Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary Information for

Porphyrin-functionalised rotaxanes for anion recognition

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Contents

^{1}H NMR spectra of new axle, macrocycle and rotaxane compounds

Compound 3·Cl

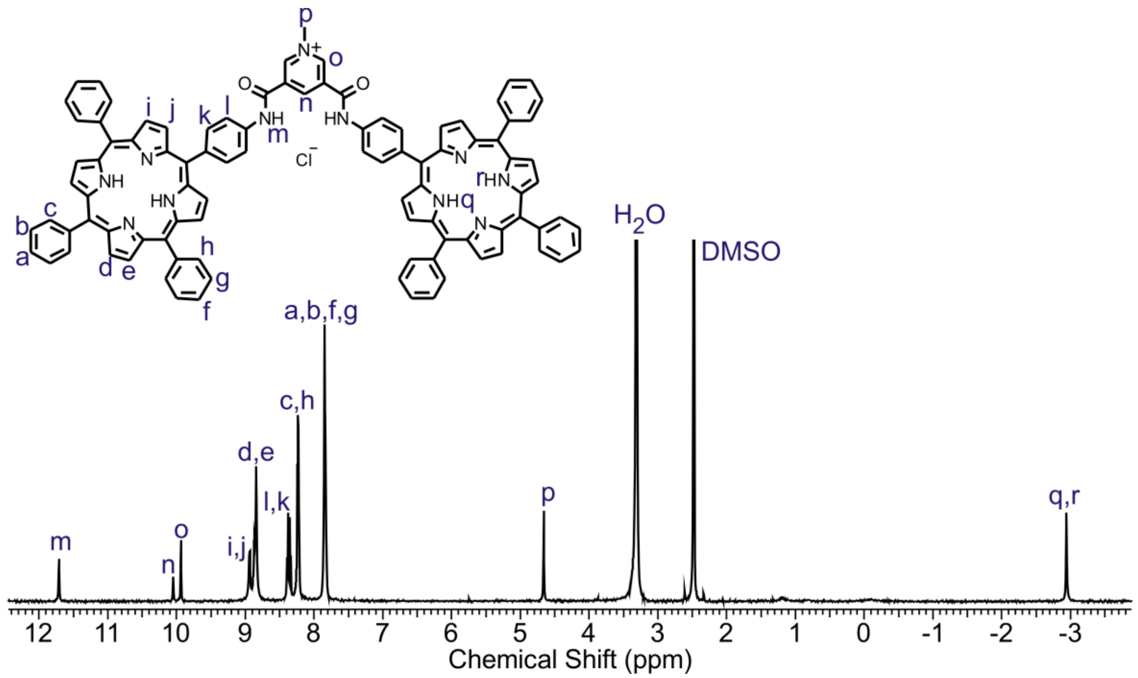


Fig S1 ^{1}H NMR spectrum of compound **3·Cl** in DMSO-d_6 at 293 K.

Compound 5·Cl

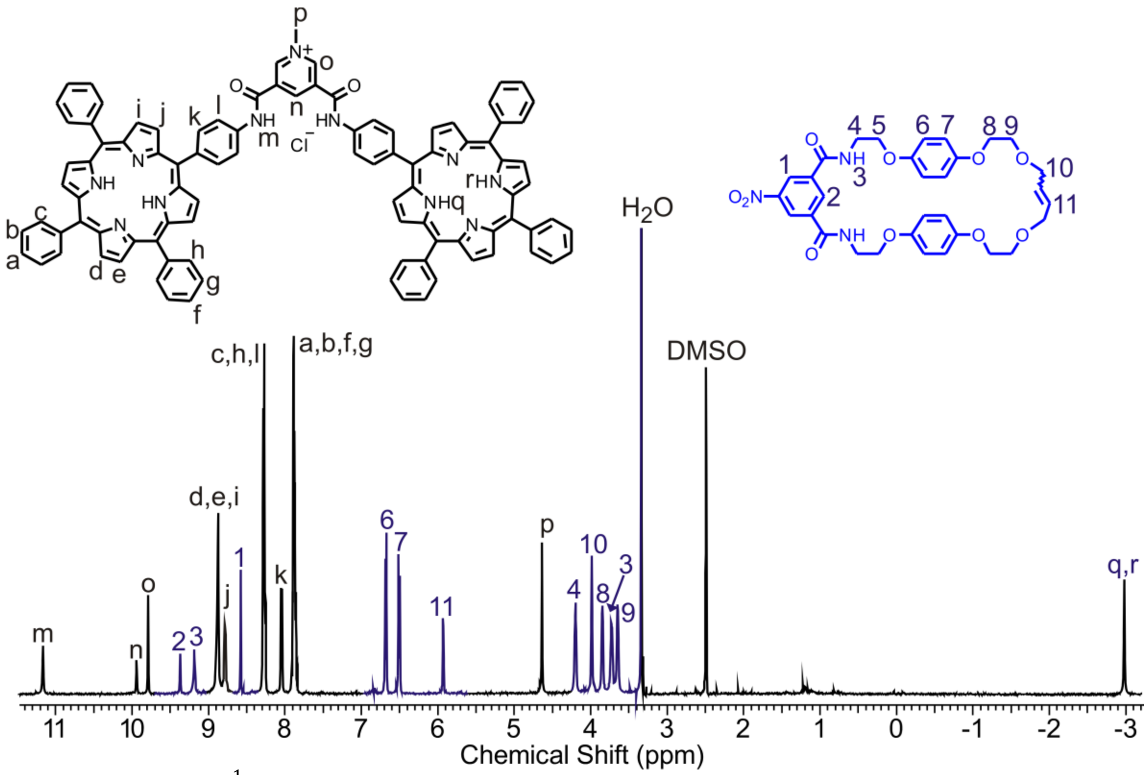


Fig S2 ^{1}H NMR spectrum of compound **5·Cl** in DMSO-d_6 at 293 K.

