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Covalent Capture of Oriented Calix[6]Arene Rotaxanes by a Metal-Free Active Template Approach

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Table of Contents

1. General Information

All solvents were dried using standard procedures. ^{1}H NMR spectra were recorded on a Bruker Avance III instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Melting points are uncorrected. Chemical shifts are expressed in ppm (δ) using the residual solvent signal as internal reference (7.26 ppm for $CHCl_3$, 3.31 for CH_3OH and 2.50 for DMSO). Mass spectra were recorded in ESI mode. Compounds **1**,[1] **3**,[2] **5**$^{+}$,[3] and **6**[4] were synthesised according to published procedures. All other reagents were of reagent grade quality obtained from commercial suppliers and were used without further purification.

2. Synthesis of the new compounds

1-octadecy-[4,4'-bipyridin]-1-ium 4-methylbenzenesulfonate (2^{+}): In a 100 ml round-bottomed flask octadecyl 4-methylbenzenesulfonate (1.0 g, 2.4 mmol) and 4,4'-dipyridyl (1.1 g, 7.1 mmol) were dissolved in CH_3CN (50ml) and the resulting solution was refluxed for 24h, then the solvent was evaporated to dryness at reduced pressure. The oily residue was triturated thrice with ethyl acetate (3×20 mL) until salt **2**$^{+}$ precipitated as a white solid compound, which was recovered by suction filtration (1.0 g, 64%). M.p. = 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$ with few drops of CD_3OD): δ(ppm) = 0.81 (t, *J* = 7.2 Hz, 3H), 1.2–1.3 (m, 30H), 1.9-2.0 (m, 2H), 2.28 (s, 3H), 4.63 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J*=6.4 Hz, 2H), 8.40 (d, *J* = 6.4 Hz, 2H), 8.82 (d, *J* = 6.4 Hz, 2H), 9.02 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$ with few drops of CD_3OD): δ(ppm) = 14.0, 21.1, 22.6, 26.0, 28.9, 29.3 (2 res.), 29.4, 29.5, 29.6 (2 res.), 31.5, 31.8, 62.1, 123.2, 125.6, 126.3, 128.8, 140.2, 142.0, 144.1, 145.3, 148.6, 152.6; ESI-MS(+): m/z (%) = 409 (100) $[M]^{+}$.

Rotaxane R'[1•8]$^{2+}$: To a solution of calix[6]arene-wheel **1** (0.1 g, 0.07 mmol) in toluene (20 mL), an equimolar ratio of stoppered salt **5**$^{+}$ (0.044 g, 0.07 mmol) and an excess of tosylate **6** (0.075 g, 0.21 mmol) were added. The orange-coloured resulting solution was refluxed for four days; afterwards, the mixture was cooled to room temperature and diphenylacetyl chloride (0.032 g, 0.14 mmol) and triethylamine (0.014 g, 0.14 mmol) were added. The solution was stirred at room temperature for 16 hours. The solvent was then evaporated under reduced pressure and the residue was purified by column chromatography (dichloromethane:methanol = 95:5) to afford 0.12 g (63%) of pure rotaxane R'[**1•8**]$^{2+}$ as a red solid compound. ^{1}H NMR (400 MHz, C_6D_6): δ(ppm) = 9.4 (broad s, 6H), 8.3-8.0 (broad s, 6H), 8.0-7.7 (m, 10 H), 7.59 (s, 6H), 7.45 (d, *J* = 7.6 Hz, 4H), 7.41 (d, *J* = 7.2 Hz, 4H), 7.2-7.1 (m, 6H), 7.1-7.0 (m, 10H), 6.92 (d, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 6.0 Hz, 2H), 6.68 (t, *J* = 6.8 Hz, 6H), 5.13 (s,1 H), 5.08 (s,1 H), 4.58 (d, *J* = 15 Hz, 6H), 4.1-4.0 (m, 4H), 3.95 (s, 9H), 3.9-3.7 (m, 8H), 3.7-3.5 (m, 8H), 3.5-3.2 (m, 12H), 2.2 (broad s, 2 H), 1.96 (s, 6H), 1.8 (broad s, 2H), 1.8-1.5 (m, 70H); ^{13}C NMR (100 MHz, C_6D_6): δ(ppm) = 172.0, 171.9, 153.5, 152.8, 148.2, 147.9, 144.4, 142.9, 141.2, 139.2, 139.2, 137.5, 133.8, 132.1, 129.3, 128.7, 128.7, 128.6, 128.6, 128.5, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 127.0, 126.5, 125.7, 124.7, 121.2, 118.1, 116.7, 72.4, 70.0, 66.3, 64.7, 60.9, 60.5, 57.4, 57.3, 34.6, 31.5, 30.0, 29.7, 29.2, 28.6, 28.3, 25.8, 25.5, 24.9, 20.8, 15.2; MS (ESI): m/z (z=2) = 1148.3 $[M\text{-}2TsO]^{2+}$.

