

Templated synthesis of cyclic [4]rotaxanes consisting of two stiff rods threaded through two bis-macrocycles with a large and rigid central plate as spacer

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X-ray crystallography

General methods

The NMR spectra were referenced to residual proton-solvent references.

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

UV-visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with 1 cm path cell. All measurements were made on toluene solutions, 1.50×10^{-6} M in rotaxane **2**⁴⁺. Guests **G1** to **G5** solutions (4.50×10^{-5} M) were added to the rotaxane sample in 10 µl aliquots via a 100 µl Hamilton syringe. UV-visible spectrophotometric titrations were analyzed by fitting the series of spectra at 1 nm intervals by using the SPECFIT/32 3.0 (Spectrum Software Associates) that takes into account the changes in volume during the titration.^{S1}

Diffusion NMR spectroscopy measurements were acquired on a Bruker Avance spectrometer, at the resonating frequency of 500.13 MHz for ¹H, using a Bruker BBI 5 nm probe. Samples were prepared in CD₂Cl₂ and the temperature was regulated at 298 K.

I. ^1H NMR and ES-MS characterization of compounds 6^{4+} , 1^{4+} , 12^{4+} and 2^{4+}

1) [4]pseudorotaxane 6^{4+} :

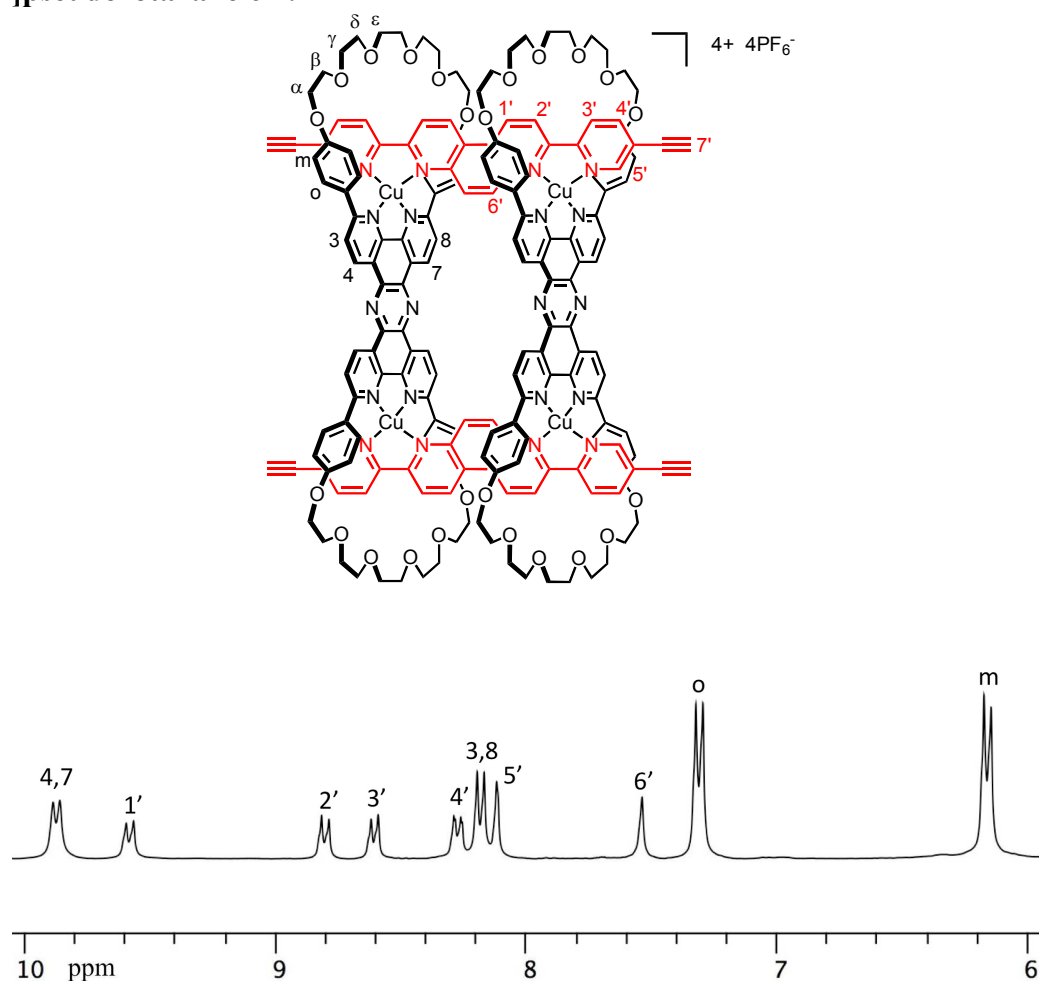


Figure S11. ^1H NMR spectrum (aromatic region, 10-6 ppm) of compound 6^{4+} in CD_2Cl_2 .

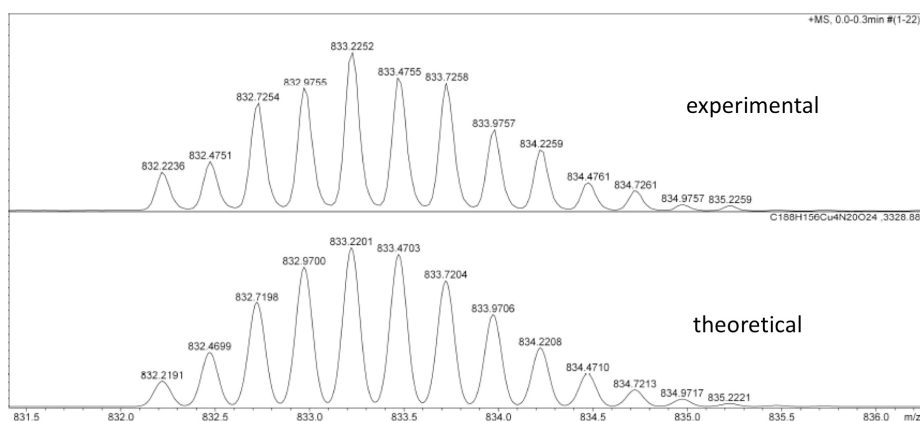


Figure S12. HR ES-MS spectrum of compound 6^{4+} (top) and the corresponding simulation (bottom).

