Supplementary Material (ESI) for New Journal of Chemistry

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

Nicholas H. Evans, Christopher J. Serpell and Paul D. Beer*

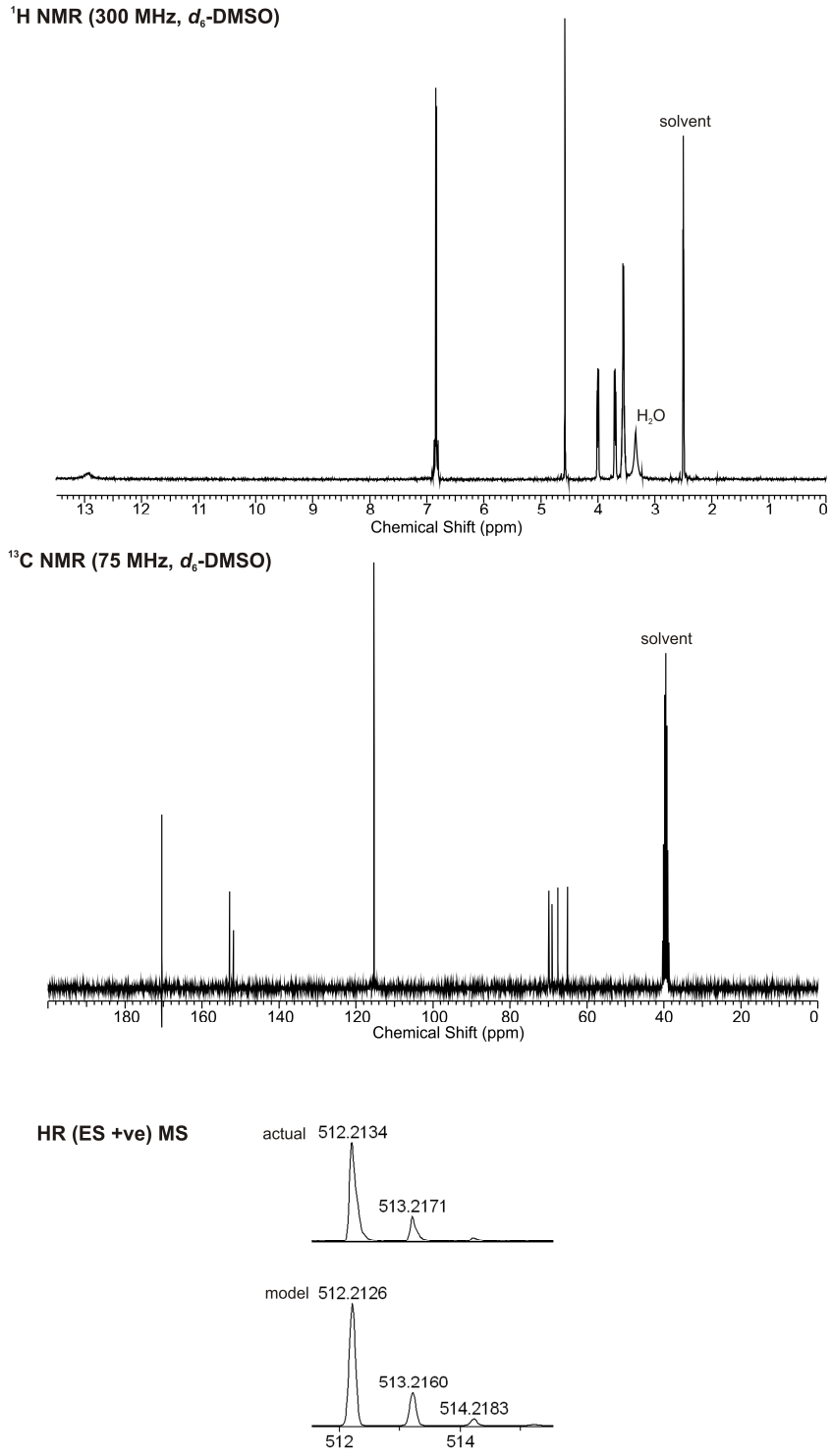
Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK. OX1 3QR.

