SUPPLEMENTARY INFORMATION

The effect of the solvent in the binding of anions and ion-pairs with a neutral [2]rotaxane

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General Information and Instruments

Rotaxane **1** was synthesized following the synthetic procedure previously described by us.[S1] Tetraalkylammonium salts were purchased from Merck and used without further purification.

NMR Titrations

^{1}H NMR spectra were recorded on Bruker Avance 500 (500 MHz for 1H NMR) ultra-shield spectrometer. Chloroform-*d*, acetone-d_6 and methanol-d_3 from Eurisotop were used.

A solution of rotaxane **1** (1 mM) in acetone-d_6 or chloroform-*d*/methanol-d_3 95/5 mixture was manually titrated with a 10 mM solution of an alkylammonium salt in the same solvent mixture using a micro syringe. A ^{1}H NMR spectrum was registered after each addition followed by hand shacking of the NMR tube for few seconds.

ITC Experiments

Isothermal titration calorimetry experiments were performed using a Microcal VP-ITC Microcalorimeter. HPLC grade solvents from Scharlab, SL were used. Titrations of rotaxane **1** with different alkylammonium salts in the different solvent mixtures were carried out by adding small aliquots (7-10 μL) of a solution of alkylammonium salts into a solution of the host in the same solvent mixture. The concentration of the guest was approximately 7-10 times more concentrated than the receptor solutions ([**1**] = 1×10^{-4} - 1×10^{-3} M). For the determination of the thermodynamic parameters of 2:1 complexes with chloride salts in acetone, higher guest's concentration solutions were used (e.g. up to 30 times more concentrated than that of the receptor solution). The association constant (K_a), TΔS and ΔH values for the binding processes were determined from the fit of the titration data to different theoretical binding models described in the main text (one set of sites or two sets of sites models implemented in Mircrocal software). Error values are reported as standard deviations.

^{1}H NMR titrations in acetone-*d*$_6$

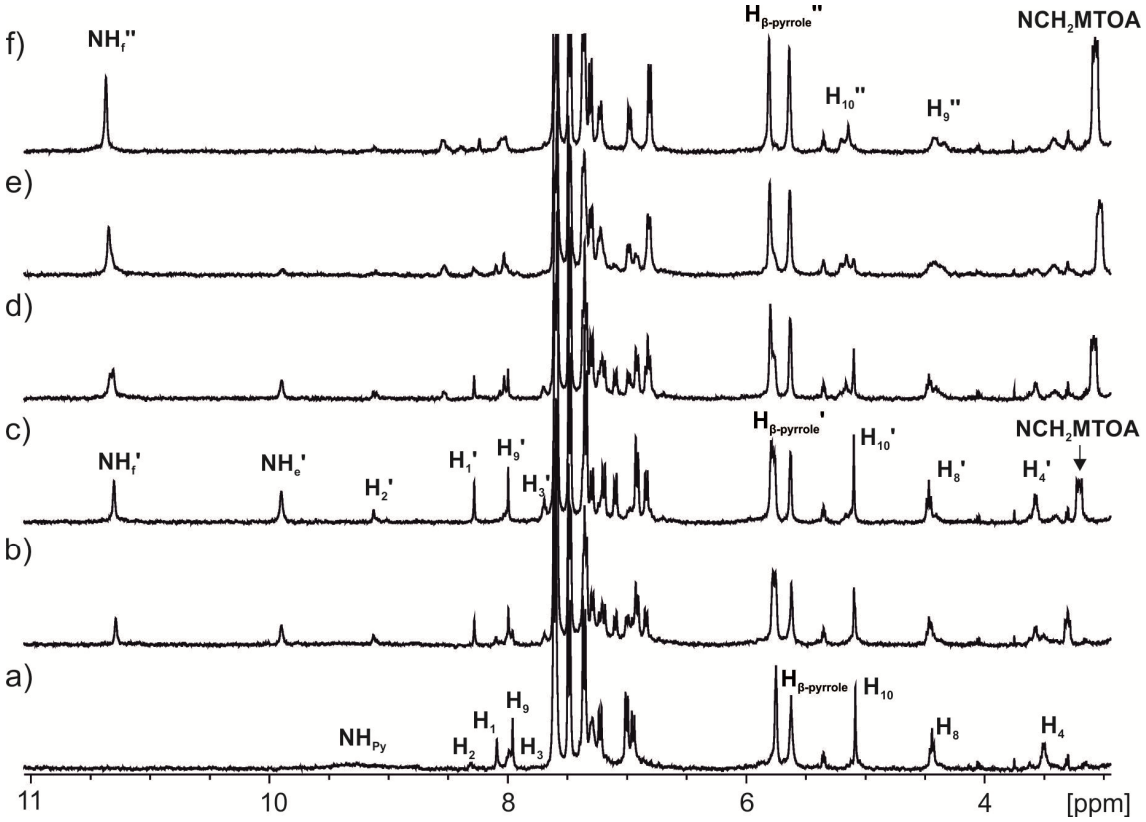

Figure S1 - Selected region of the ^{1}H NMR spectra (acetone-*d*$_6$, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv, b) 0.5 equiv., c) 1.0 equiv., d) 1.5 equiv., e) 2.0 equiv., and f) 4.0 equiv. of methyltrioctylammonium chloride (**2d**).