3. NMR Spectra of the new compounds

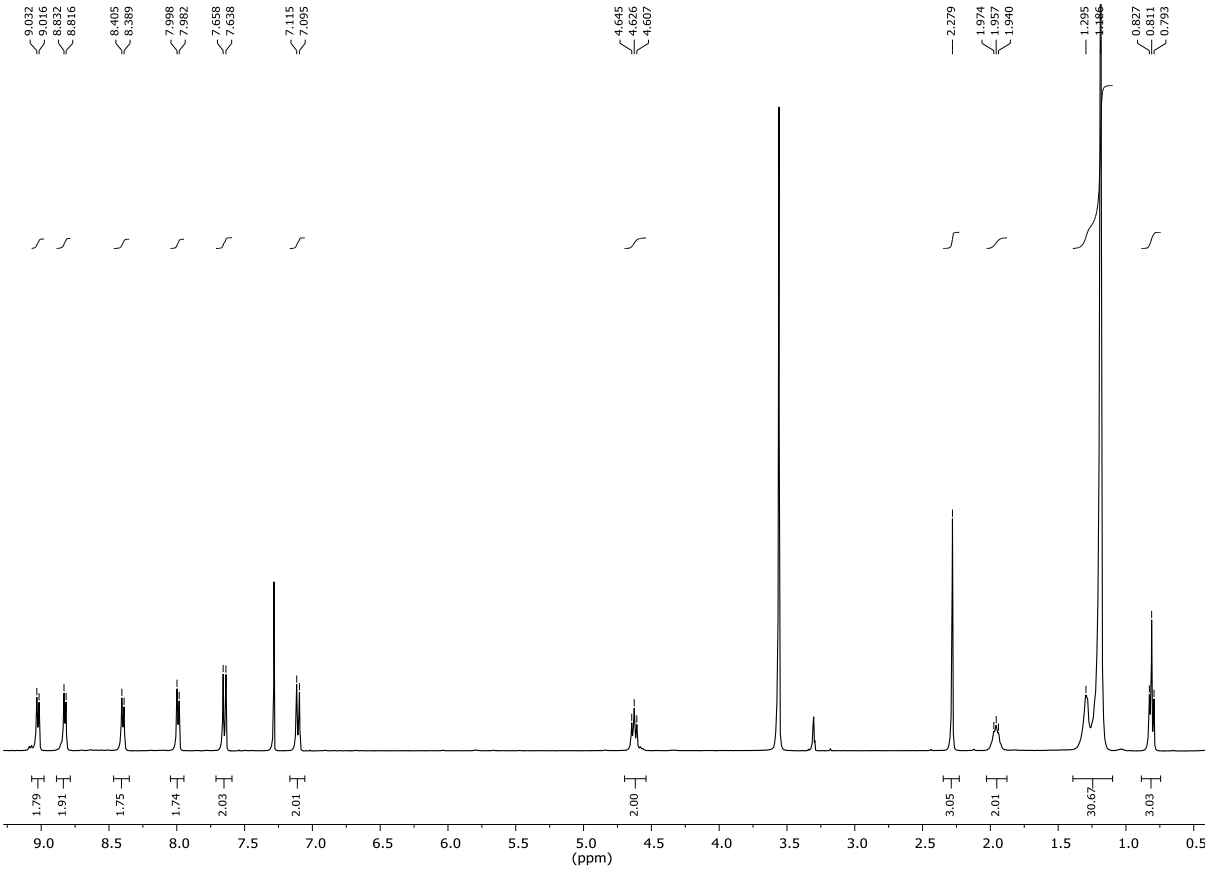

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$ with few drops of CD_3OD) of **2**$^{+}$.