Compound 5·PF$_6$

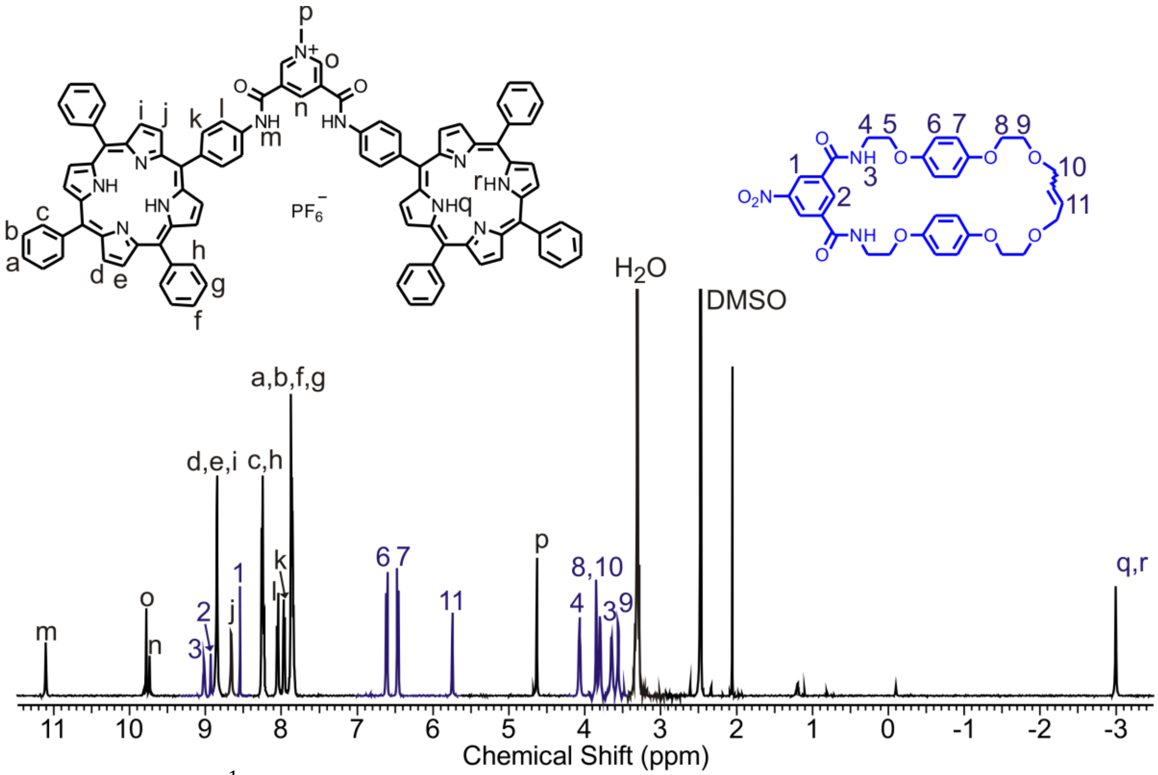


Fig S3 ^{1}H NMR spectrum of compound **5·PF$_6$** in DMSO-d$_6$ at 293 K.

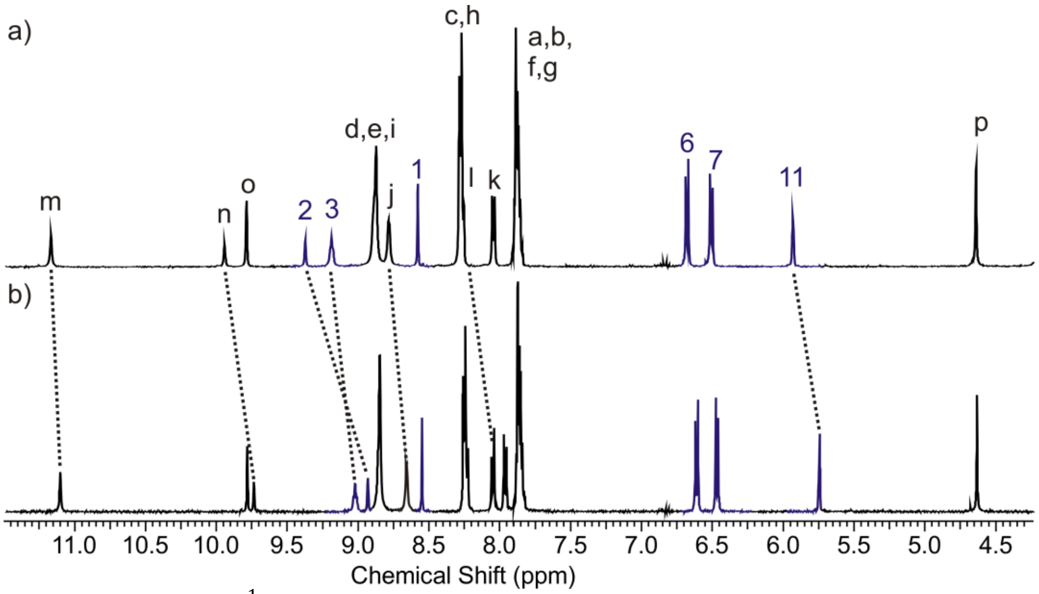


Fig S4 Comparison of the ^{1}H NMR spectra of a) compound **5·Cl** and b) compound **5·PF$_6$** in DMSO-d$_6$ at 293 K.

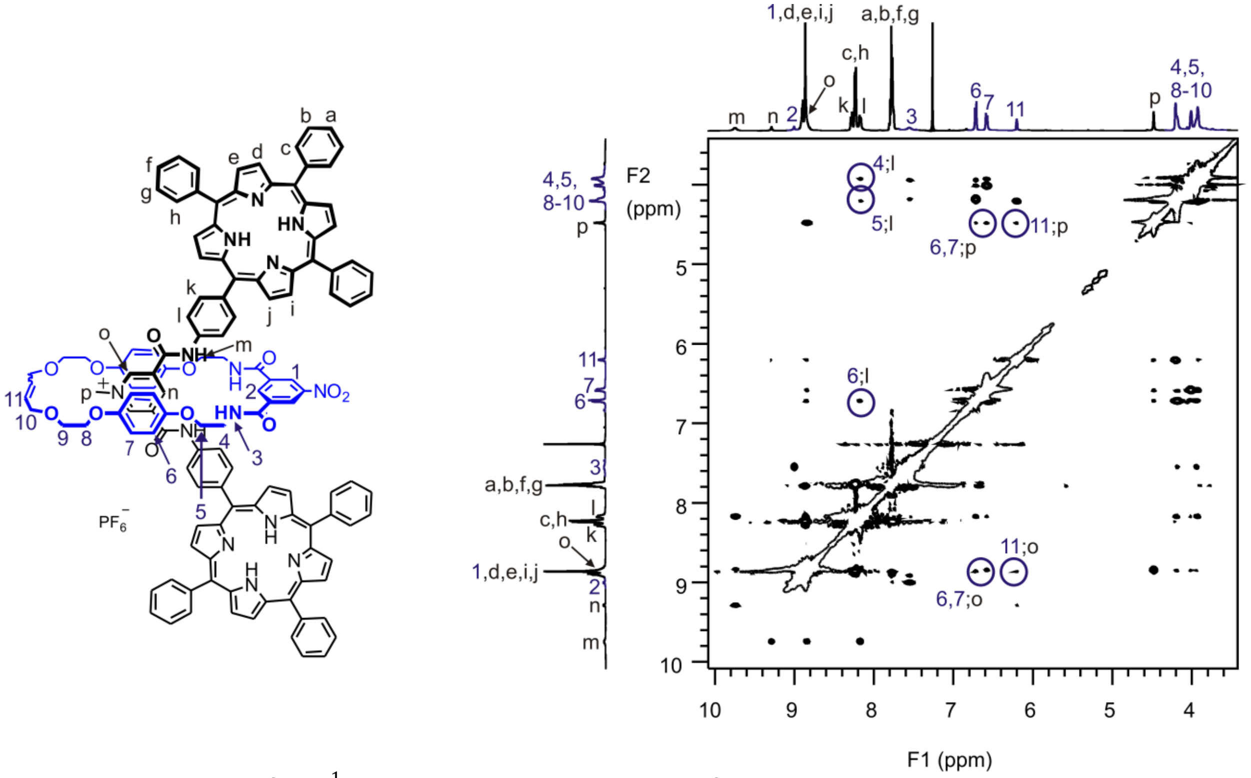


Fig S5 Section of the ^{1}H NMR ROESY spectrum of compound **5·PF$_6$** in CDCl$_3$ at 293 K.