Please note that the addition of more than 2 equiv. of **MTOACl** provokes a gradual downfield shift of the proton signal corresponding to the methylene protons alpha to nitrogen of the $MTOA^+$ cation. This is attributed to the existence of a chemical exchange between the free and bound that is fast on the chemical shift time scale, as well as to the increase in concentration of the free cation in solution.

We quantified the ratio of the concentrations of the 1:1 and 2:1 complexes at 1.5 equiv. of MTOACl using the intensity values of two separate doublets resonating at 6.91 and 6.99 ppm, respectively. Using the intensity values of the signals we calculated a K(1:1)/β(2:1) ratio of 3 $\times 10^{-4}$ M^{-1} (considering β(2:1)= K(1:1)$\times$ K(1:2)). This value is in reasonably good agreement with the magnitude determined using the measured binding constants (3 $\times 10^{-5}$ M^{-1}) given the difficulties of the accurate quantification of the concentration of the species.

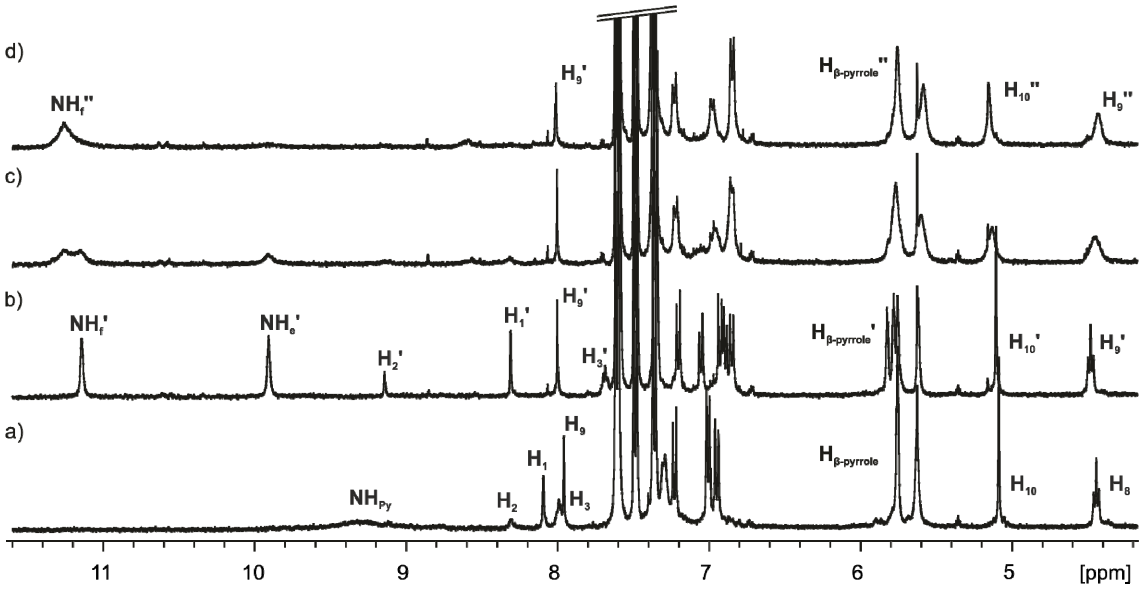

Figure S2 - Selected region of the ^{1}H NMR spectra (acetone-d_6, 500 MHz, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 1.0 equiv., c) 3.0 equiv. and d) 5.0 equiv. of tetrabutylammonium cyanate (**2b**).

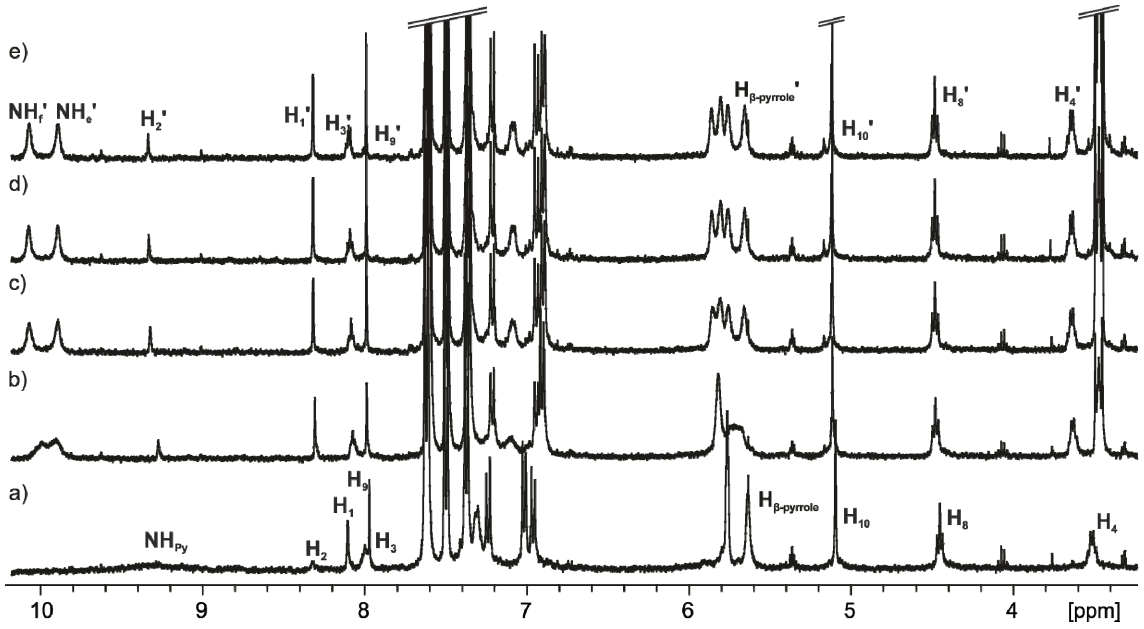

Figure S3 - Selected region of the ^{1}H NMR spectra (acetone-d_6, 500 MHz, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 1.0 equiv., c) 2.0 equiv., d) 4.0 equiv. and e) 6 equiv. of tetrabutylammonium nitrate (**2c**).