2) [4]rotaxane 1^{4+} :

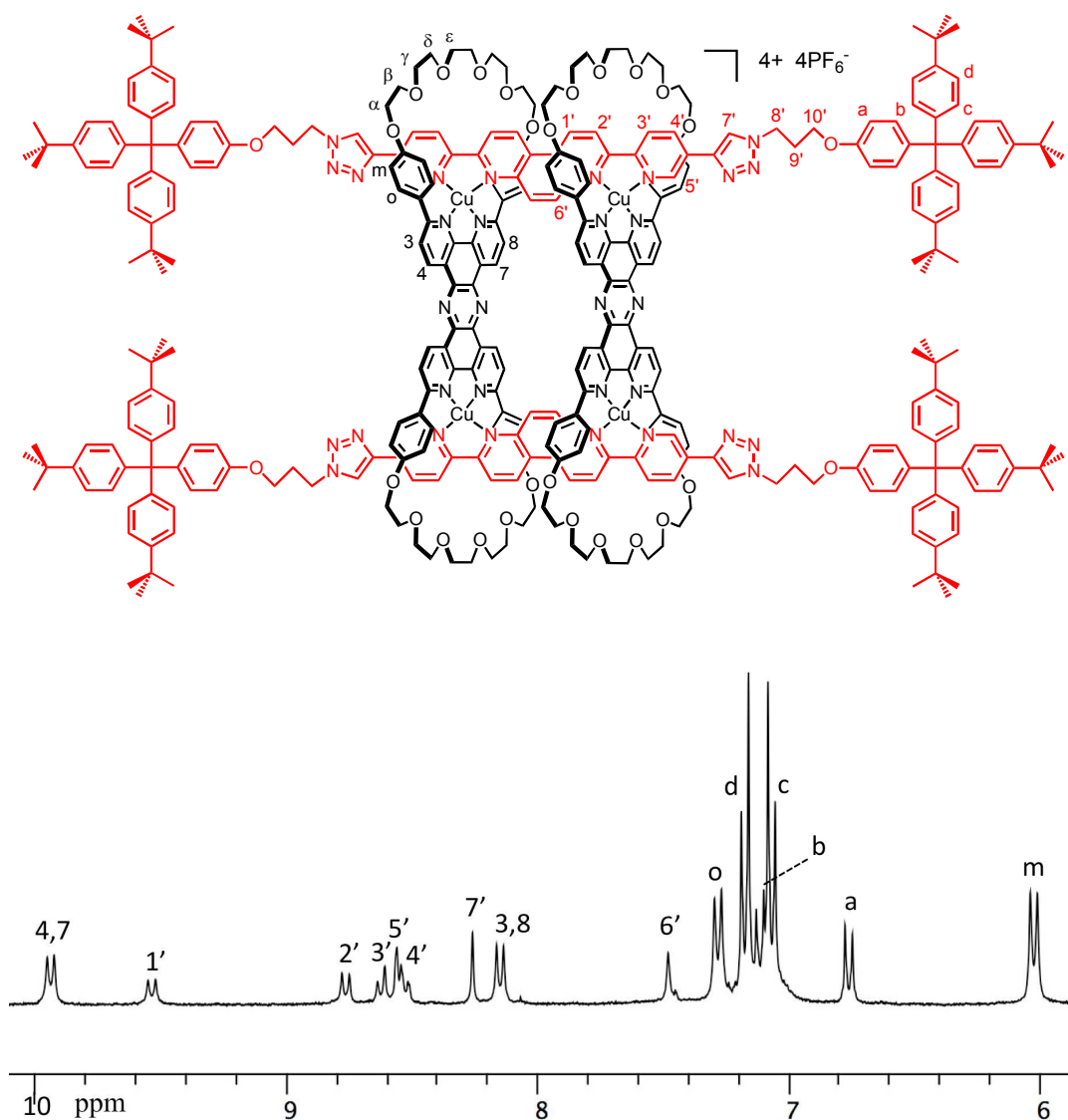


Figure SI3. ^1H NMR spectrum (aromatic region, 10-6 ppm) of compound 1^{4+} in CD_2Cl_2 .

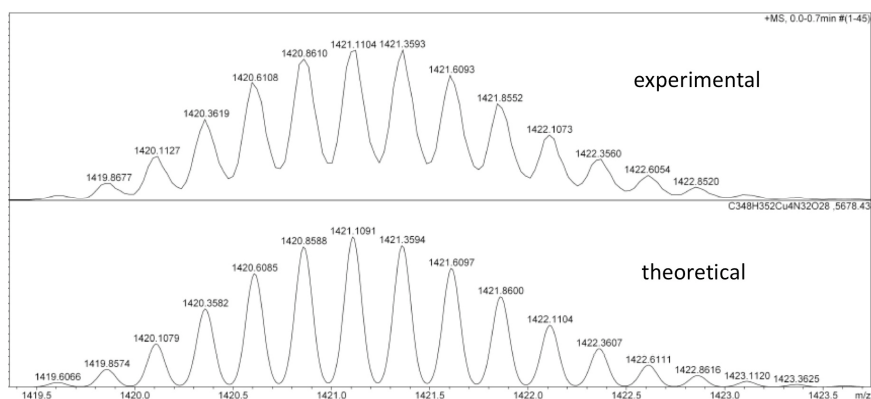


Figure SI4. HR ES-MS spectrum of compound 1^{4+} (top) and the corresponding simulation (bottom).