Compound 12

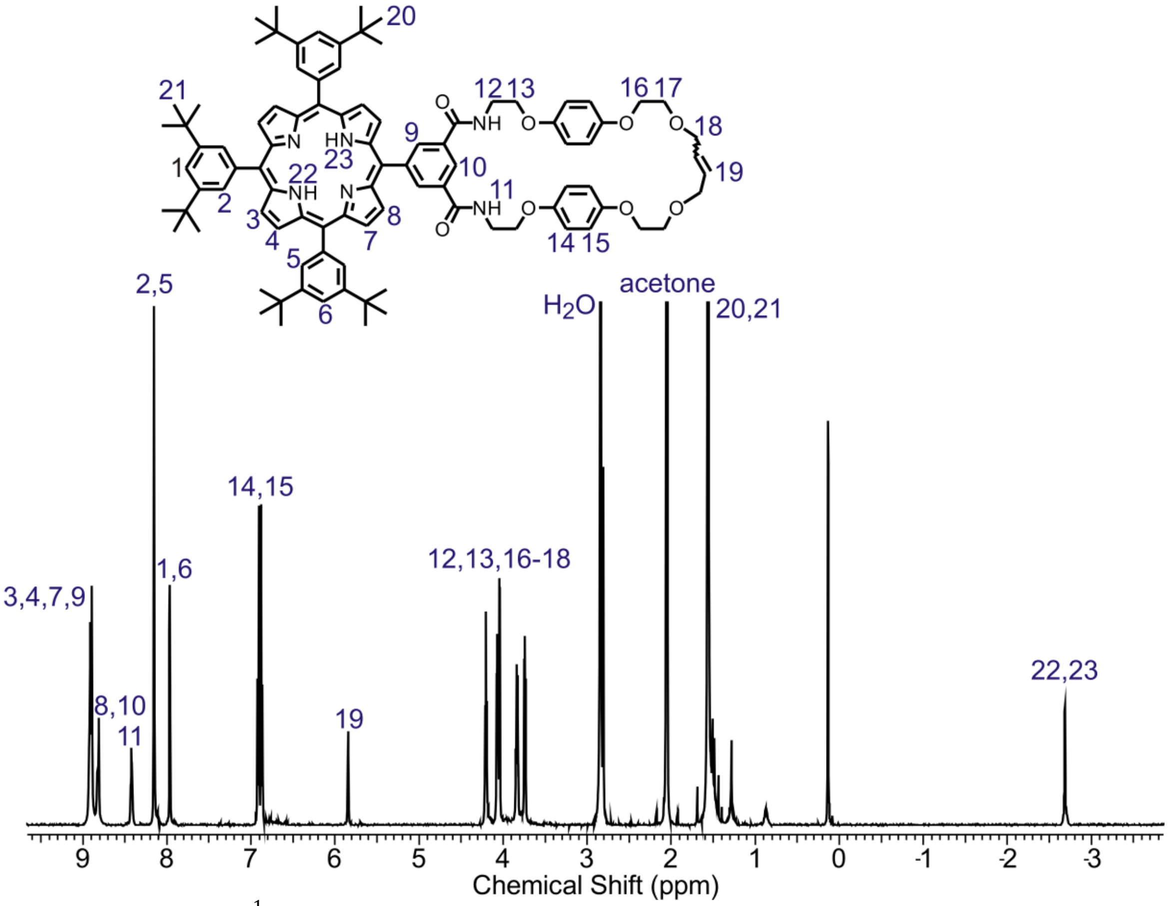


Fig S6 ^{1}H NMR spectrum of compound **12** in acetone-d$_6$ at 293 K.

Compound 14·Cl

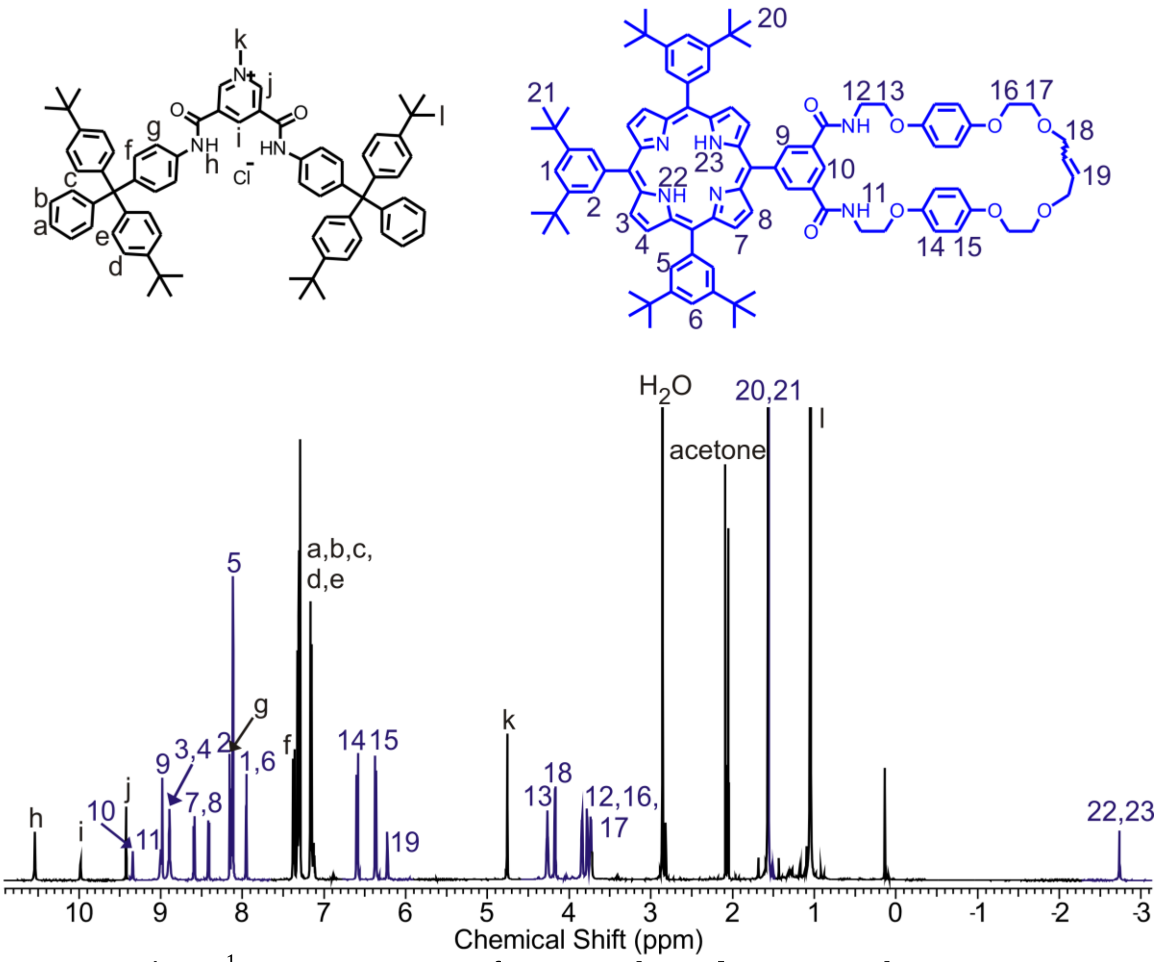
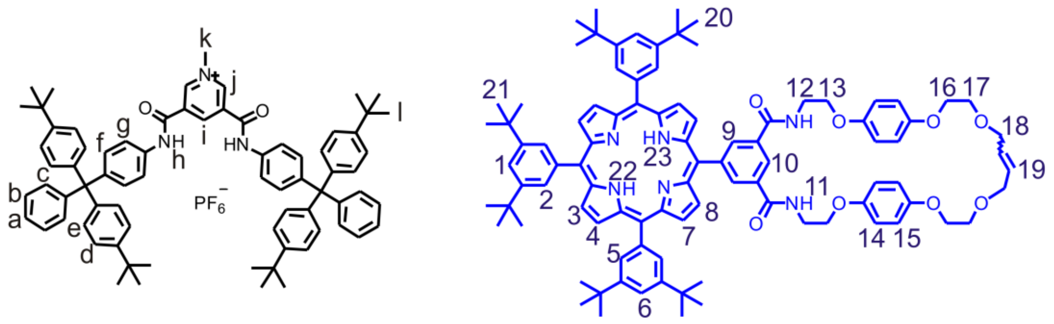