SUPPLEMENTARY INFORMATION

TABLE OF CONTENTS

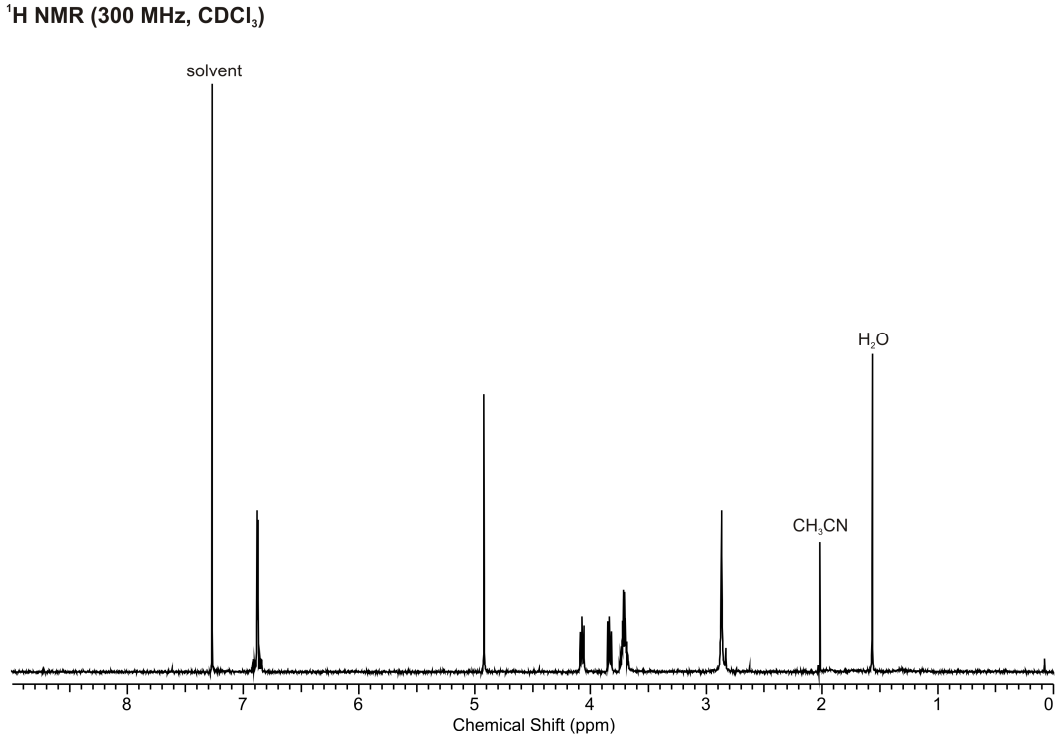
Part I: Copies of NMR and Mass Spectra of Novel Compounds

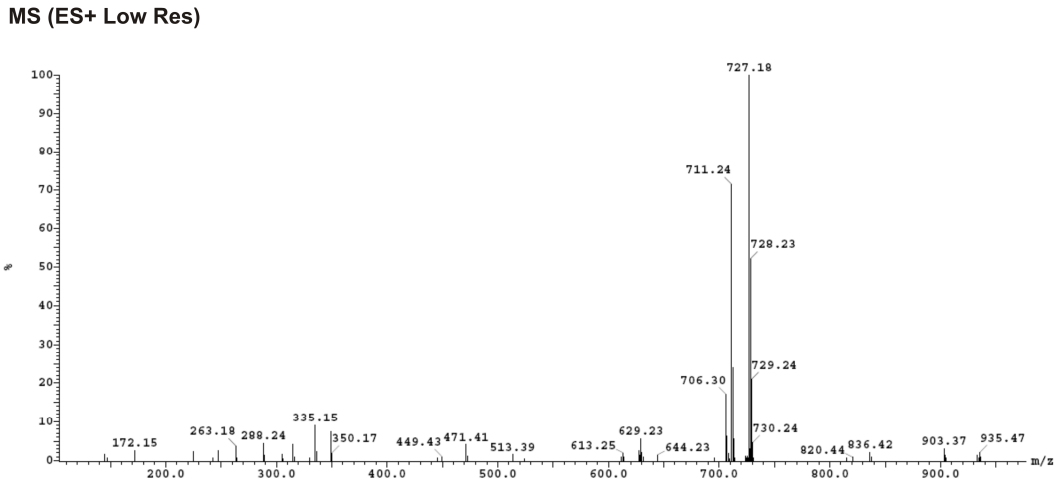
Dicarboxylic acid **2**



Supplementary Fig. 1 ^{1}H and ^{13}C NMR and HR mass spectra of dicarboxylic acid **2**.