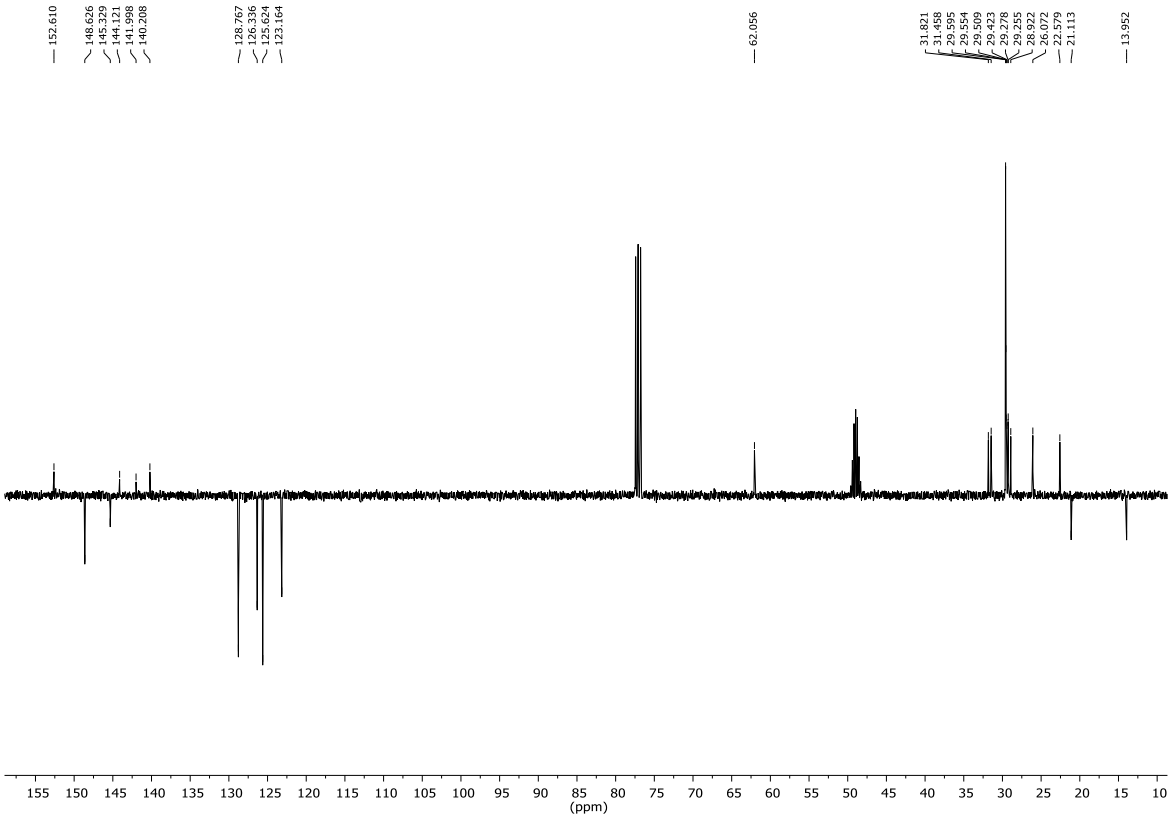

Figure S2. APT - ^{13}C NMR spectrum (100 MHz, $CDCl_3$ with few drops of CD_3OD) of **2**$^{+}$.

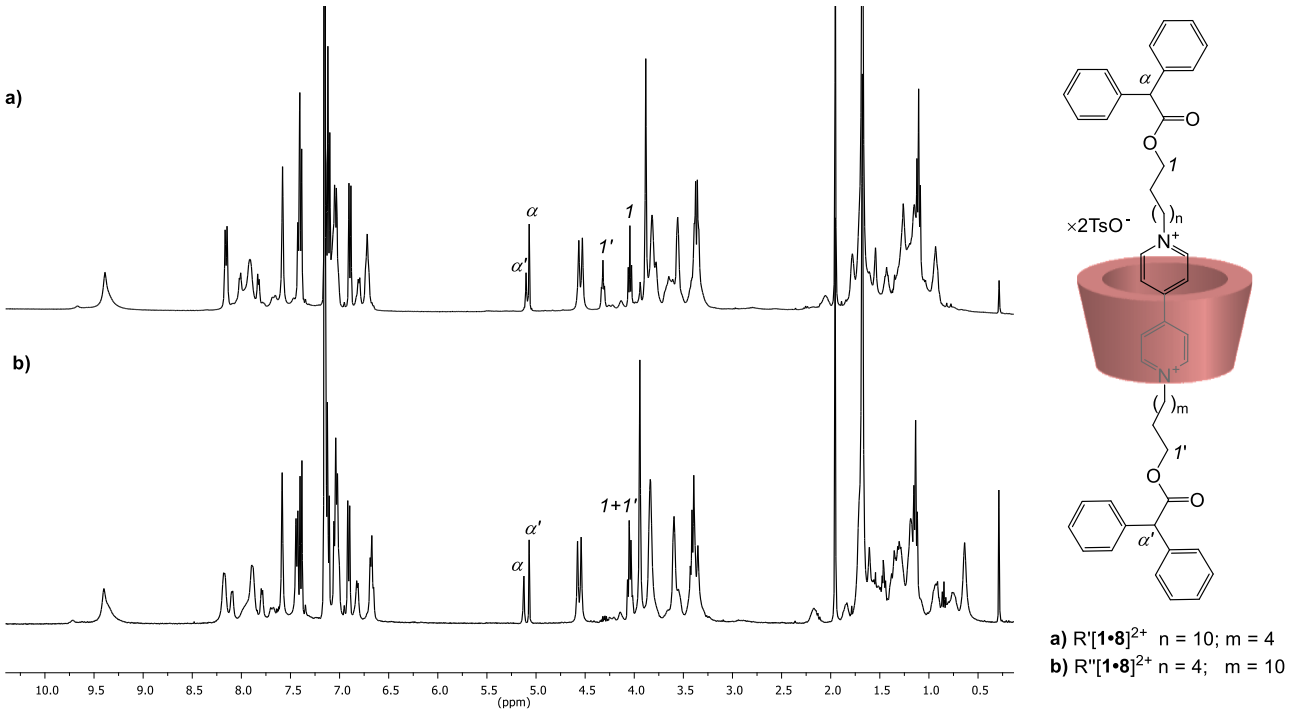

Figure S3. ^{1}H NMR (C_6D_6, 400 MHz) stack plot of orientational rotaxane isomers R'[**1●8**]$^{2+}$ (a) and R''[**1●8**]$^{2+}$ (b). The ^{1}H NMR spectrum of R''[**1●8**]$^{2+}$ was used for comparison to derive the structural assignment of R'[**1●8**]$^{2+}$; see on the right the schematic representation of the two orientational rotaxane isomers with the labelling of the protons used for the assignment of their structures. The orientational rotaxane isomer R''[**1●8**]$^{2+}$ was prepared using previously reported methods.[1,3]