Fig S7 ^{1}H NMR spectrum of compound **14·Cl** in acetone-d_6 at 293 K.

Compound 14·PF_6



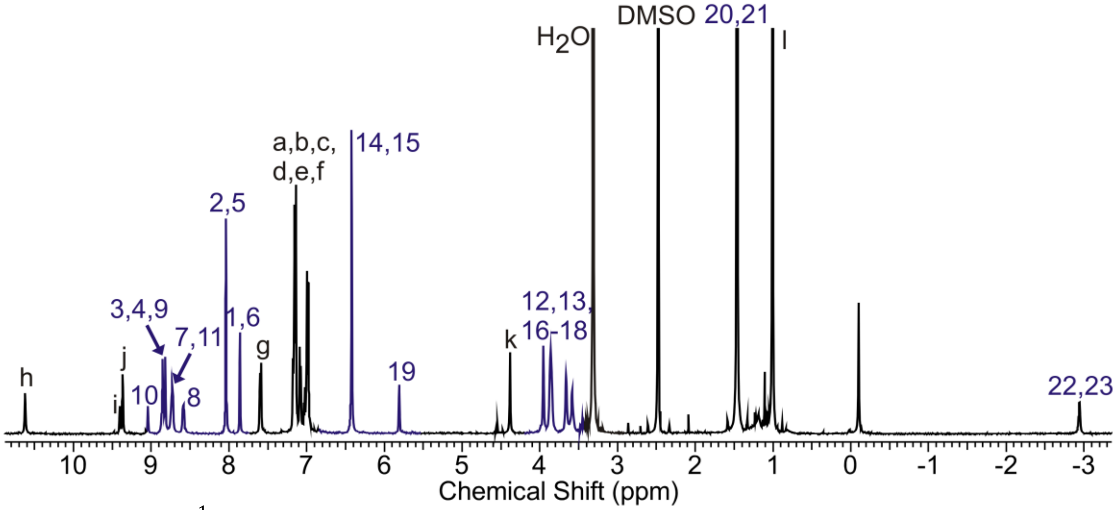


Fig S8 ^1H NMR spectrum of compound **14·PF_6** in DMSO-d_6 at 293 K.

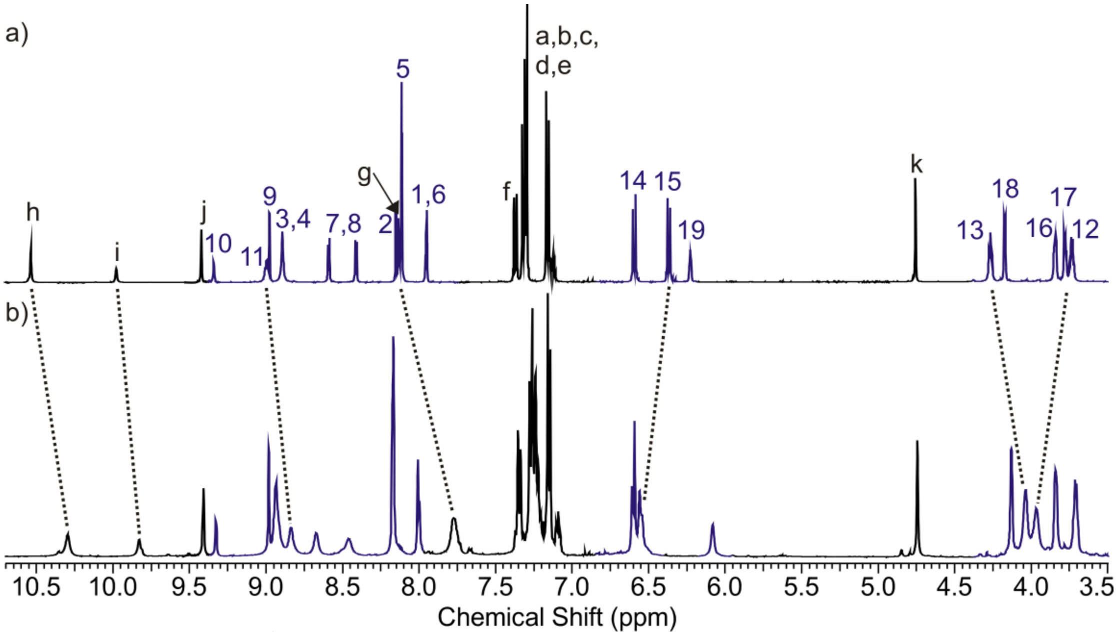


Fig S9 Comparison of the ^1H NMR spectra of a) compound **14·Cl** and b) compound **14·PF_6** in acetone-d_6 at 293 K.