Activated diester **3**

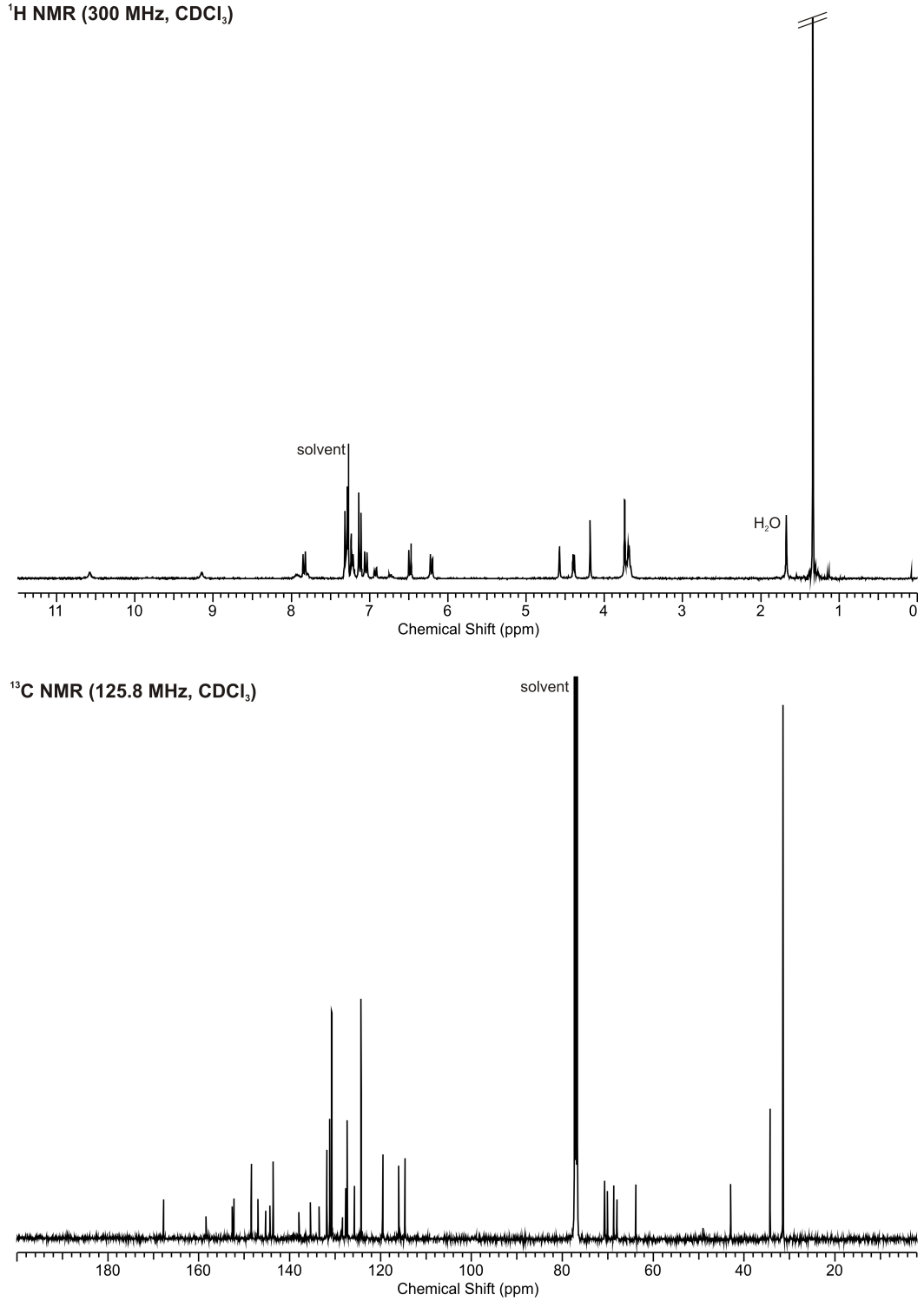




Supplementary Fig. 2 ^{1}H NMR and low resolution mass spectra of activated diester **2**.

δ_H (300 MHz, $CDCl_3$): 6.64-6.91 (8H, m, Ar*H*), 4.92 (4H, s, OCH_2CO), 4.06-4.09 (4H, m, OCH_2), 3.82-3.85 (4H, m, OCH_2), 3.67-3.74 (8H, m, 2 x OCH_2), 2.87 (8H, s, CH_2); *m/z:* (ES) 727.2 ($[M + K]^+$, 100%), 711.2 ($[M + Na]^+$, 72), 706.3 ($[M + NH_4]^+$, 18).