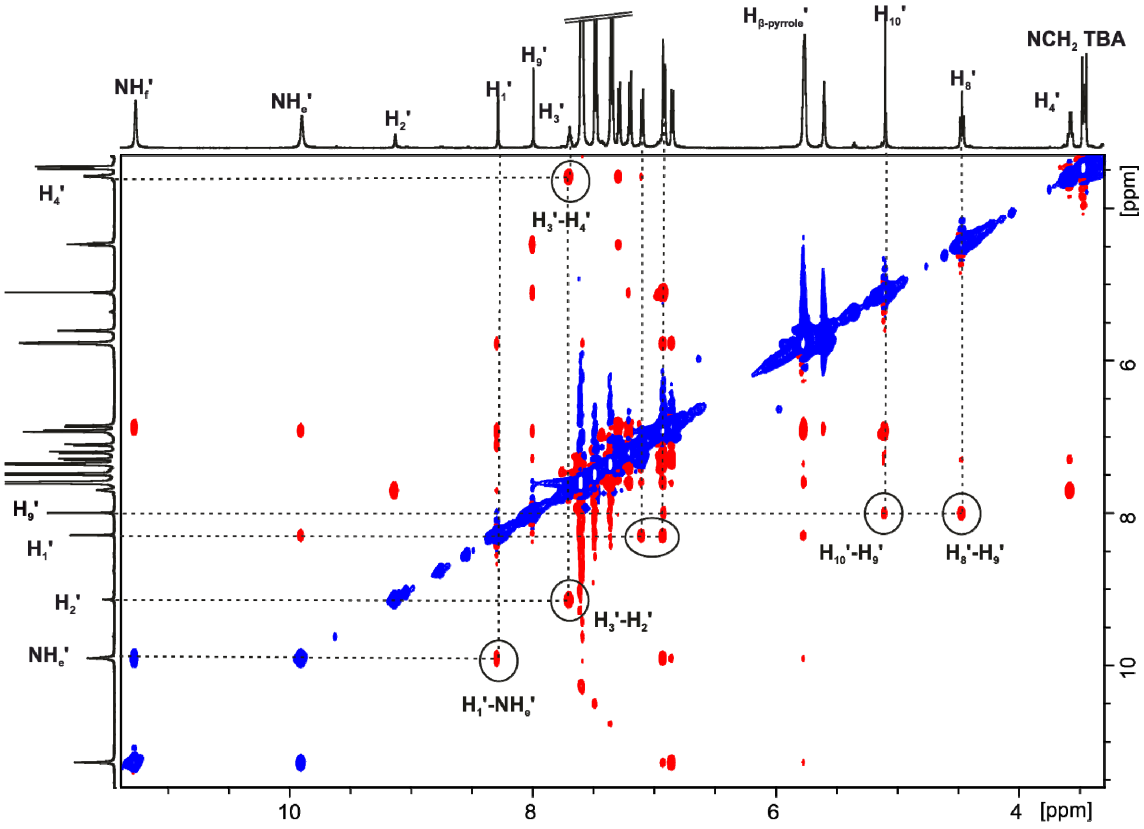

Figure S4 - Selected region of a ROESY experiment (acetone-d_6, 500 MHz, 298 K) of an equimolar mixture of [2]rotaxane **1** and tetrabutylammonium chloride (**2a**). The most relevant cross-peaks are marked.