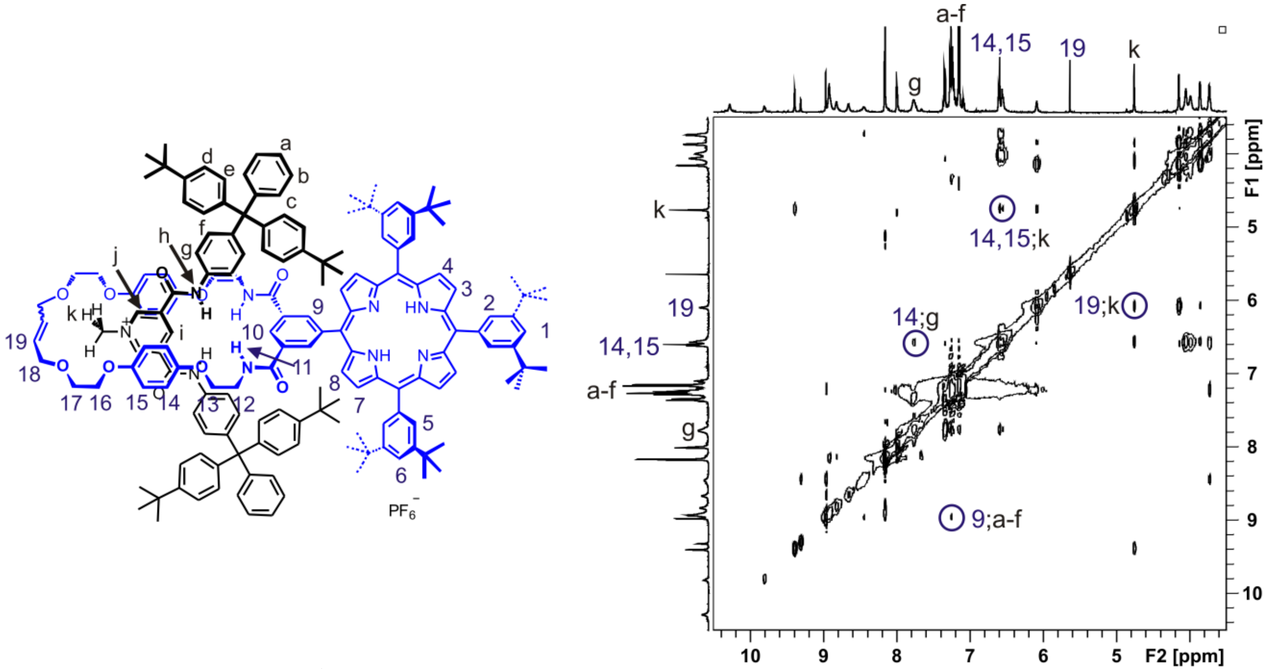


Fig S10 Section of the ^{1}H NMR ROESY spectrum of compound **14·PF$_6$** in acetone-d$_6$ at 293 K.

MALDI-TOF mass spectra of rotaxane compounds 5·Cl, 5·PF$_6$, 14·Cl and 14·PF$_6$

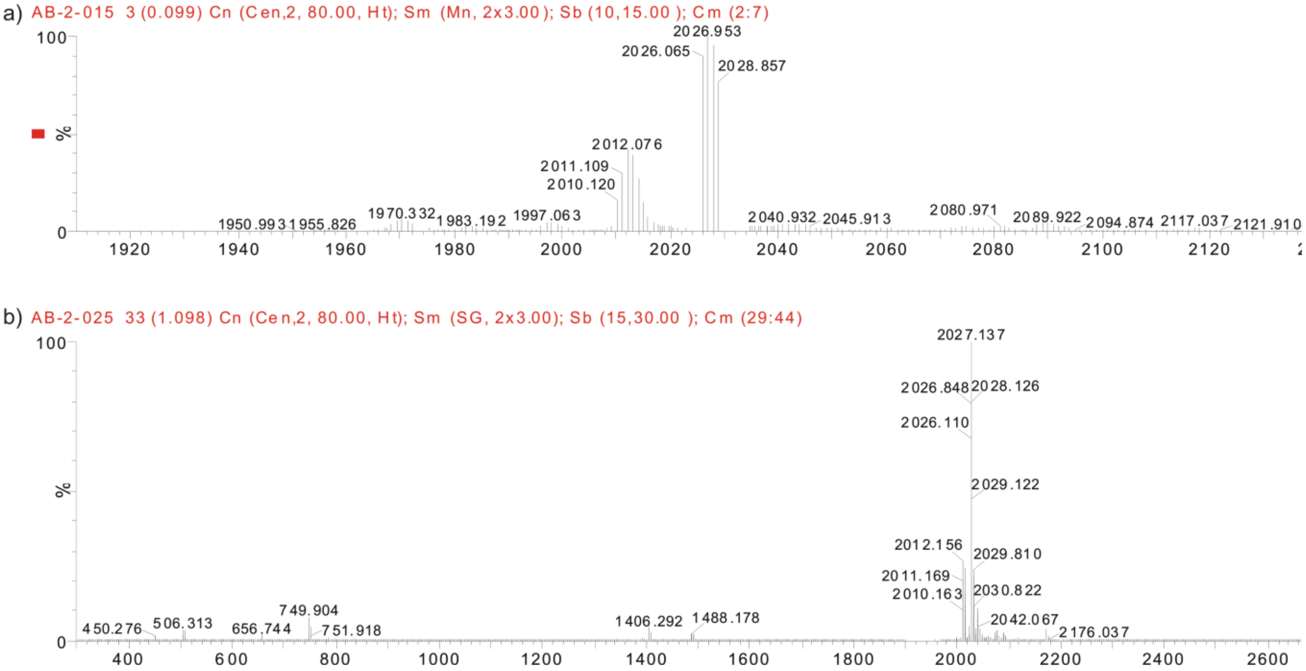


Fig S11 MALDI-TOF mass spectra of a) compound **5·Cl** and b) compound **5·PF$_6$**.