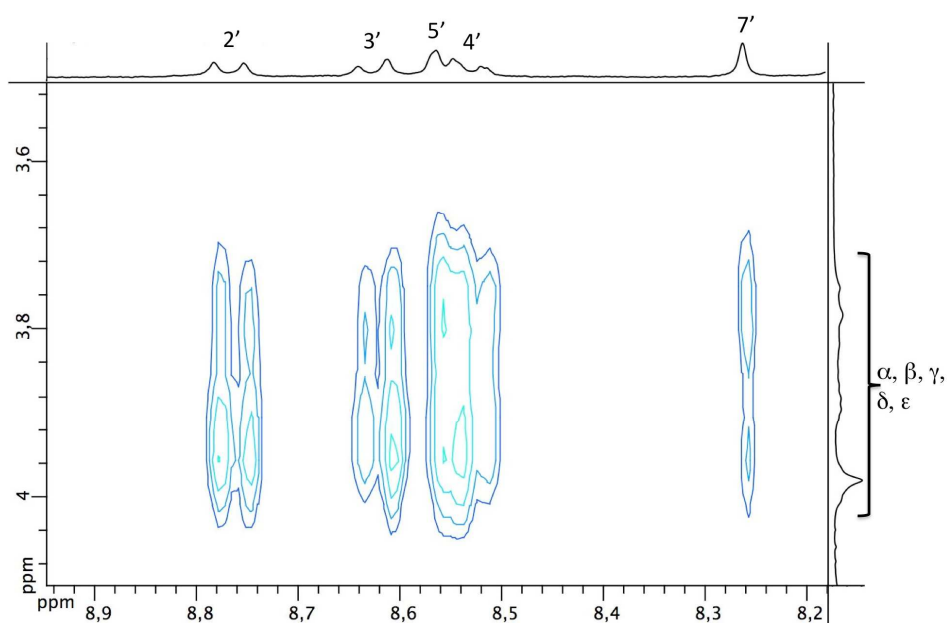


Figure SI5. Part of the NOESY spectrum of compound **1⁴⁺** showing the NOE correlations between protons of the rod (H-2', H-3', H-4', H-5' and H-7') and protons of the polyethylene glycol chain of the bis-macrocycle.

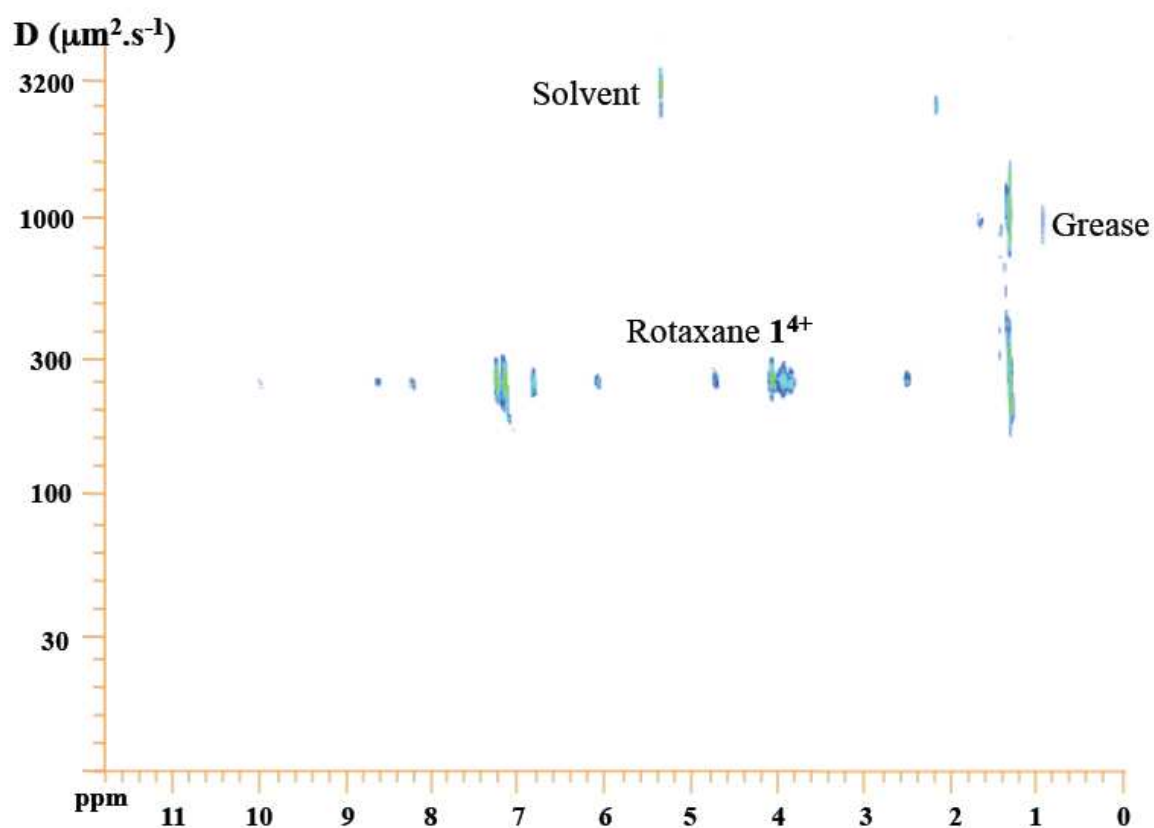


Figure SI6. DOSY spectrum of rotaxane **1⁴⁺** in CD₂Cl₂.

3) [4]pseudorotaxane 12⁴⁺:

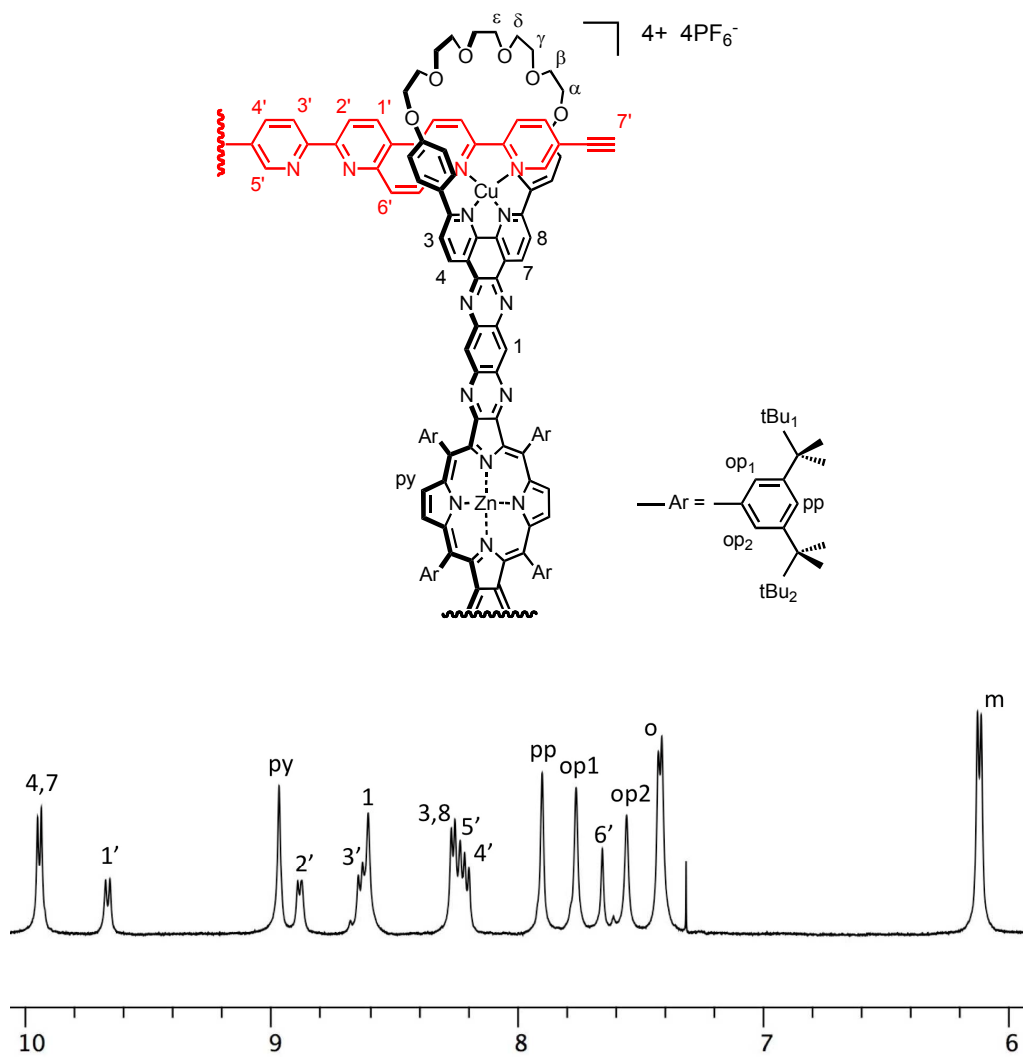


Figure SI7. ^1H NMR spectrum (aromatic region, 10-6 ppm) of compound **12**⁴⁺ in CD_2Cl_2 .

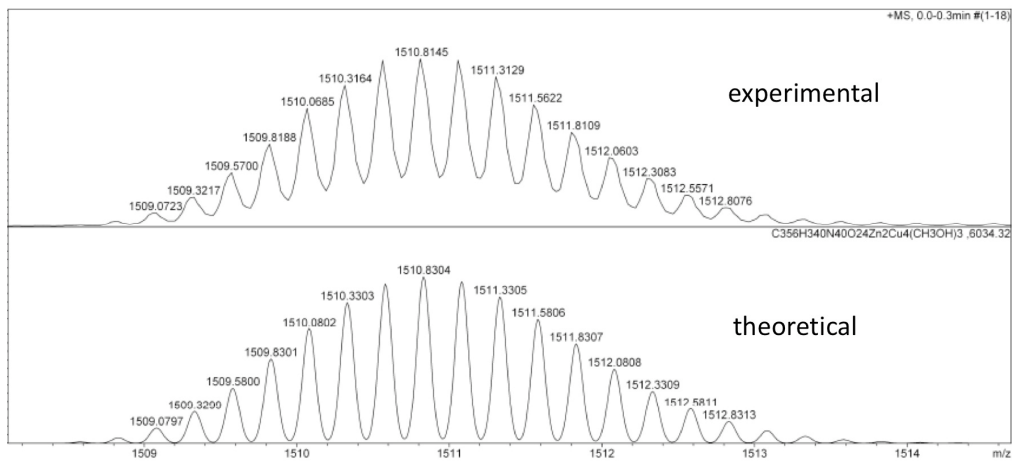


Figure SI8. HR ES-MS spectrum of compound **12**⁴⁺(CH₃OH)₃ (top) and the corresponding simulation (bottom).

4) [4]rotaxane 2^{4+} :

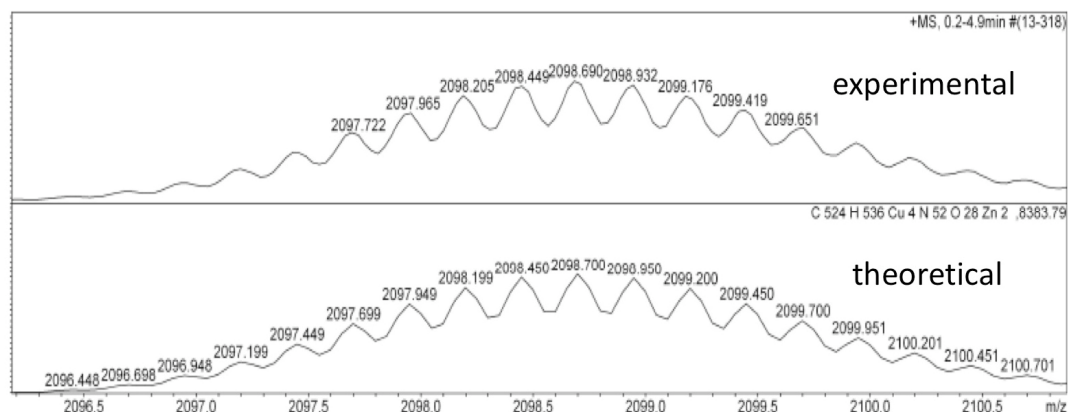


Figure SI9. HR ES-MS spectrum of compound 12^{4+} (top) and the corresponding simulation (bottom).