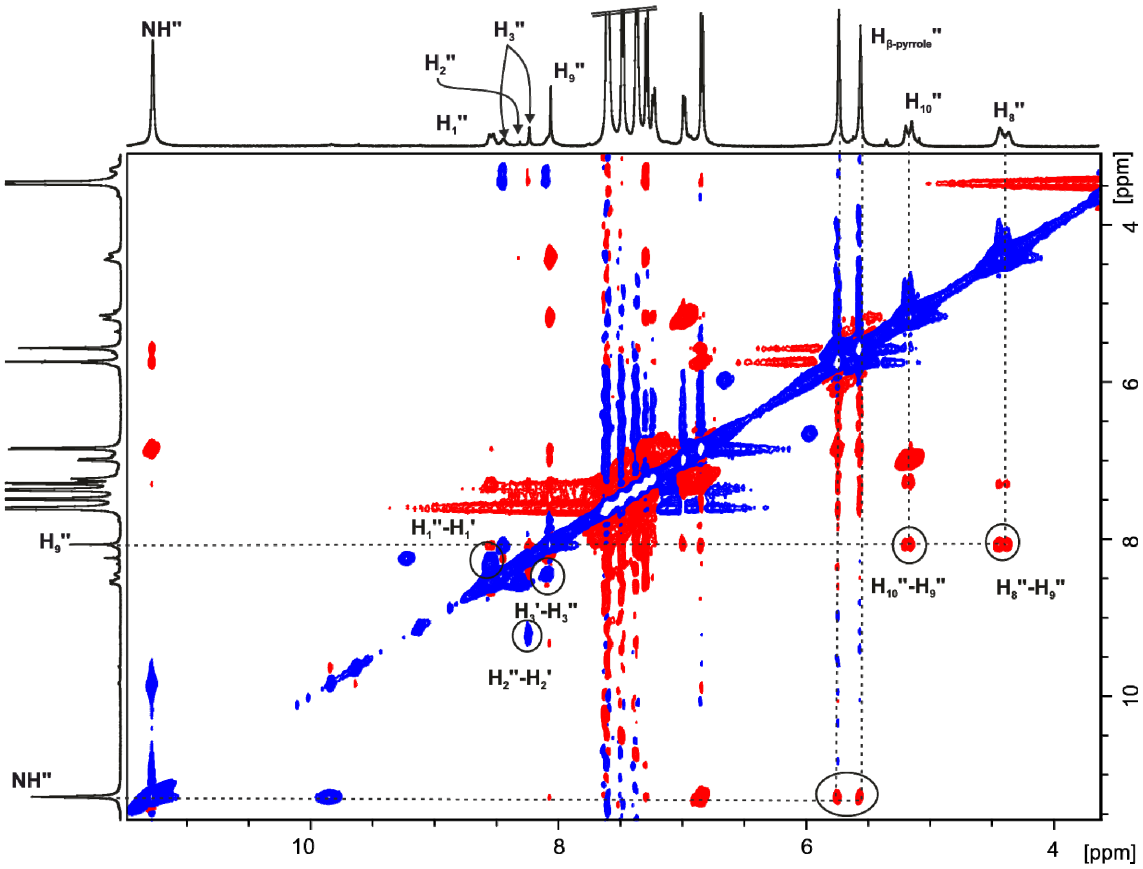

Figure S5 - Selected region of a ROESY experiment (acetone-d_6, 500 MHz, 298 K) of [2]rotaxane **1** with 3 equiv. of tetrabutylammonium chloride (**2a**). The most relevant cross-peaks are marked.

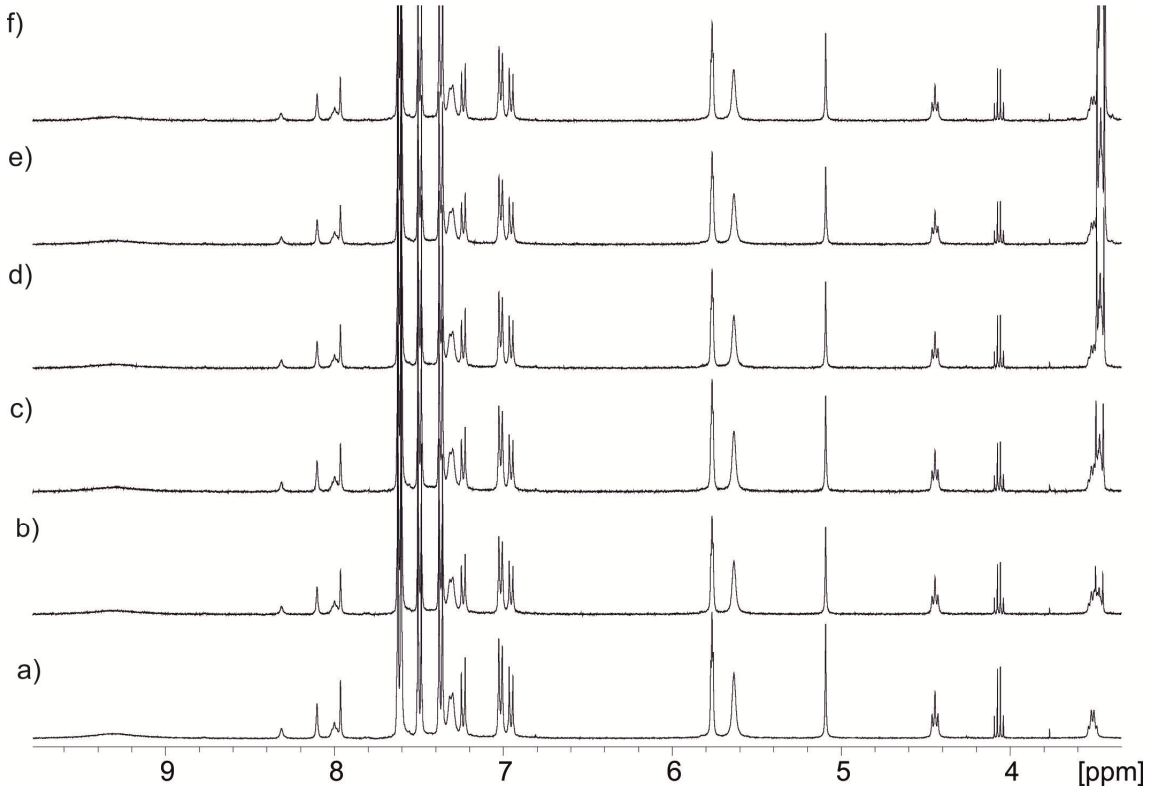

Figure S 6. Selected region of the ^{1}H NMR spectra (acetone-d_6, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 0.5 equiv., c) 1.0 equiv., d) 1.5 equiv., e) 2.0 equiv., and f) 4.0 equiv. of $TBAPF_6$. Please note that the addition of incremental amounts of $TBAPF_6$ does not provoke changes on the proton signals of the host. This result indicates that no significant binding of the cation TBA+ takes place with the free rotaxane in acetone solution using a non-coordinating anion.