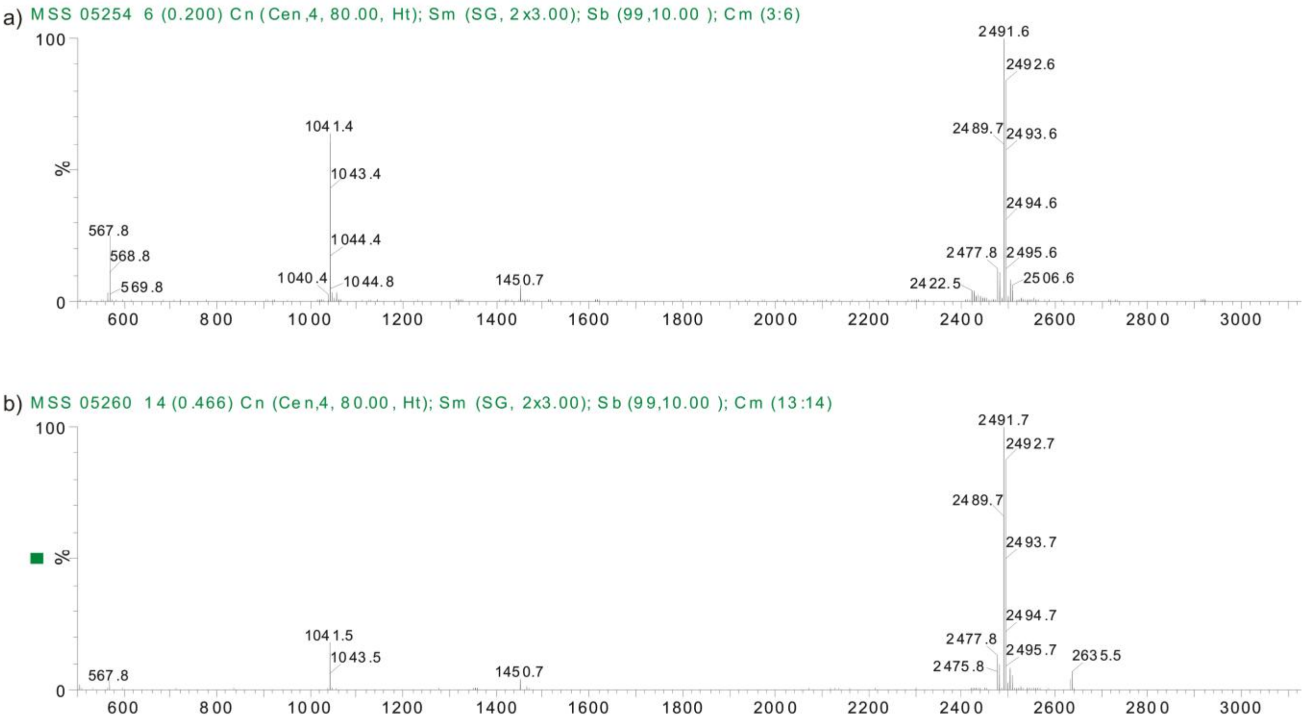


Fig S12 MALDI-TOF mass spectra of a) compound **14·Cl** and b) compound **14·PF$_6$**.

Anion recognition studies

^{1}H NMR titration experiments

All ^{1}H NMR titration experiments were conducted on an Oxford Instruments Varian Unity Plus 500 MHz spectrometer, at 293K. Initial sample volumes were 600 μl. The starting concentration of the host was 2 mM (for all titrations involving compound **5·PF$_6$**) or 1.5 mM (for all titrations involving compound **14·PF$_6$**). All anions were added as their TBA salts. The concentrations of the TBAX solutions were 60 mM (for all titrations involving compound **5·PF$_6$**) or 45 mM (for all titrations involving compound **14·PF$_6$**). 17 aliquots of the TBAX solutions were added until a total of 10 equivalents of the anion had been added. Spectra were recorded after each addition, and the sample shaken thoroughly before measurement.

Stability constants were obtained by analysis of the resulting titration data using the WinEQNMR (M. J. Hynes, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 311) computer program. Estimates for each binding constant, the limiting chemical shifts and the complex stoichiometry were also added to the input file. The various parameters were refined by non-linear least-squares analysis to achieve the best fit between observed and calculated chemical shifts. The parameters were varied until the values for the stability constants converged. Comparison of the calculated binding isotherm with that obtained experimentally demonstrated that the model used was appropriate.

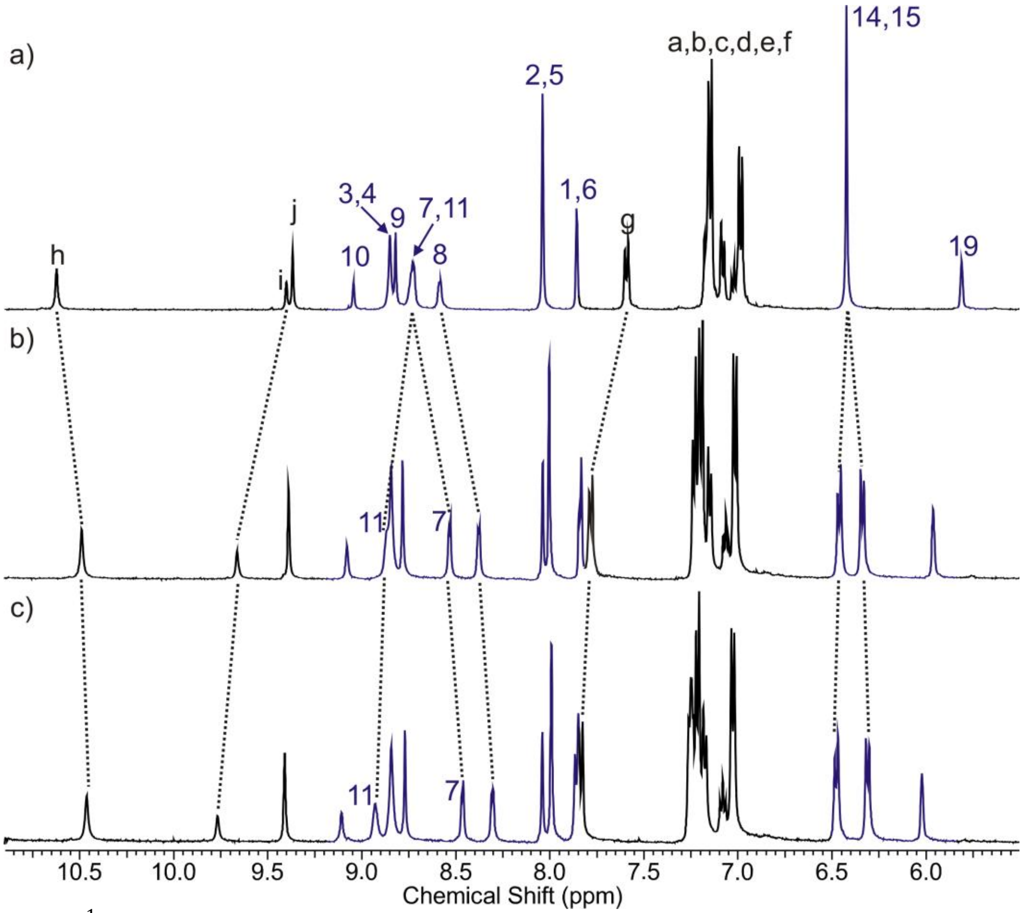


Fig S13 Partial ^{1}H NMR spectra of compound **14·PF$_6$** in the presence of a) 0, b) 1 and c) 5 equivalents of TBACl in DMSO-d$_6$ at 293 K.