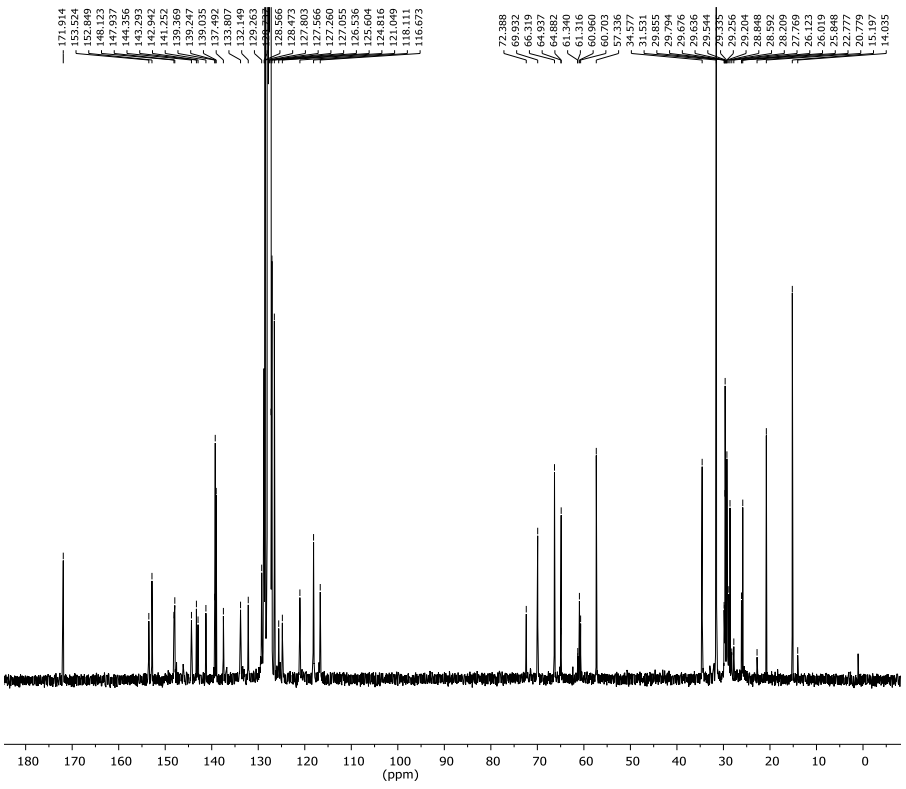

Figure S4. ^{13}C NMR spectrum (100 MHz, C_6D_6) of R'[**1●8**]$^{2+}$.