^{1}H NMR titrations in a 95/5 chloroform-*d*/methanol-d_3 mixture

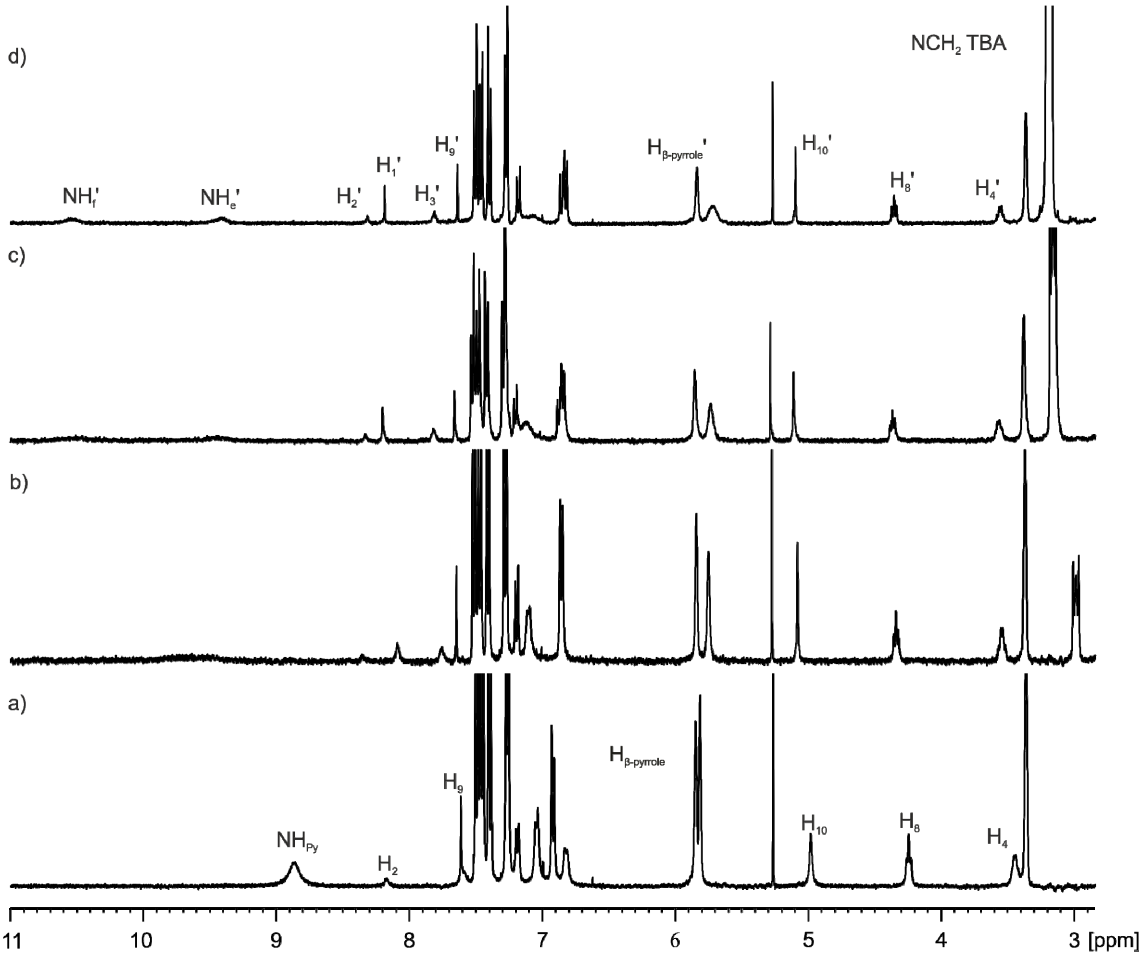

Figure S 7. - Selected region of the ^{1}H NMR spectra (95/5 $CDCl_3/CD_3OH$, 500 MHz, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 1.0 equiv., c) 5.0 equiv., and d) 20 equiv. of tetrabutylammonium chloride (**2a**).