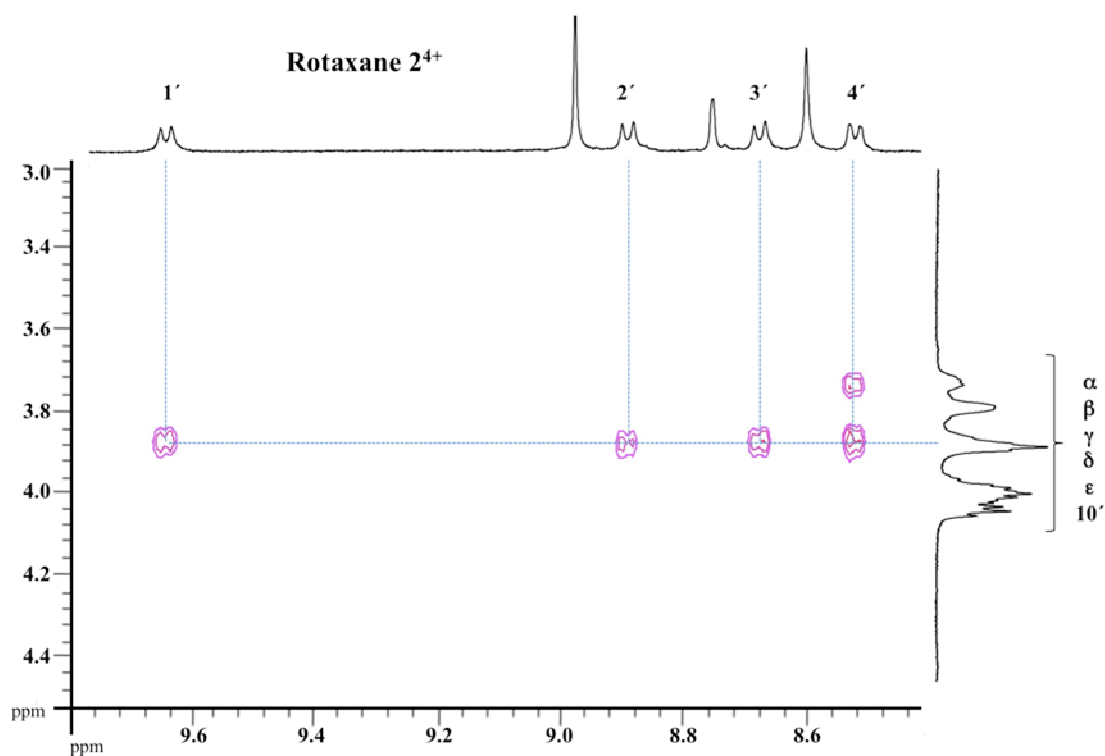


Figure SI10. Part of the ROESY spectrum of compound 2^{4+} in CD_2Cl_2 showing the NOE correlations between protons of the rod (H-1', H-2', H-3' and H-4') and protons of the polyethylene glycol chain of the bis-macrocycle.

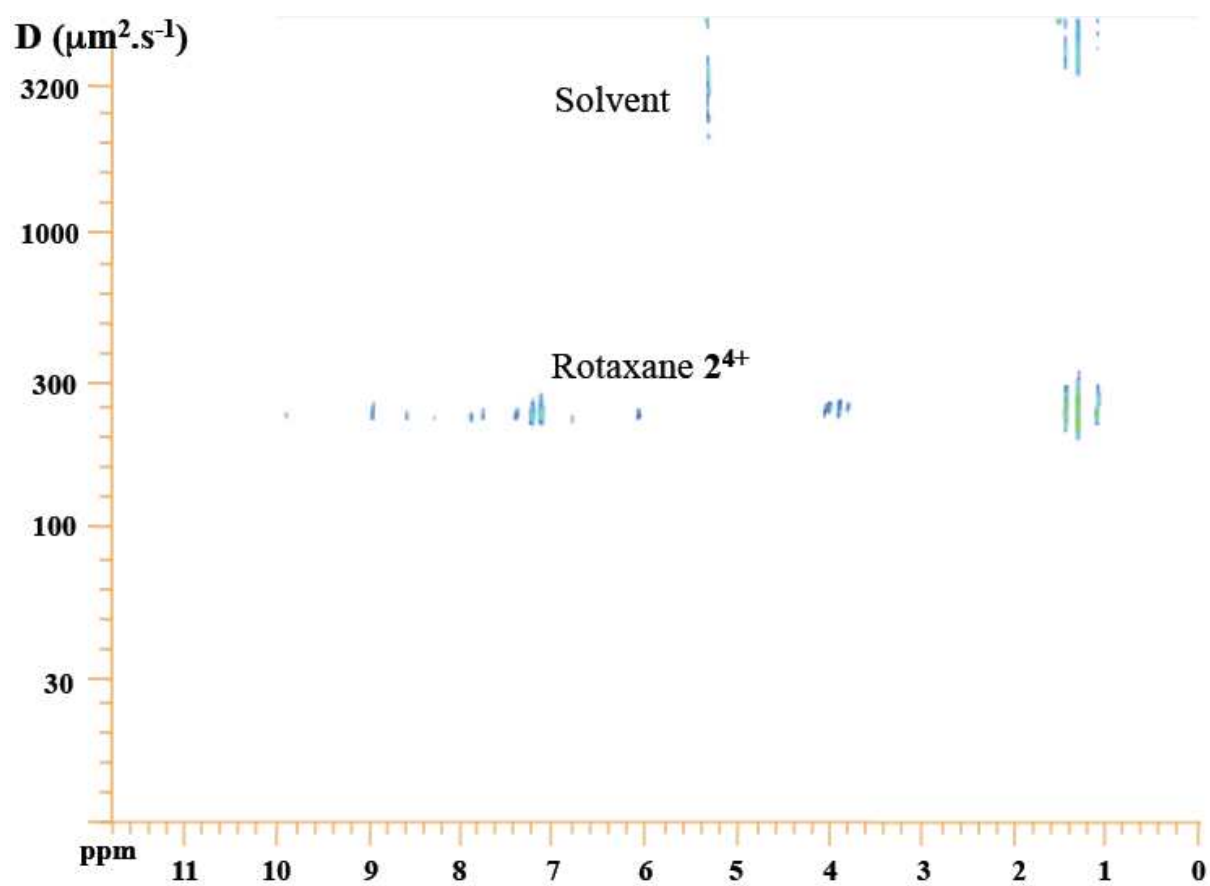


Figure S111. DOSY spectrum of rotaxane 2^{4+} in CD_2Cl_2 .