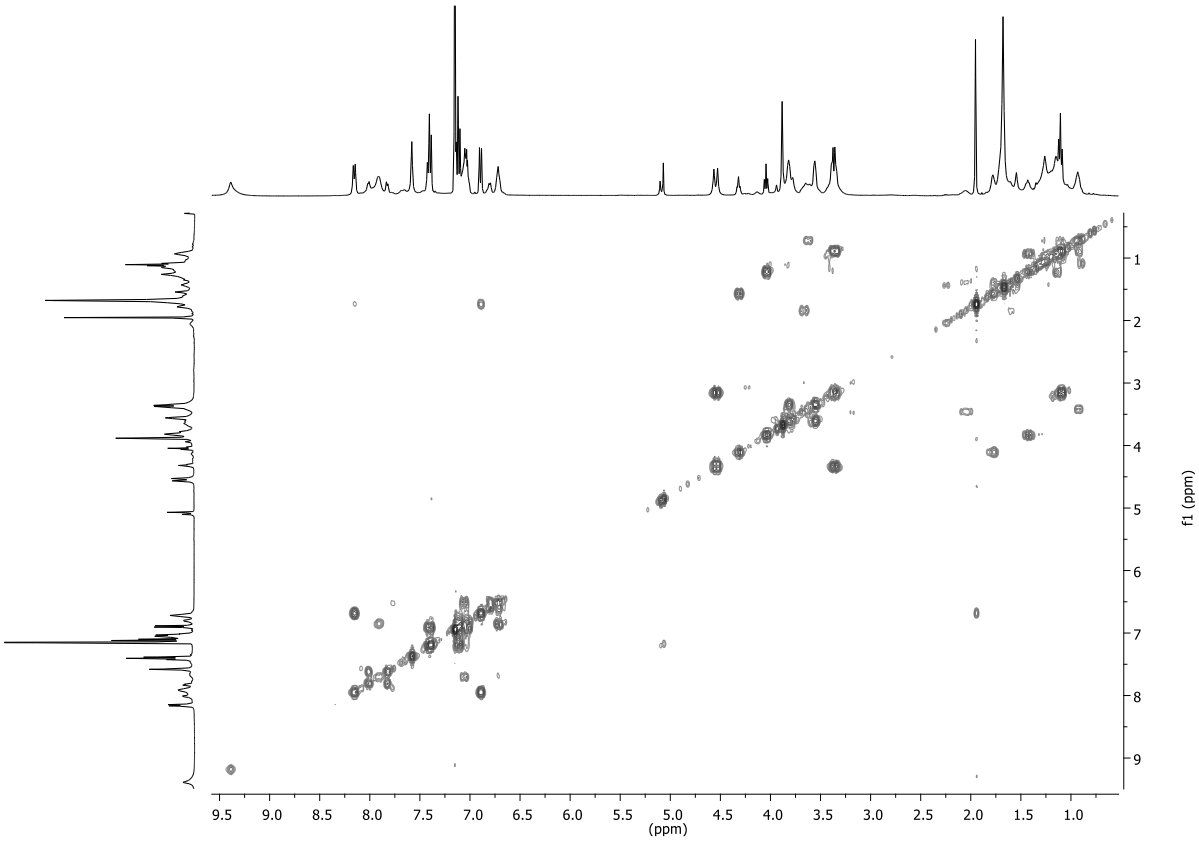

Figure S5. COSY NMR spectrum (400 MHz, C_6D_6) of R'[**1●8**]$^{2+}$.

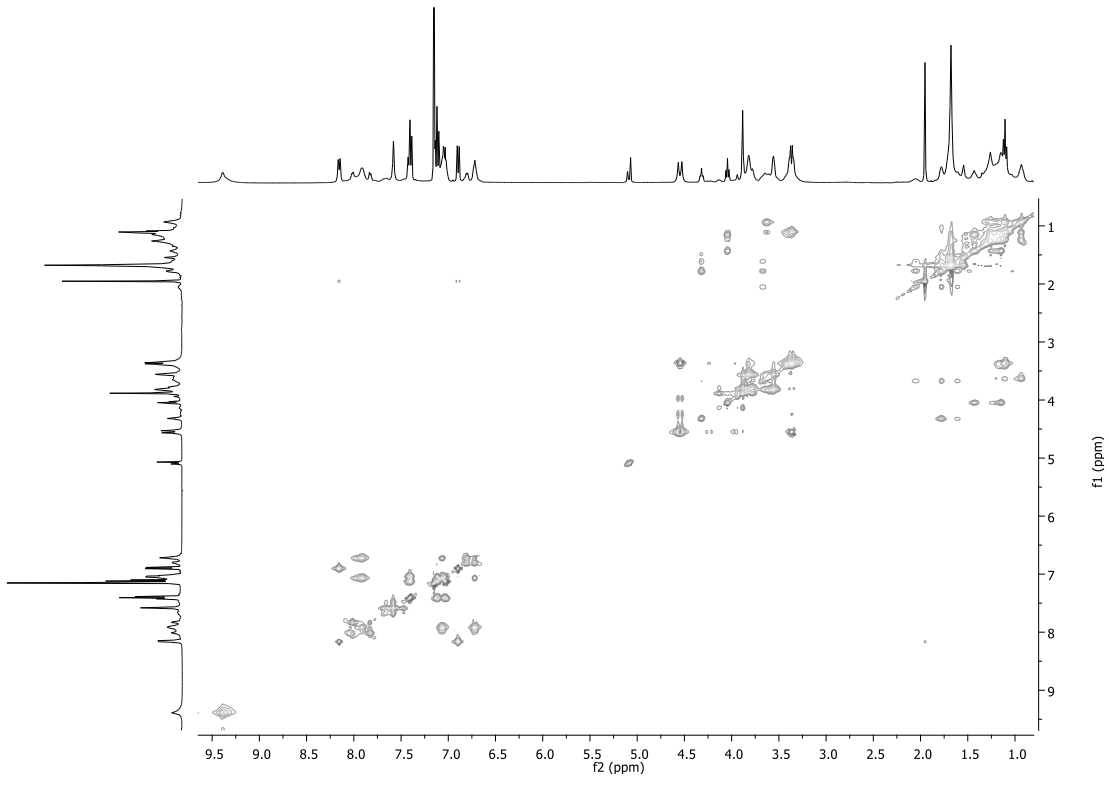

Figure S6. TOCSY NMR spectrum (400 MHz, C_6D_6) of R'[**1●8**]$^{2+}$.