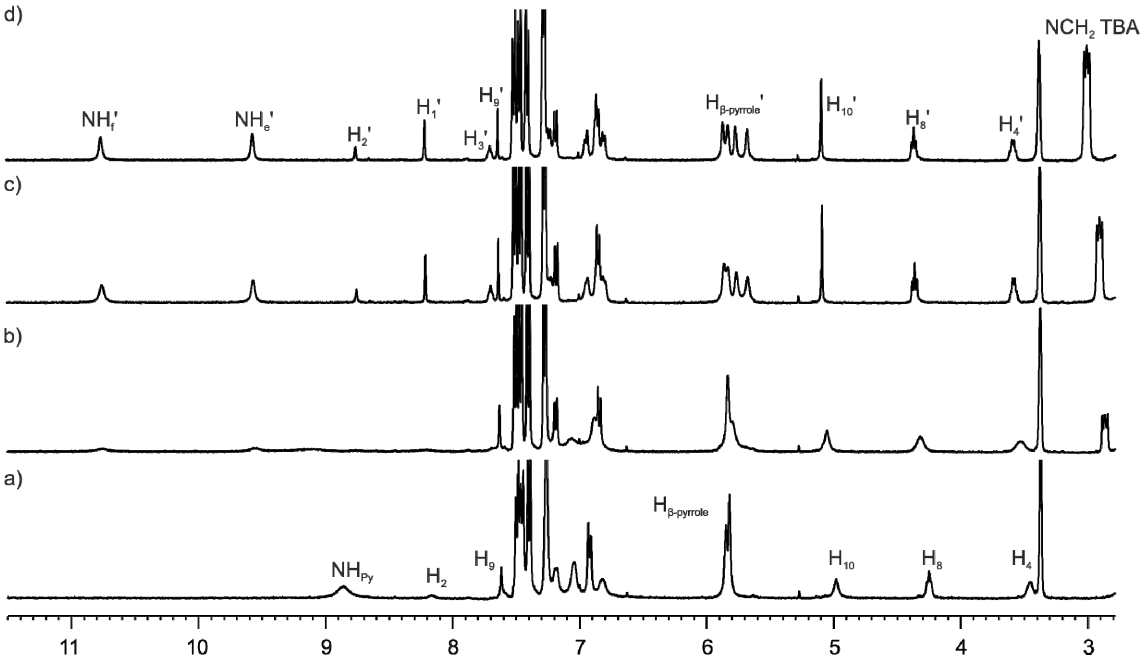

Figure S 8. - Selected region of the ^{1}H NMR spectra (95/5 $CDCl_3/CD_3OH$, 500 MHz, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 1.0 equiv., c) 2.0 equiv. and d) 3.0 equiv. of tetrabutylammonium cyanate (**2b**).

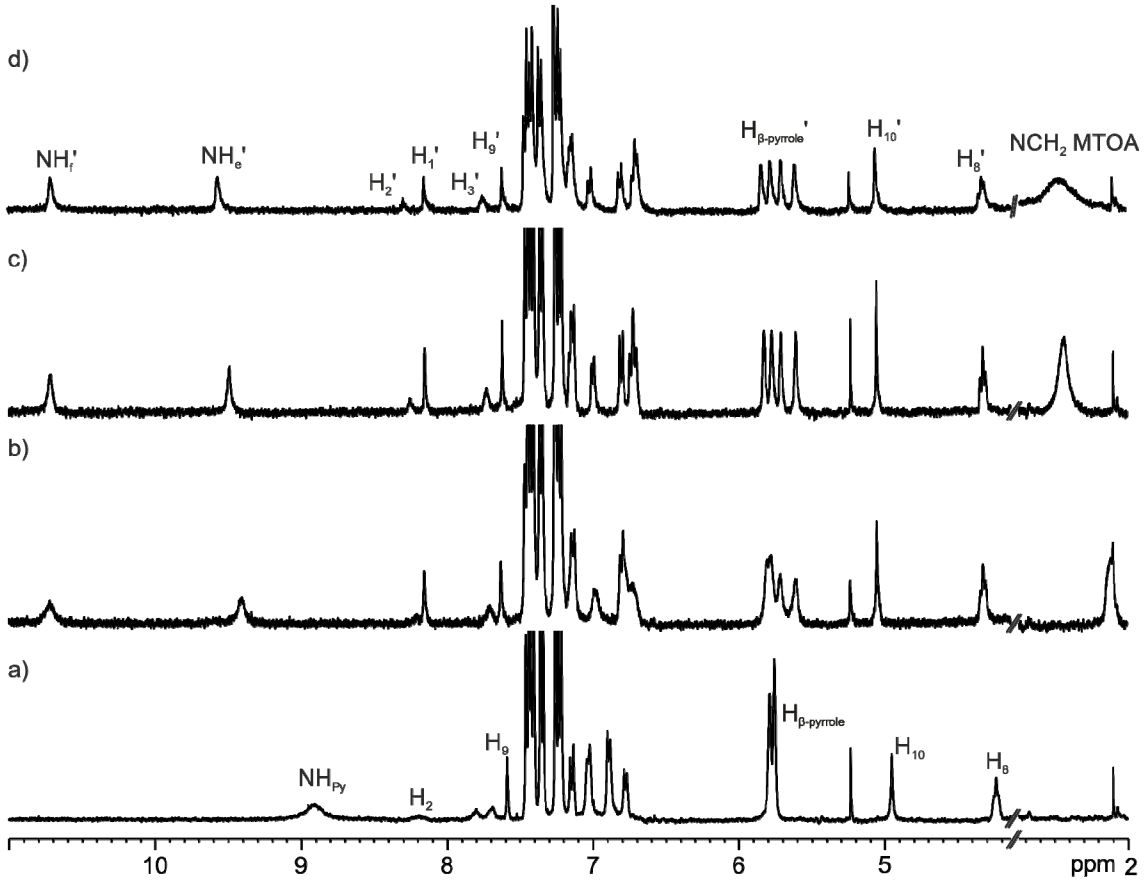

Figure S9 - Selected region of the ^{1}H NMR spectra (95/5 $CDCl_3/CD_3OH$, 500 MHz, 298 K) of the titration experiment of a 1 mM solution of [2]rotaxane **1** with a) 0 equiv., b) 1.0 equiv., c) 2.0 equiv. and d) 10.0 equiv. of methyl-trioctylammonium chloride (**2d**).