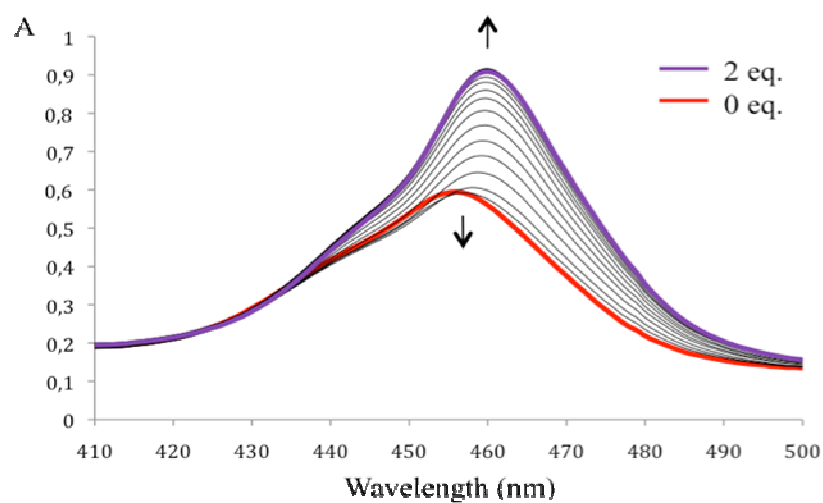
II. X-ray crystallography of rotaxane 2⁴⁺

Brown crystals of 2⁴⁺ were obtained by slow diffusion of diethylether into dichloromethane solution of 2(PF₆)₂. The structural analysis was performed using Bruker Kappa Apex II diffractometer with graphite-monochromatized Cu-K α (λ = 1.54184 Å) radiation. Collect software^{S2} was used for the data measurement and DENZO-SMN^{S3} for the processing. The structure were solved by direct methods with SIR97^{S4} and refined by full-matrix least-squares methods with 4153 restraints (see below) using the WinGX-software,^{S5} which utilizes the SHELXL-97 module.^{S6} No absorption correction was applied. All C-H hydrogen positions were calculated using a riding atom model with $U_H = 1.2 \times U_C$. The very sensitive crystals were transferred as soon as possible into a loop containing perfluorinated oil. Despite of the rapid capture of the crystals, some of the crystallinity was lost and in addition the large molecular weight of the 2⁴⁺ molecule resulted in a very weakly diffracting crystals much like protein crystals which do not allow any detectable diffraction peaks above 100° in 2 θ . After several attempts a crystal giving a clear diffraction pattern at low angles was subjected to data collection. The data processing and reduction provided a data set with *ca.* 25 % of the reflections missing due to the unsuccessful integration of intensities in some of the frames. After successful structure solution and initial isotropic refinement revealed severe disorder and very large thermal movement of the polyoxaethylene rings. Due to this geometrical constraints (DFIX) were applied to the hexafluorophosphate anions and O-CH₂-CH₂-O moieties to fix the bond lengths and angles to chemically acceptable values. Due to the very small amount of strong enough reflections extensive thermal parameter restraints (ISOR and SIMU) were applied to all non-H atoms. The use of DFIX, ISOR and SIMU resulted in a very large number of restrains. The crystal lattice contains very large voids filled with a lot of scattered electron density of the disordered solvent molecules and the SQUEEZE protocol inside PLATON^{S7} was used to remove the void electron density resulting in a marked decrease in the final R-values. Crystal data for 2(PF₆)₂: brown prism, 0.10 x 0.30 x 0.30 mm³, $M = 90004.82$, C₅₂₄H₅₃₄N₅₂O₃₀P₄F₂₄Cu₄Zn₂, triclinic, space group *P*-1, $a = 15.9812(19)$ Å, $b = 27.908(4)$ Å, $c = 34.355(4)$ Å, $\alpha = 70.843(5)^\circ$, $\beta = 79.695(6)^\circ$, $\gamma = 73.704(6)^\circ$, $V = 13829(3)$ Å³, $Z = 1$, $D_c = 1.081$ g/cm³, $F_{000} = 4734$, $\mu = 0.922$ mm⁻¹, $T = 173.0(1)$ K, $2\theta_{\max} = 100^\circ$, 21362 reflections used, 5573 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.1117$, 2695 parameters, 4153 restraints, $\text{GoF} = 0.821$, $R = 0.122$ [$I_o > 2\sigma(I_o)$], $wR = 0.357$ (all reflections), $0.438 < \Delta\rho < -0.347$ e/Å³.

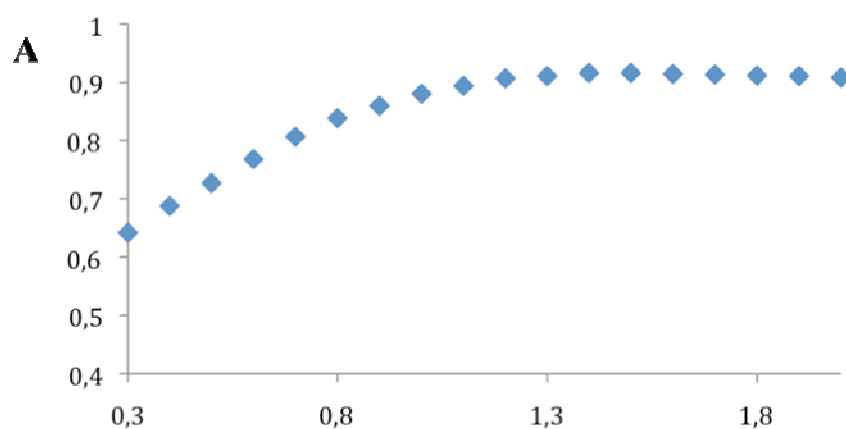
III. UV titration of rotaxane 2^{4+} with guests G1, G3, G4 and G5