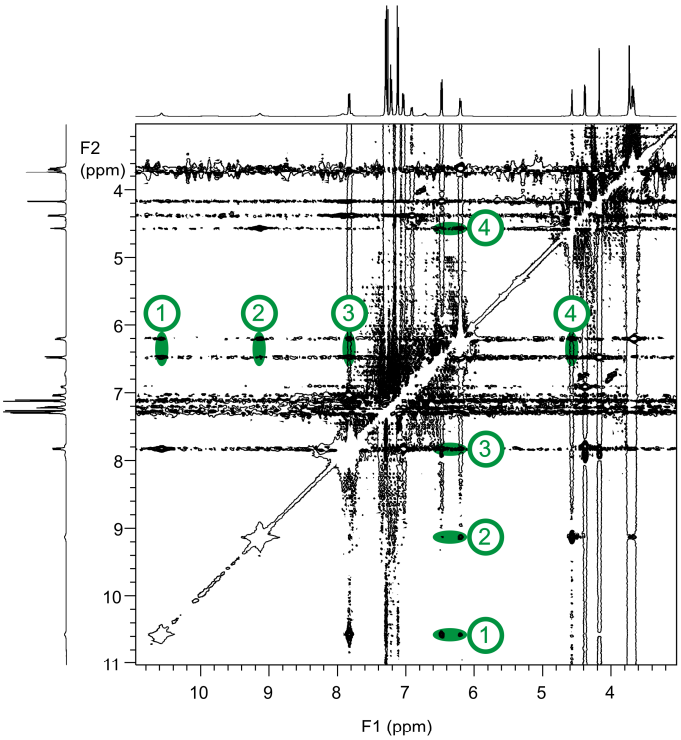
Rotaxane $\mathbf{5}^{+}Cl^{-}$

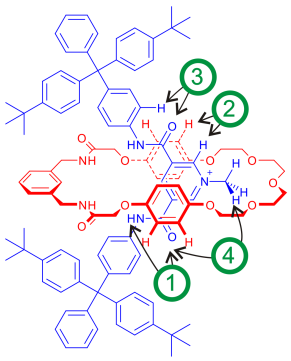


Supplementary Fig. 3 ^{1}H and ^{13}C NMR spectra of rotaxane $\mathbf{5}^{+}Cl^{-}$.

Rotaxane $\mathbf{5}^{+}Cl^{-}$ (cont.)

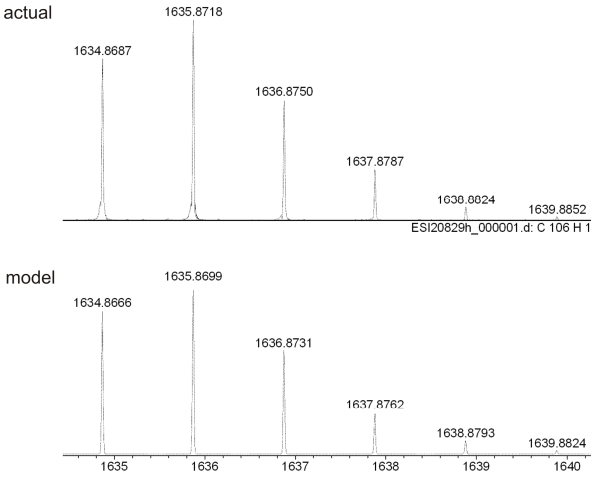
^{1}H ROESY NMR ($CDCl_3$, 500 MHz)





