
18 J. A. Wisner, P. D. Beer and M. G. B. Drew, *Angew. Chem. Int. Ed.*, 2001, **40**, 3606–3609.