1) Substrate G1

a)



b)



Equivalents of guest molecule G1

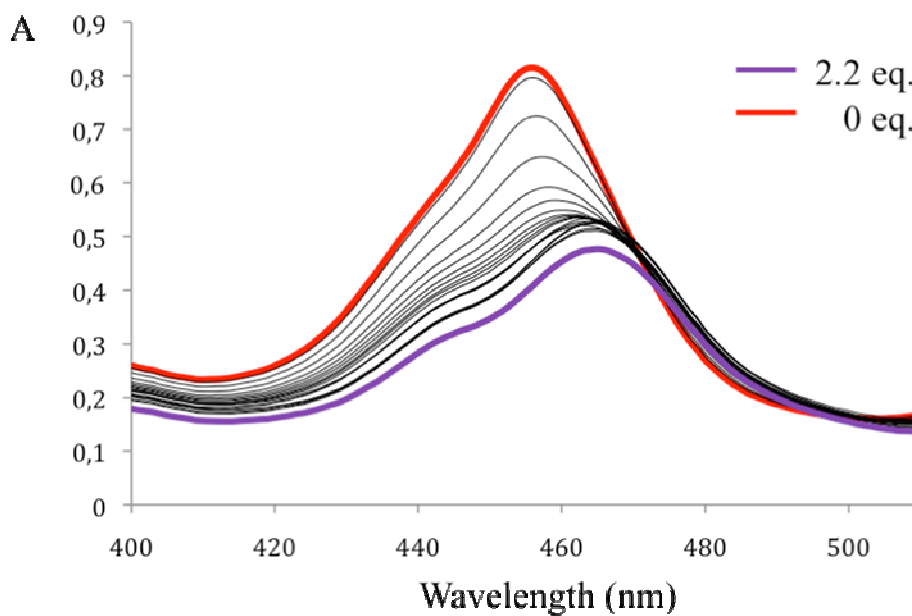
Host : Guest [1:1]

$\log K = 7.4 \pm 0.1$

Figure SII2. Titrations studies in toluene of rotaxane 2^{4+} with substrate **G1**; a) evolution of Soret band during titration from 0 (red curve) to 2 (blue curve) equivalents; b) evolution of the absorbance at $\lambda = 460$ nm.

2) Substrate G3

a)



b)

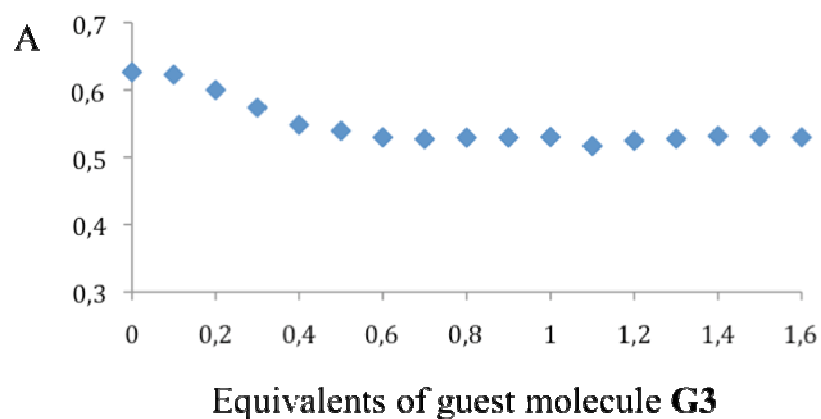
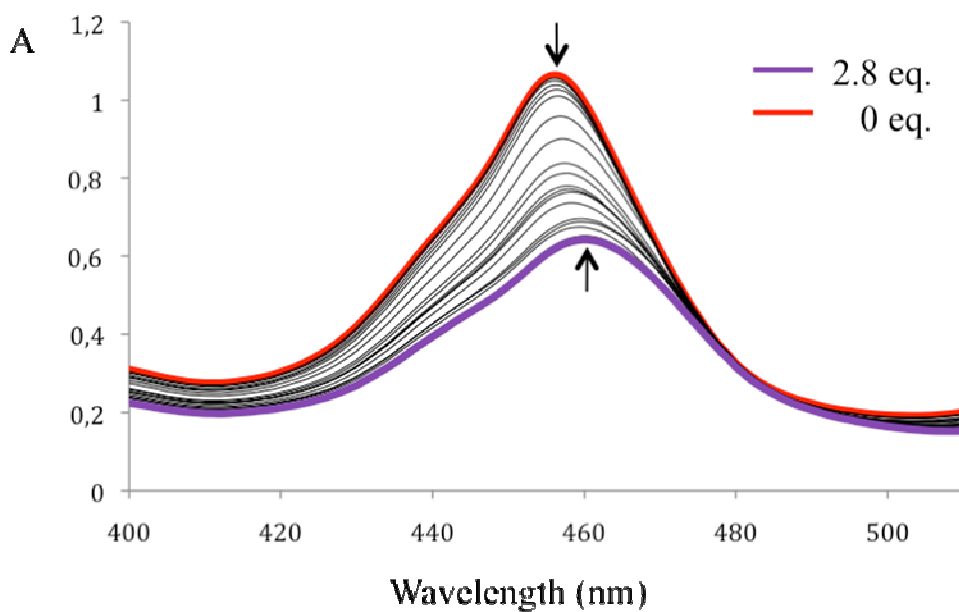