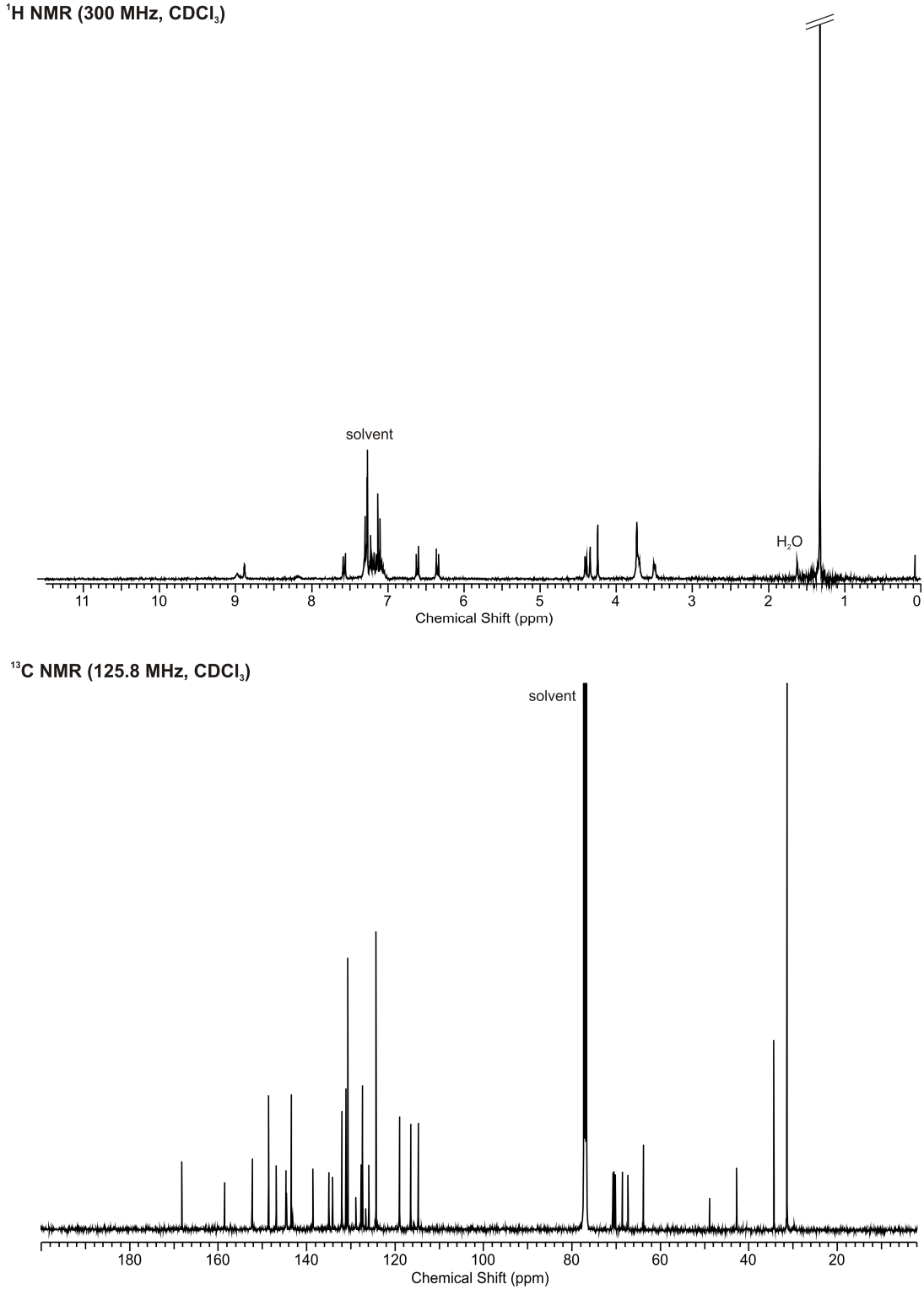
some principal intercomponent
through-space interactions highlighted