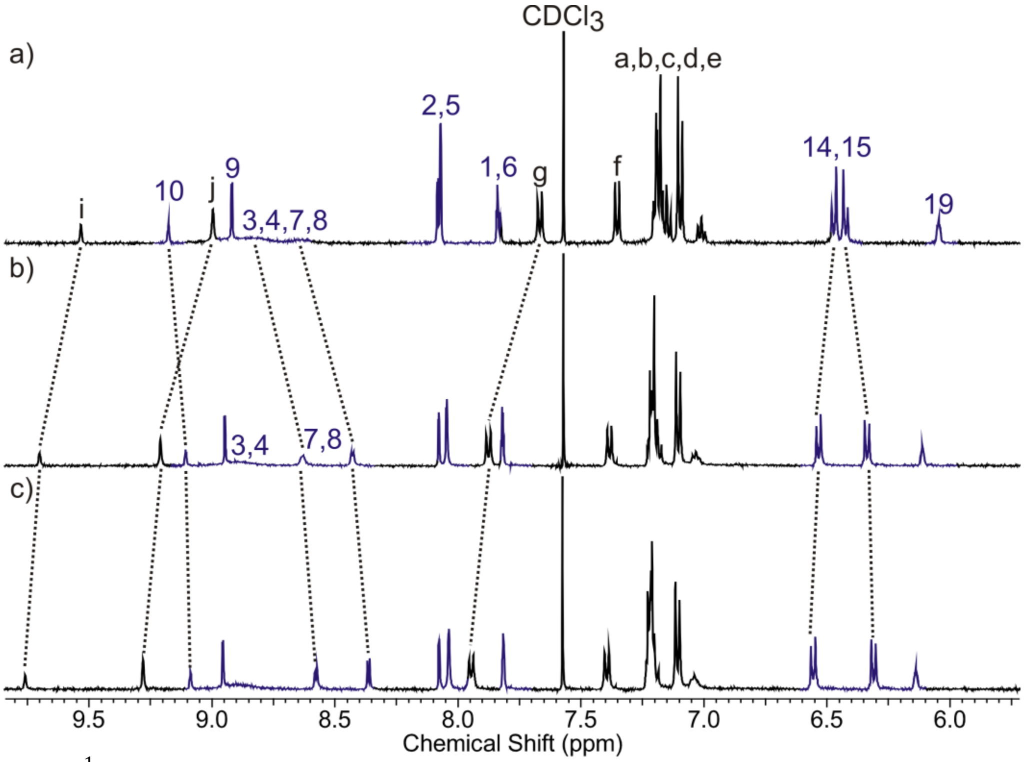


Fig S14 Partial ^{1}H NMR spectra of compound **14·PF$_6$** in the presence of a) 0, b) 1 and c) 5 equivalents of TBACl in $CDCl_3$:CD_3OD 1:1 at 293 K.

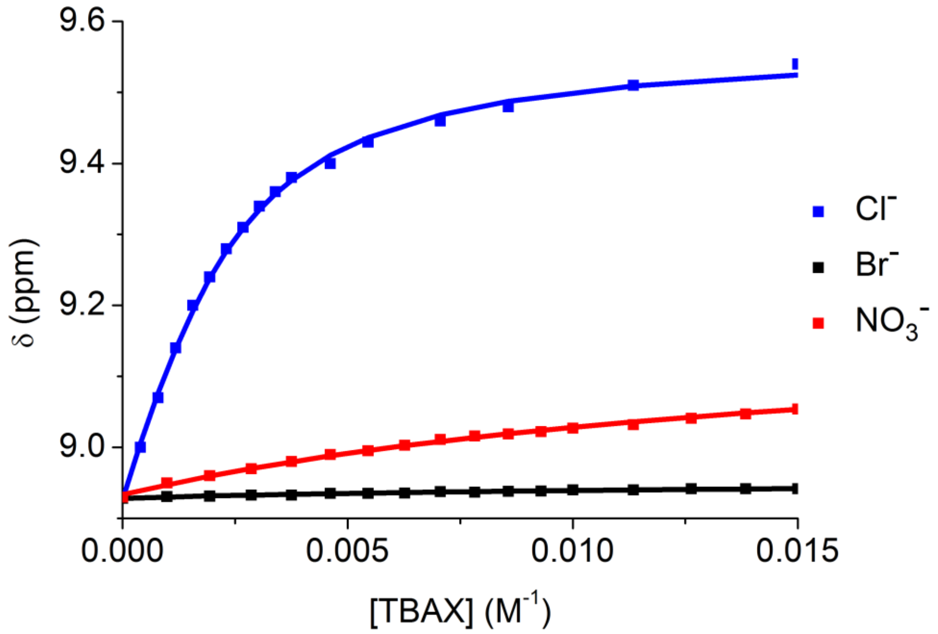


Fig S15 Changes in the chemical shift of proton 2 on addition of the TBA salts of Cl$^-$, Br$^-$ and NO_3^- anions to 2 mM solutions of compound **5·PF$_6$** in DMSO-d$_6$ at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms.

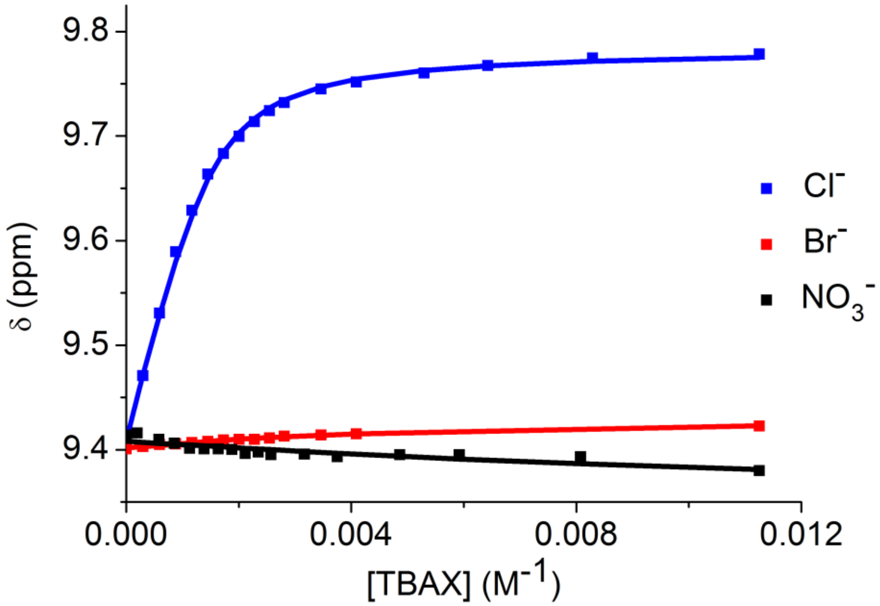


Fig S16 Changes in the chemical shift of the internal pyridinium proton i on addition of anions as their TBA salts to 1.5 mM solutions of compound **14·PF$_6$** DMSO-d$_6$ at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms.