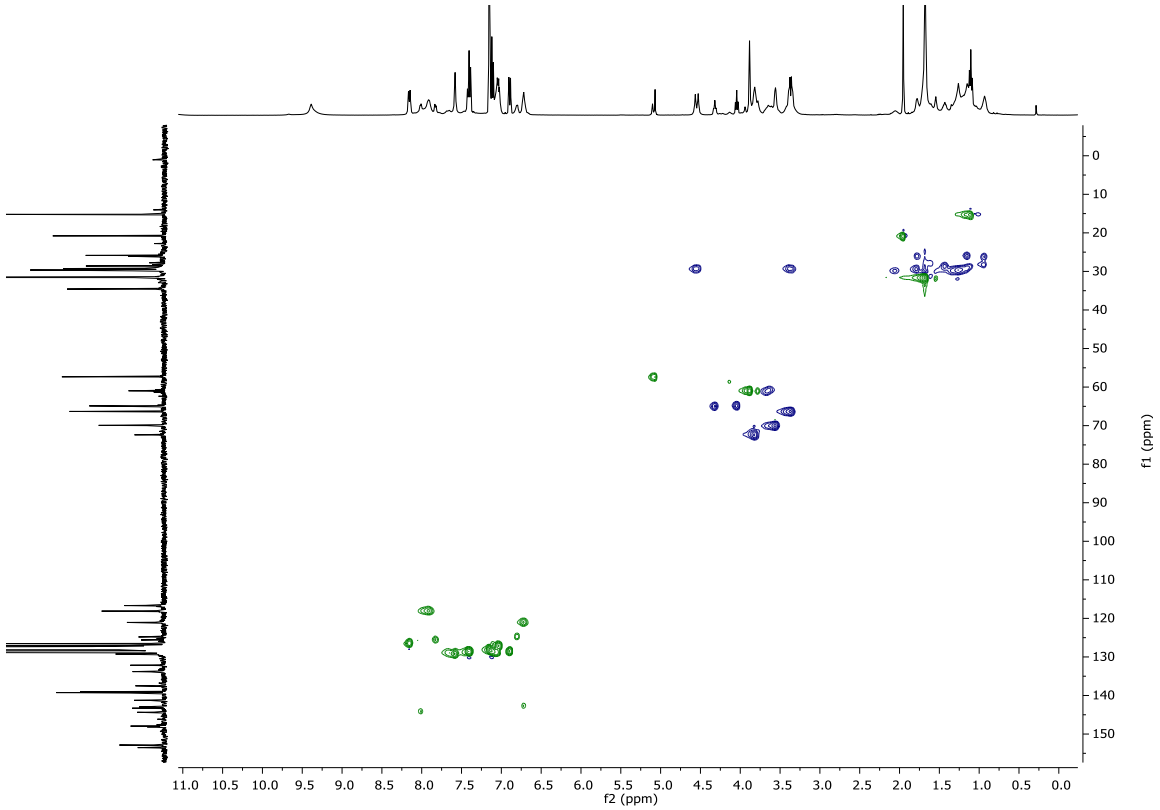

Figure S7. Edited HSQC NMR spectrum (400 MHz, C_6D_6) of R'[**1●8**]$^{2+}$.