HR (ES +ve) MS



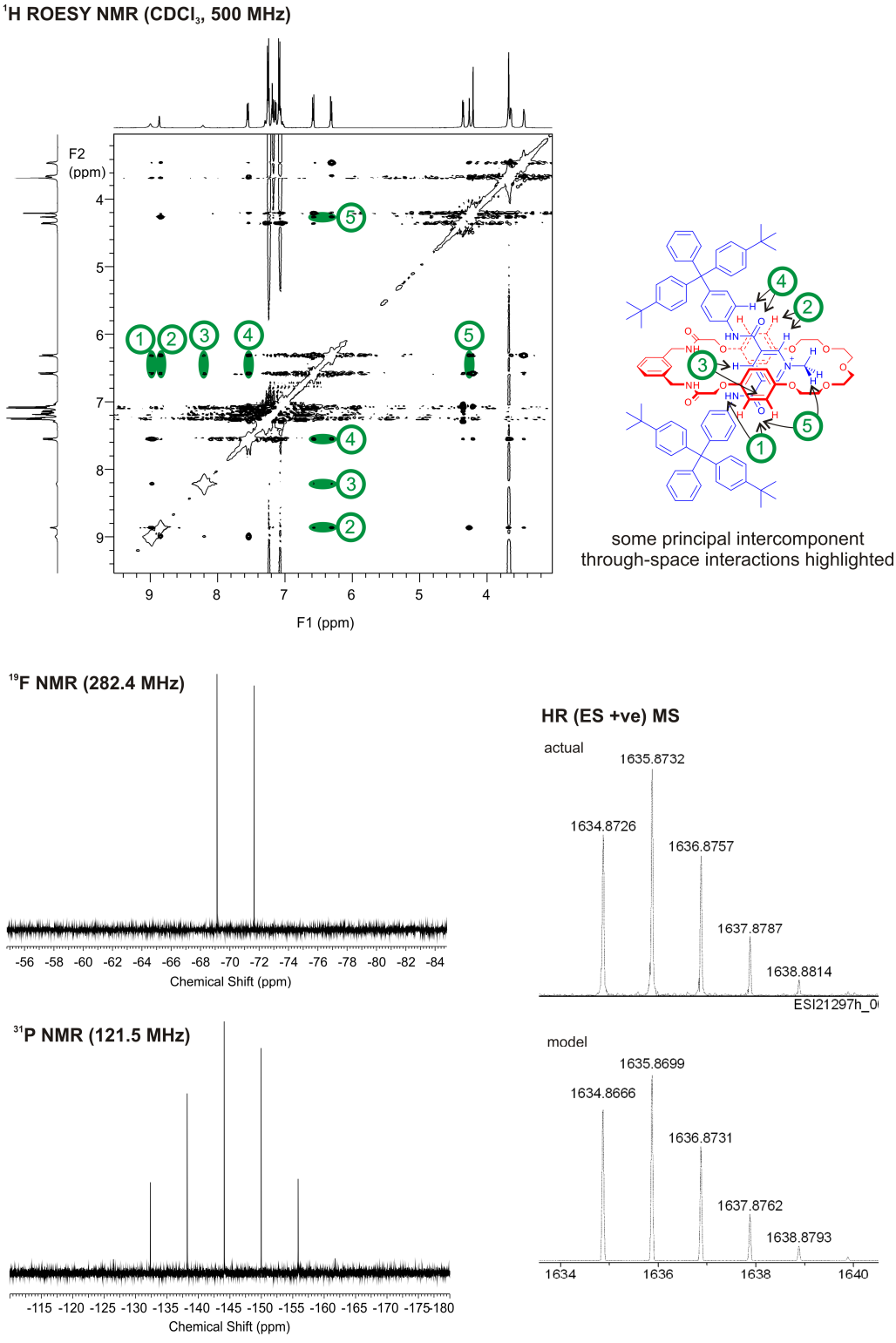
Supplementary Fig. 4 ^{1}H ROESY NMR and HRMS spectra of rotaxane $\mathbf{5}^{+}Cl^{-}$.

Rotaxane $\mathbf{5}^{+}PF_6^{-}$



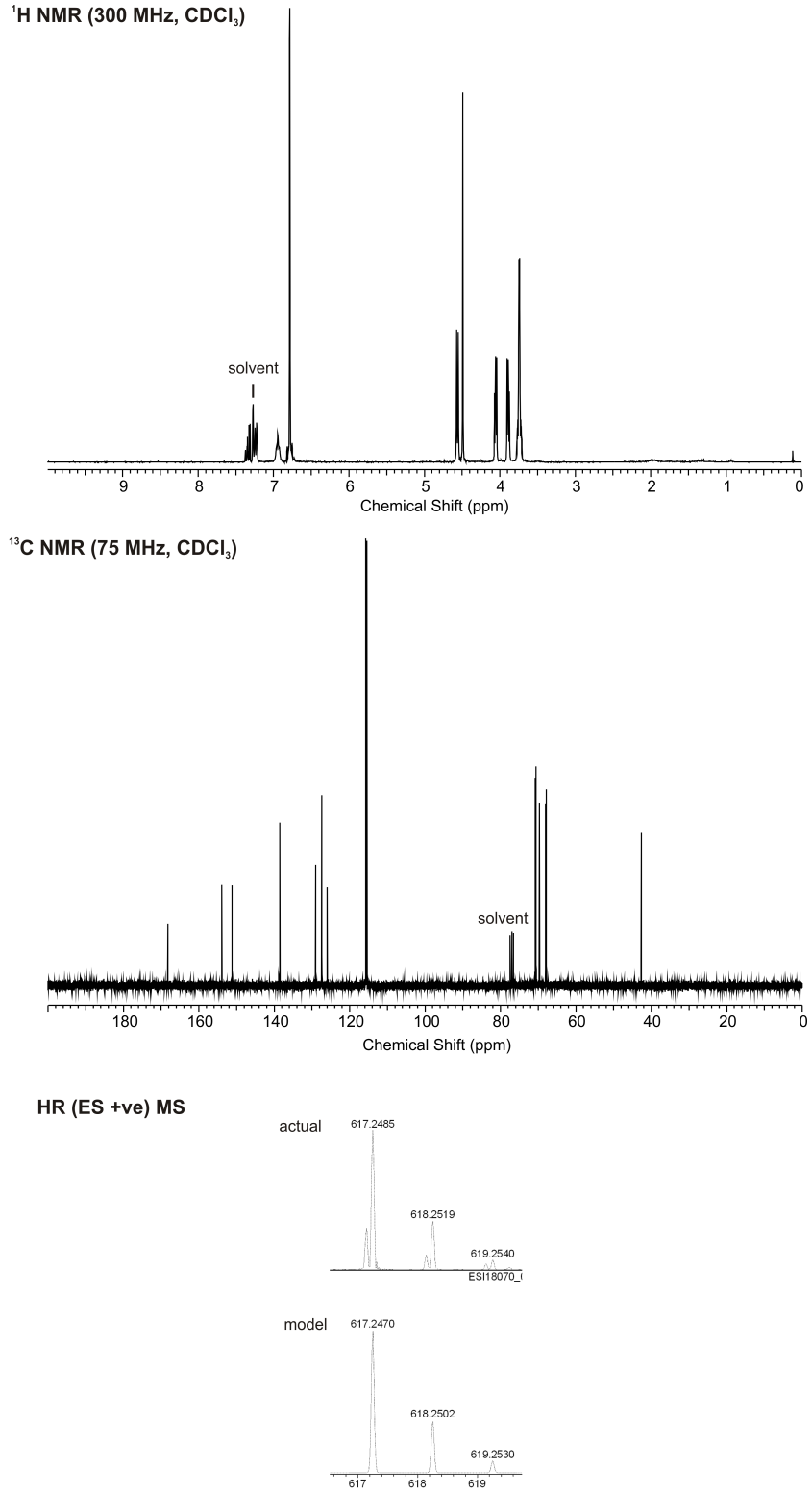
Supplementary Fig. 5 ^{1}H and ^{13}C NMR spectra of rotaxane $\mathbf{5}^{+}PF_6^{-}$.