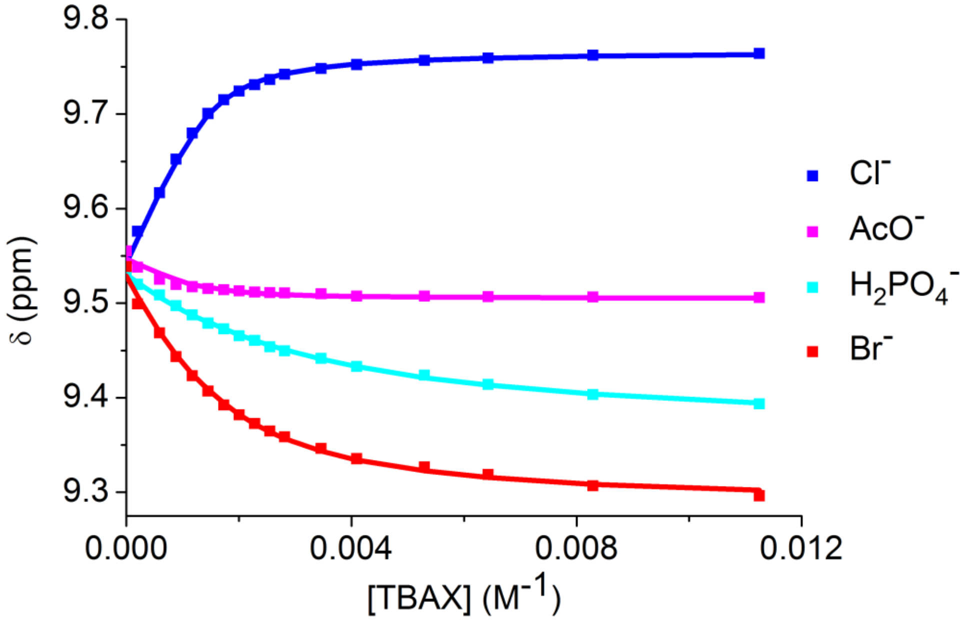


Fig S17 Changes in the chemical shift of the internal pyridinium proton i on addition of anions as their TBA salts to 1.5 mM solutions of compound **14·PF$_6$** in CDCl$_3$:CD$_3$OD 1:1 at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms.

UV-Visible and fluorescence experiments

UV-visible titration experiments were conducted using a Shimadzu UV-2401PC spectrometer or a PG instruments T60U spectrometer. Fluorescence titration experiments were conducted using a Hitachi F-4500 fluorescence spectrophotometer. During each titration experiment, aliquots of a TBAX guest solution were repeatedly added to a solution of the [2]rotaxane host compound in a cuvette. After each addition, the sample was mixed thoroughly and the spectrum was recorded. The concentration of the host compound was kept constant throughout each experiment.

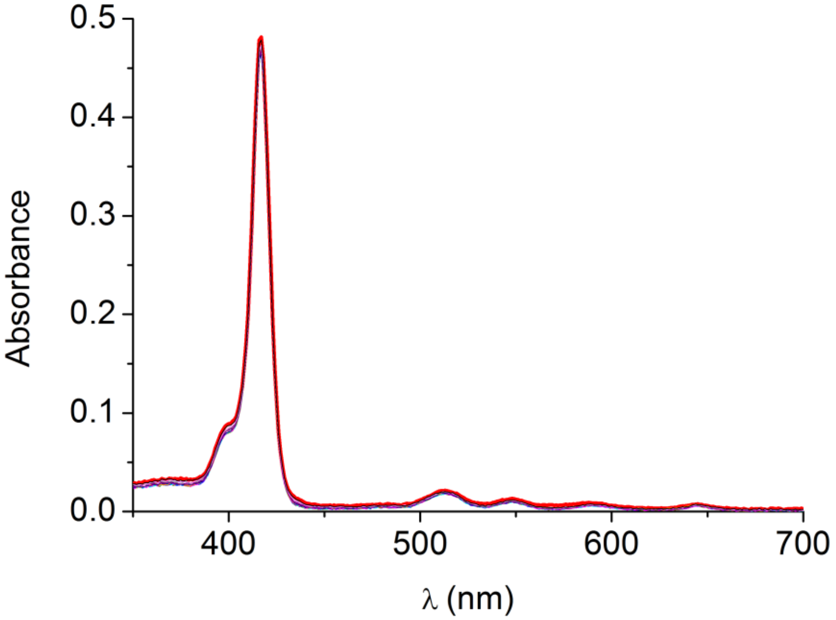


Fig S18 Representative example to demonstrate the negligible effect of anions on the optical properties of compounds **5·PF$_6$** and **14·PF$_6$**: observed changes in the UV-visible absorbance spectrum of a 2 μM solution of the [2]rotaxane **14·PF$_6$** in acetone at 293 K on addition of increasing concentrations of TBACl up to a final concentration of 1.3 mM.

Electrochemical titration protocol

Square wave voltammetry was performed on an Autolab PGSTAT12 controlled by General Purpose Electrochemical System Software, v. 4.9 (Eco Chemie). A standard one-compartment three-electrode electrochemical cell was used with a glassy carbon solid disc working electrode, a platinum wire auxiliary electrode and a Ag/AgNO$_3$ reference electrode (silver wire in 10 mM AgNO$_3$ in an electrolyte solution). The entire cell was housed in a Faraday cage to minimise noise from external fields. For all experiments the electrolyte solution was 0.1 M TBAPF$_6$ in CH$_2$Cl$_2$:CH$_3$CN 1:1. Before undertaking studies with the [2]rotaxane receptors **5·PF$_6$** and **14·PF$_6$**, the voltammograms of a 1 mM solution of ferrocene in the CH$_2$Cl$_2$/CH$_3$CN electrolyte solution were recorded to check the reference electrode and internal resistance of the equipment.

Square wave voltammograms were recorded with a 2 s equilibration time, a scan increment of 1 mV and a frequency of 30 Hz. The working electrode was cleaned between scans using by polishing with commercially available microcloth, rinsing with EtOH and drying.

In a typical experiment, 2.5 mL of a 0.2 mM solution of the [2]rotaxane host compound in the electrolyte solution was placed in the electrochemical cell. The solution was de-gassed by purging with Ar and subsequently maintained under an atmosphere of Ar. The square wave voltammograms of the solution were recorded. Chloride anion binding experiments were performed by addition of 0, 1, 2 and 5 equivalents of TBACl (1 x 0 μL, 2 x 5μL and 1 x 15 uL aliquots of a 0.1 M solution of TBACl in the electrolyte solution). The square wave voltammogram was recorded after each addition.