4. Characterization of the mixture of pseudorotaxane isomers P'[1⊃2]$^{+}$ and P''[1⊃2]$^{+}$

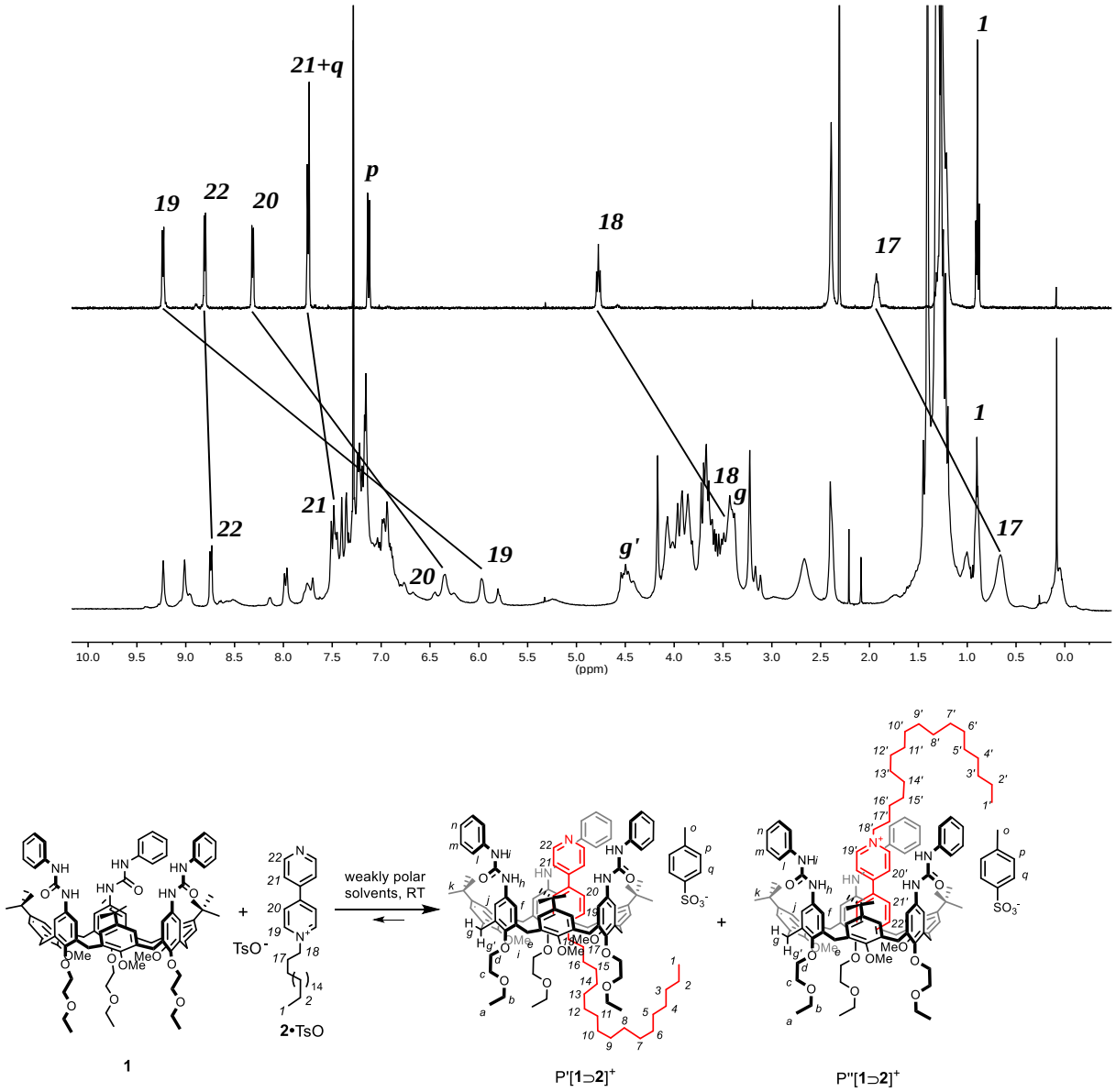

Figure S8. (top) ^{1}H NMR ($CDCl_3$, 300 MHz) stack plot of a) **2**$^{2+}$ and b) mixture of pseudorotaxane isomers P'[**1**⊃**2**]$^{2+}$ and P''[**1**⊃**2**]$^{2+}$ (T = 253 K); (bottom) Schematic representation of the formation of the mixture orientational pseudorotaxane isomers with the proton labelling used for the NMR resonances assignment.

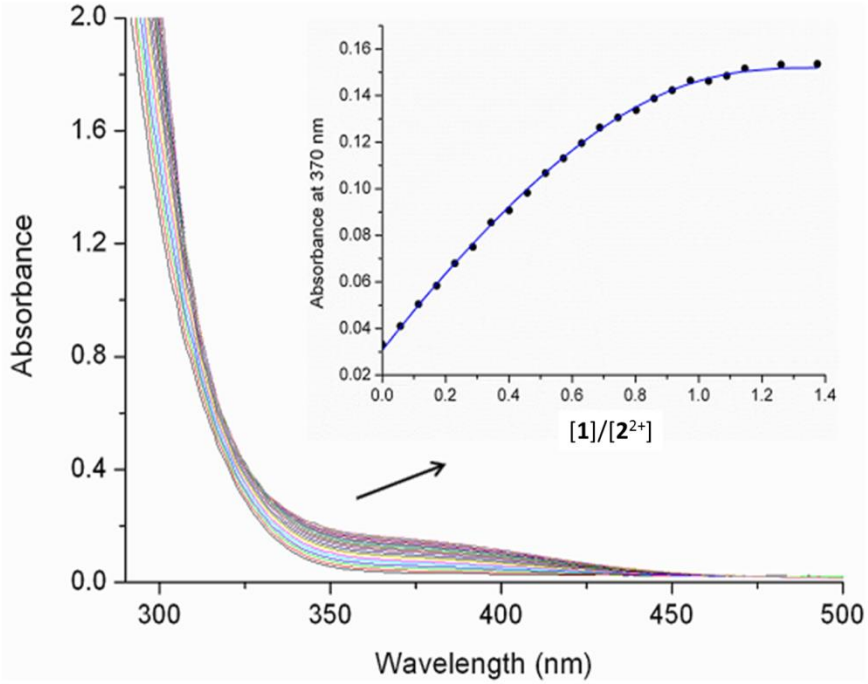

Figure S9. Collection of UV/Vis absorption spectra (toluene, *T* = 333 K) of pyridylpyridinium tosylate $\mathbf{2}^{2+}$ upon titration with calix[6]arene **1**. Inset: plot of the absorption changes at λ = 370 nm (black dots) vs equivalents of calix and fitting of the data (solid blue line).