Rotaxane $\mathbf{5}^{+}PF_6^{-}$ (cont.)



Supplementary Fig. 6 ^{1}H ROESY, ^{19}F & ^{31}P NMR and HRMS spectra of rotaxane $\mathbf{5}^{+}PF_6^{-}$.

Macrocycle **7**



Supplementary Fig. 7 ^{1}H and ^{13}C NMR and HR mass spectra of macrocycle **7**.

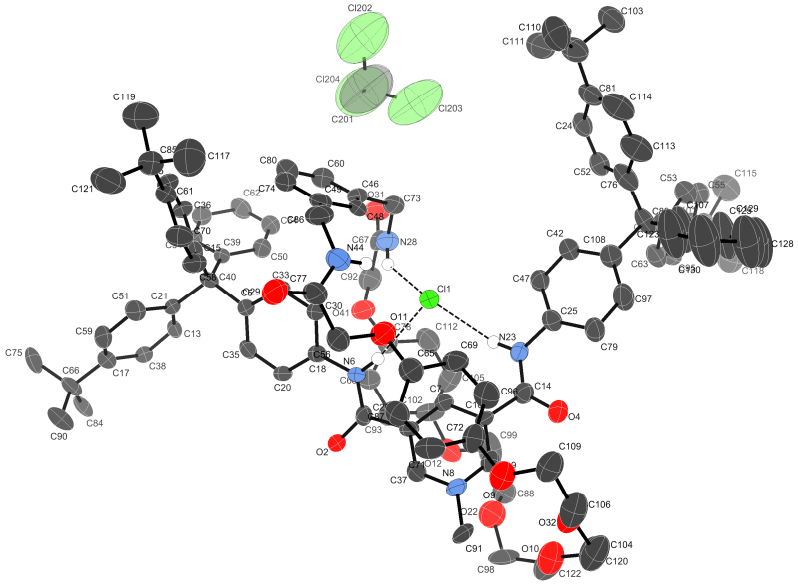
Part II: Crystallographic Information for Structure of Rotaxane $5^{+}Cl^{-}$

Crystals were grown by slow diffusion of diisopropyl ether into a chloroform solution of rotaxane $\mathbf{5}^{+}Cl^{-}$. Single crystal X-ray diffraction data were collected using silicon double crystal monochromated synchrotron radiation (λ = 0.68890 Å) at Diamond Light Source beamline I19 using a custom-built Rigaku diffractometer equipped with a Cryostream N_2 open-flow cooling device.[1] The data were collected at 150(2) K via a series of ω-scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å. Cell parameters and intensity data (including inter-frame scaling) were processed using the CrystalClear package.[2] The structure was solved by direct methods using SIR92[3] and refined against F with a 2σ cutoff within the CRYSTALS suite.[4]

The sample diffracted very weakly, and at high angles the reflections were completely absent, even when subjected to synchrotron radiation. This is ascribed to the large cavity containing disordered solvent. After structure solution, the entire main residue could be modeled as well as a single partially occupied chloroform molecule.