Isothermal Titration Calorimetry (ITC)

Acetone

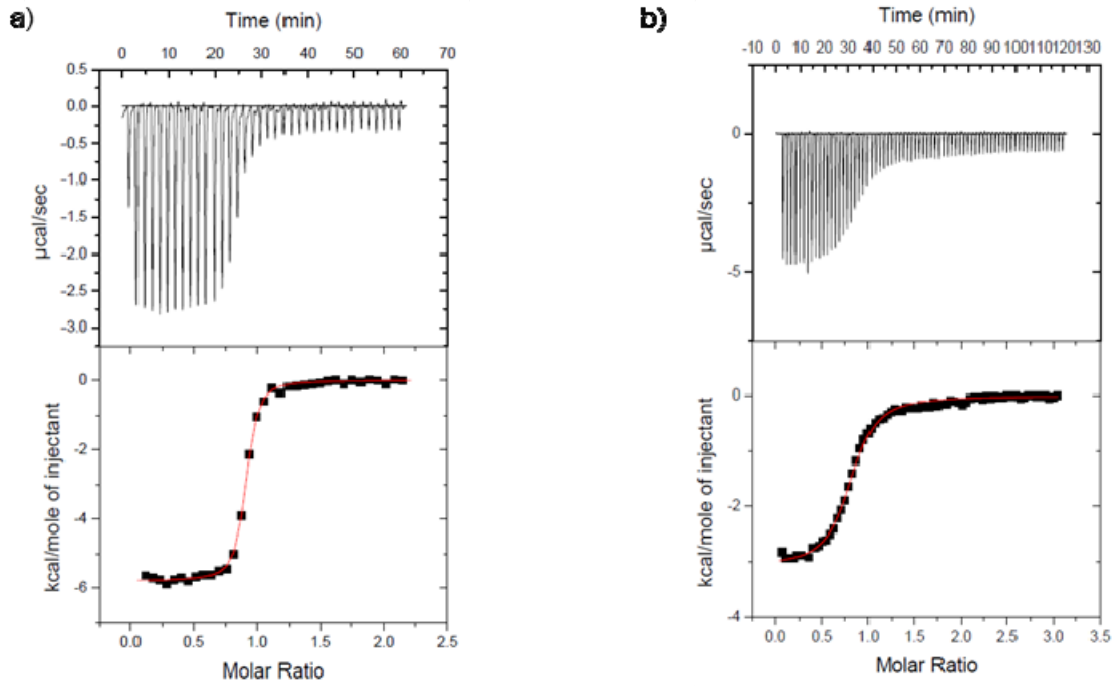

Figure S 10. Top – Traces of the raw data of the titration experiment of a $1.2 \cdot 10^{-4}$ M and $5.3 \cdot 10^{-4}$ M solution of [2]rotaxane **1**, with the **2b** and **2c** salts, respectively ([TBAOCN] = $1.2 \cdot 10^{-3}$ M (left) and [$TBANO_3$] = $7.3 \cdot 10^{-3}$ M (right)) in acetone. Bottom – Binding isotherms of the calorimetric titration shown on top. To determine the values of the thermodynamic variables the ITC data was fitted to a 1:1 binding model (red line).

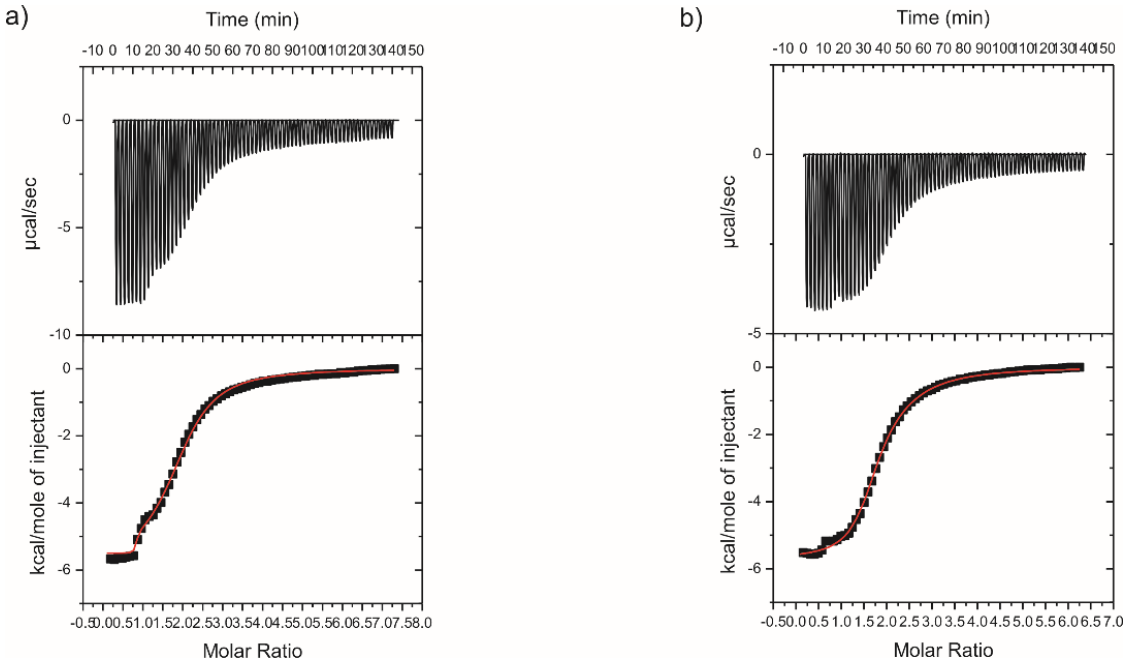

Figure S11 - Top – Traces of the raw data of the titration experiment of a 5.0×10^{-4} M and $3.2 \cdot 10^{-4}$ M solution of [2]rotaxane **1**, with **2a** and **2d,** respectively ([TBACl] = $17 \cdot 10^{-3}$ M (left) and [MTOACl] = $8.7 \cdot 10^{-3}$ M (right)) in acetone. Bottom – Binding isotherms of the calorimetric titration shown on top. To determine the values of the thermodynamic variables the ITC data was fitted to a model that considers the formation of 1:1 and 2:1 complexes (red line).