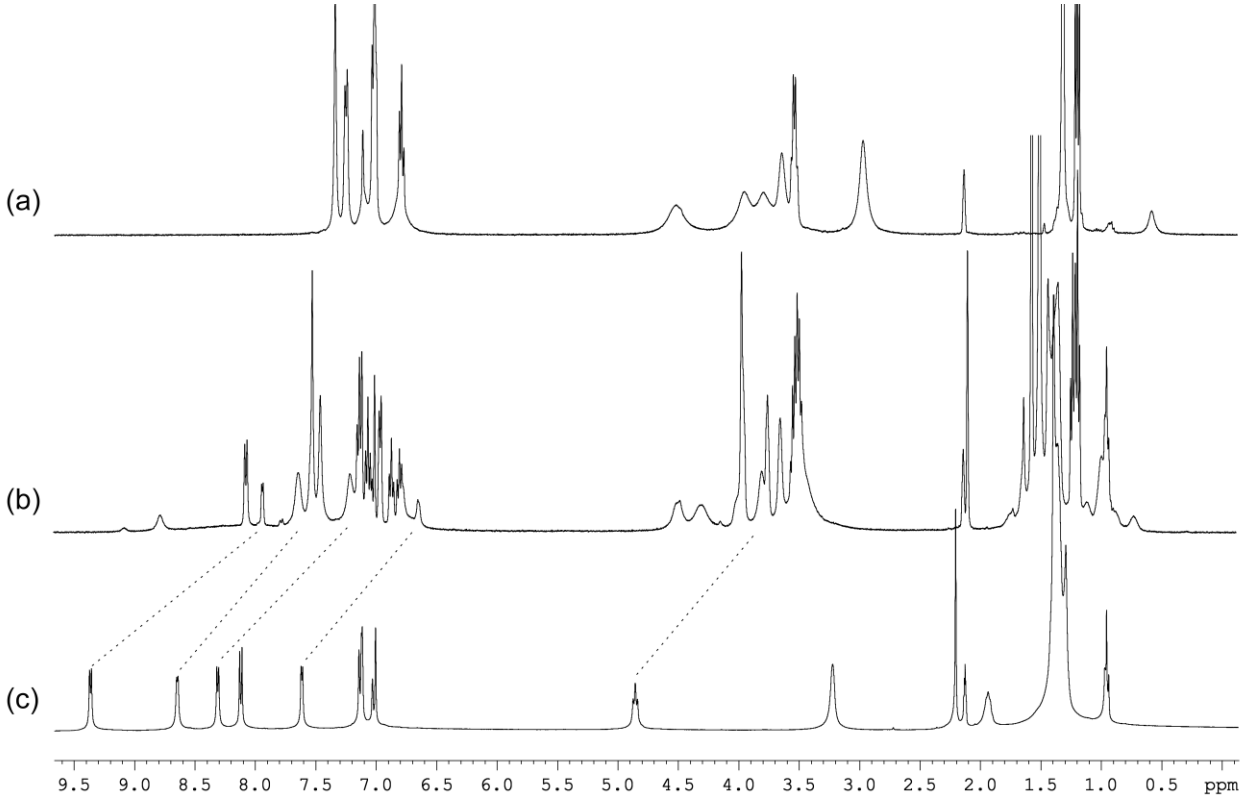

Figure S10. ^{1}H NMR stack plot of (a) calix[6]arene host **1**, (c) guest $\mathbf{2}^{+}$ and (b) of their 1:1 mixture (c = 1×10^{-2} M). The spectra were taken in toluene[D8] at *T* = 353 K. Dotted lines indicate the up-field shift of the most representative aromatic resonance of $\mathbf{2}^{+}$ upon complexation with **1**.

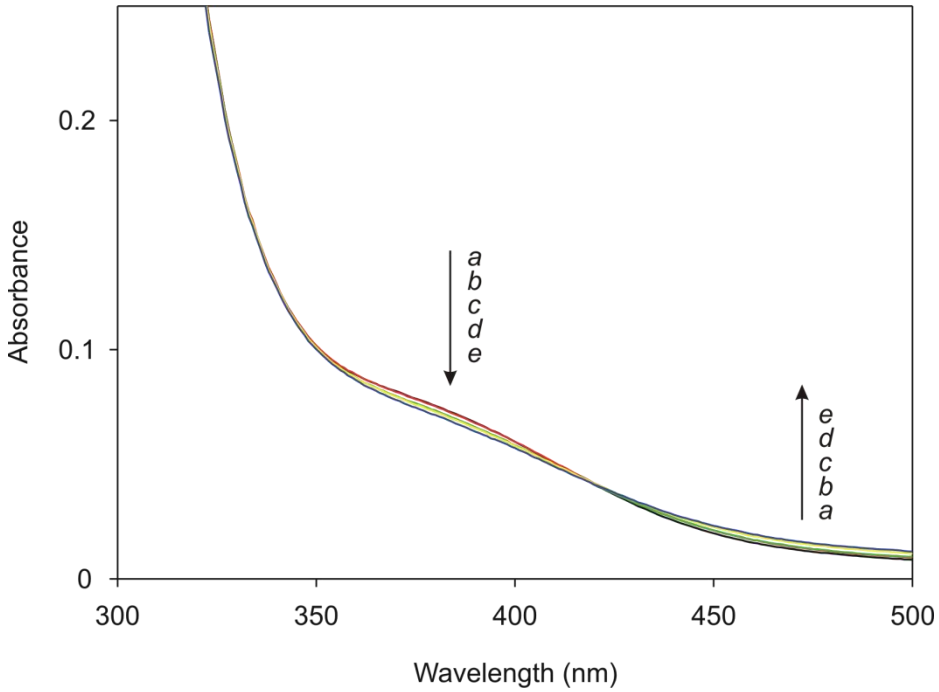

Figure S11. Absorption spectra of a toluene solution containing calixarene **1** and guest $\mathbf{2}^{+}$ in a 1:1 ratio at a concentration of 1.1×10^{-4} M at the following temperatures: (a) 319 K, (b) 327 K, (c) 333 K, (d) 342 K, and (e) 351 K.

5. References

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2. A. Arduini, R. Bussolati, A. Credi, G. Faimani, S. Garaudee, A. Pochini, A. Secchi, M. Semeraro, S. Silvi, and M. Venturi, *Chem. - A Eur. J.*, 2009, **15**, 3230-3242.

3. A. Arduini, F. Ciesa, M. Fragassi, A. Pochini, and A. Secchi, *Angew. Chemie, Int. Ed*., 2005, **44**, 278-281.

4. S. Ballot, and N. Noiret, *Tetrahedron Lett*. 2003, **44**, 8811-8814.