The PLATON/SQUEEZE routine[5] was used to model the remainder of the disordered solvent cavity because there was no discernible structure in the Fourier difference map within this volume. It is very difficult to know what proportion of the two solvents used in crystallisation occupy the cavity (even considering the electron count derived using SQUEEZE), and therefore it was deemed inappropriate to include such speculative information in the data reported in Supplementary Table 1.

Thermal restraints were applied where appropriate to the main residue, while geometric restraints were also required for the chloroform molecule. Hydrogen atoms were placed geometrically and subsequently constrained using rides. Absent high angle data were omitted from the refinement using the Wilson plot.



Supplementary Fig. 8 X-ray structure for compound $\mathbf{5}^{+}Cl^{-}$ Thermal ellipsoids displayed at 50% probability

Supplementary Table 1 Selected crystallographic data for compound $\mathbf{5}^{+}Cl^{-}$

Compound reference	$\mathbf{5}^{+}Cl^{-}$
Chemical formula	$C_{106\cdot48}H_{116\cdot48}Cl_{2\cdot45}N_5O_{11}$
Formula Mass	1729.39
Crystal system	Monoclinic
a/Å	11.498(6)
b/Å	29.702(16)
c/Å	31.391(17)
α/°	90
β/°	97.333(5)
γ/°	90
Unit cell volume/Å^3	10630(10)
Temperature/K	293
Space group	$P2_1/n$
No. of formula units per unit cell, *Z*	4
No. of reflections measured	23420
No. of independent reflections	23420
R_{int}	0.162
Final R_1 values ($I > 2\sigma(I)$)	0.1371
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0616
Final R_1 values (all data)	0.2083
Final $wR(F^2)$ values (all data)	0.0616

[1] J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105.
[2] CrystalClear (Version 2.0, 2009), Rigaku Americas, 9009 TX, USA 77381-5209.
[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
[4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.
[5] A. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7; P. van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, *A46*, 194.

Part III: ^{1}H NMR Titrations

Protocol

^{1}H NMR spectra were recorded on a Varian Unity Plus 500 spectrometer. In a typical experiment, a solution of guest was added to a solution of the host at 293 K. The chemical shift of specific proton(s) was monitored for seventeen titration points (for 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 and 10.0 equivalents of added guest), with the resulting data analysed using the WinEqNMR2 computer program[1], as the association of guest and host was found to be fast on the NMR timescale for all systems.

The anion binding titration experiments were carried out using salts of the non-complexing tetrabutylammonium (TBA) cation as the guest species, titrated into the dissolved host. A 0.075 M solution of anion was added to 0.50 mL of a 1.50 mM solution of host, i.e. 10 μL is 1 equivalent. The volumes of TBA salt added were 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL and 1 x 30 μL.

The values of the observed chemical shift and the guest concentration were entered into winEQNMR2 for every titration point and, estimates for the binding constant and limiting chemical shifts were made. The parameters were refined using non-linear squares analysis to obtain the best fit between observed and calculated chemical shifts for a 1:1 binding stoichiometry. The program plots the observed chemical shift versus the guest concentration, revealing the accuracy of the experimental data and the suitability of the model used. The input parameters were varied until the best-fit values of the stability constants, and their errors, converged.

Complete set of calculated association constants for rotaxane $\mathbf{5}^+PF_6^-$

Supplementary Table 2 1:1 Anion association constants, *K*, of rotaxane $\mathbf{5}^+PF_6^-$ [a]

Anion	*ortho*-pyridinium proton *y*	*para*-pyridinium proton *x*	internal xylyl cavity proton *c*
Cl^-	810	660	700
Br^-	1070	1370 [b]	920
$H_2PO_4^-$	645	495 [b]	[c]
OAc^-	285	220 [b]	[c]

[a] Anions added as TBA salts. Solvent: 1:1 $CDCl_3$:CD_3OD. T = 293 K. Association constants, *K*, calculated using winEQNMR2, errors < 10%. [b] Upfield shift observed. [c] Negligible shift (< ± 0.01 ppm) observed

[1] M. J. Hynes, *J. Chem. Soc. Dalton Trans.*, 1993, 311.