Chloroform/methanol 95/5

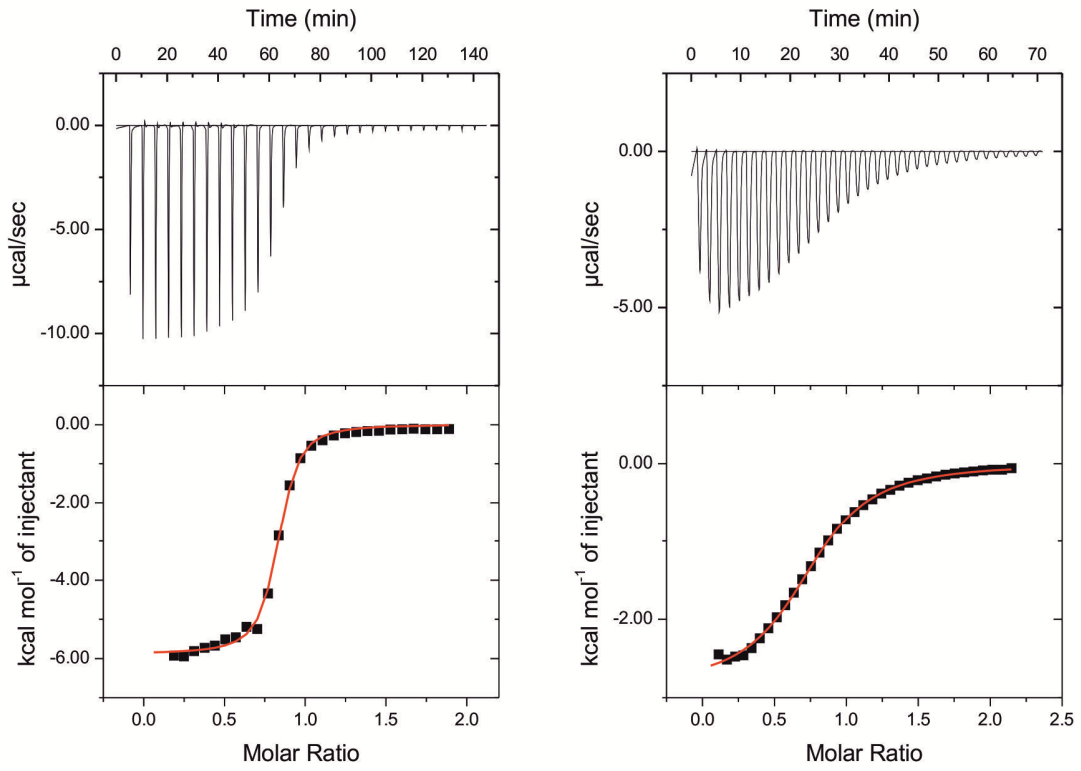

Figure S12 Top – Traces of the raw data of the titration experiment of a $1.0 \cdot 10^{-3}$ M and $5.0 \cdot 10^{-4}$ M rotaxane **1**, with the **2a** and **2b**, respectively ([TBACl] = $1 \cdot 10^{-2}$ M (right) and [TBAOCN] = $4 \cdot 10^{-3}$ M (left)) in a 95/5 mixture of chloroform/methanol. Bottom – Binding isotherms of the calorimetric titration shown on top. To determine the values of the thermodynamic variables the ITC data was fitted considering a 1:1 binding model (red line).

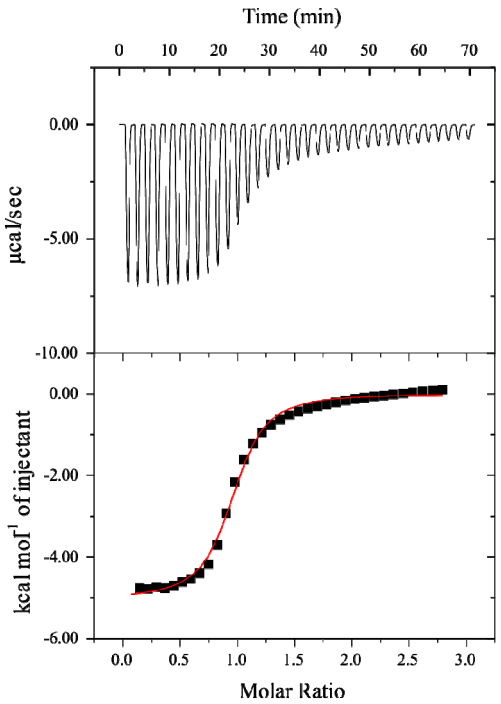

Figure S13 Top – Traces of the raw data of the titration experiment of a $5.0 \cdot 10^{-4}$ M rotaxane **1**, with **2d** ([MTOACl] = $5 \cdot 10^{-3}$ M) in a 95/5 mixture of chloroform/methanol. Bottom – Binding isotherm of the calorimetric titration shown on top. To determine the values of the thermodynamic variables the ITC data was fitted considering a 1:1 binding model (red line).

References

S1 J. R. Romero, G. Aragay and P. Ballester, *Chem. Sci.*, 2017, **8**, 491-498.