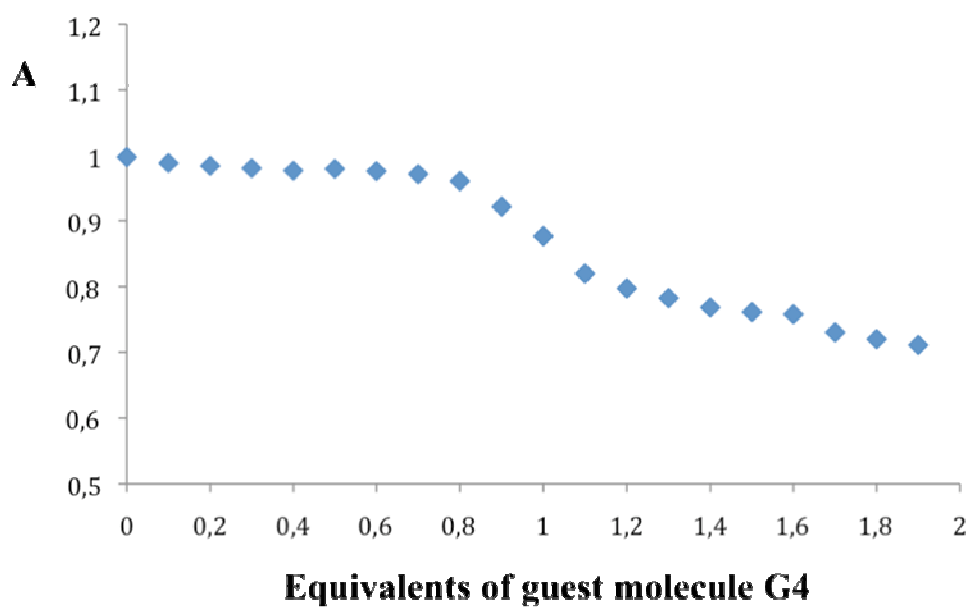
Figure S113. Titrations studies in toluene of rotaxane 2^{4+} with substrate G3; a) evolution of Soret band during titration from 0 (red curve) to 2.2 (blue curve) equivalents; b) evolution of the absorbance at $\lambda = 465$ nm.

3) Substrate G4

a)



b)



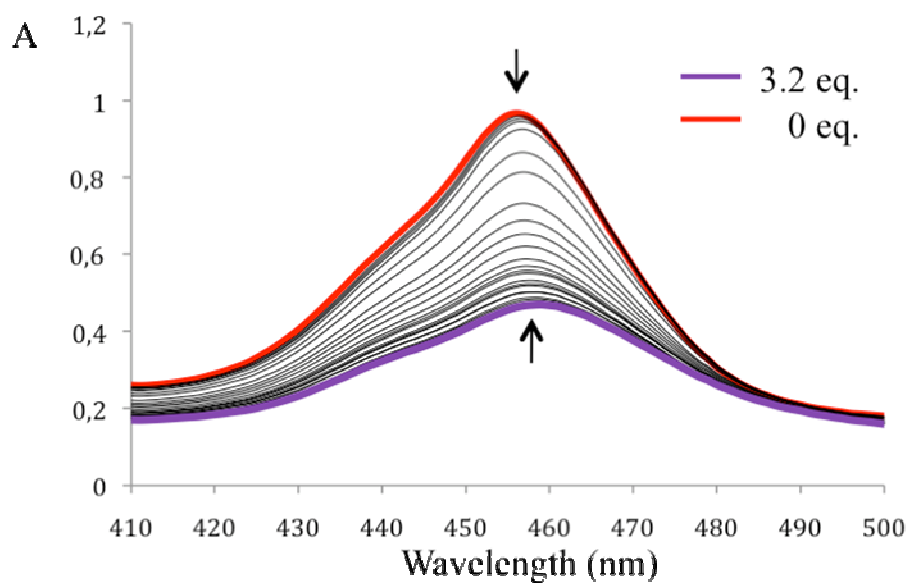
Host : Guest [1:2]

$\log K = 13.6 \pm 0.4$

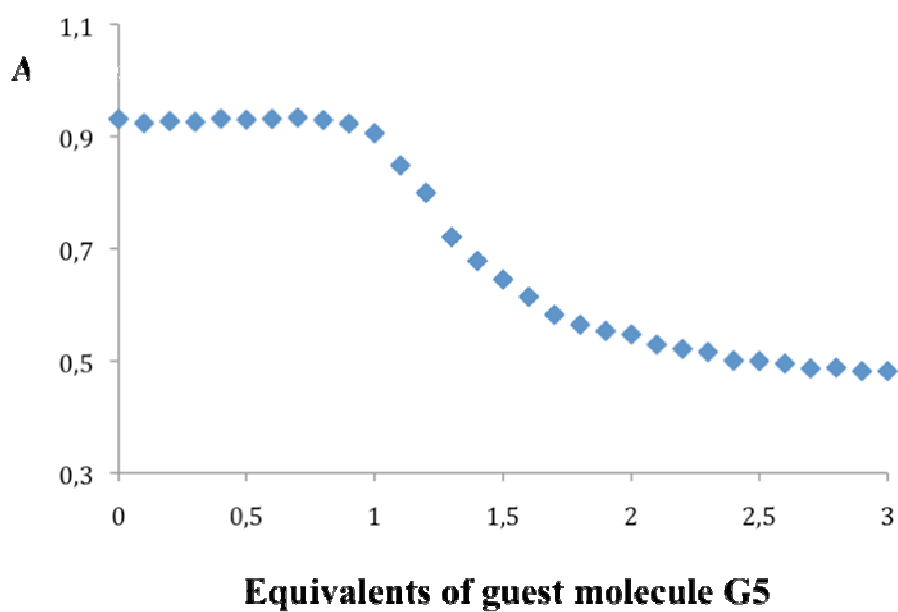
Figure S114. Titrations studies in toluene of rotaxane 2^{4+} with substrate G4; a) evolution of Soret band during titration from 0 (red curve) to 2.8 (blue curve) equivalents; b) evolution of the absorbance at $\lambda = 460$ nm.

4) Substrate G5

a)



b)



Host : Guest [1:2]

$\log K = 11.9 \pm 0.2$

Figure SII5. Titrations studies in toluene of rotaxane 2^{4+} with substrate G5; a) evolution of Soret band during titration from 0 (red curve) to 3.2 (blue curve) equivalents; b) evolution of the absorbance at $\lambda = 459$ nm.

References

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