

Dynamics of a [2]rotaxane wheel in a crystalline molecular solid

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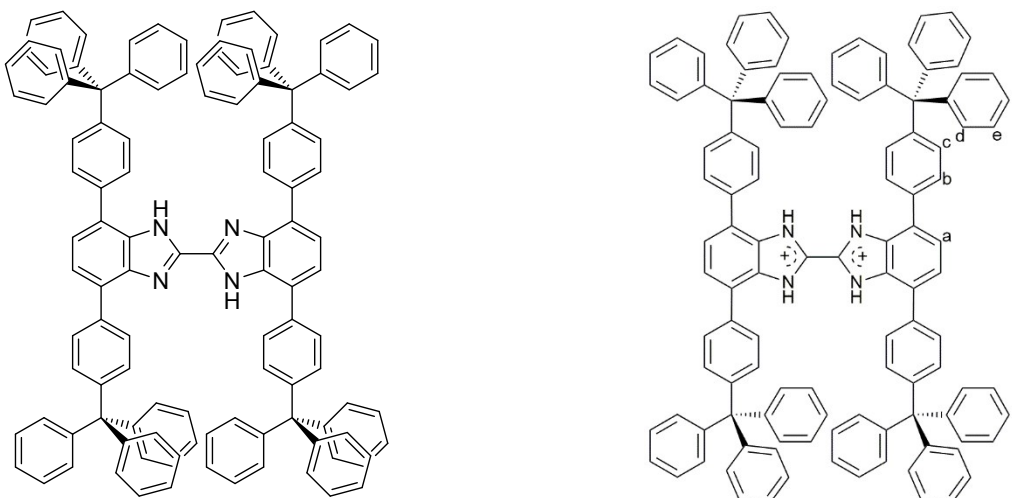
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Materials and Methods

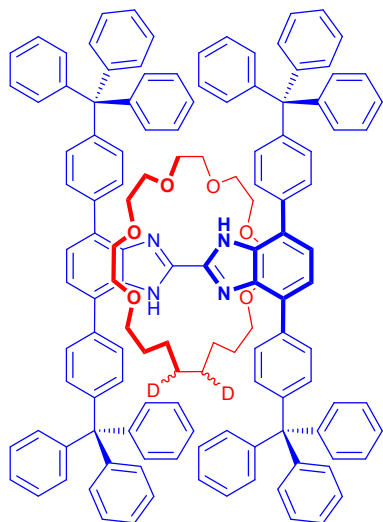
Melting point measurements were performed on MPA100 melting point apparatus. PXRD measurements were performed on a PROTO AXRD benchtop diffractometer for 2 to 30° 2theta values. VT measurements were performed using an Anton Paar BTS500 stage with temperatures ramped at 10 K min⁻¹ and allowed to stabilise for 2 minutes. TGA was performed using a TA TGA5500 and samples were allowed to isotherm for 10 min at ambient temperature unless otherwise stated and then heated at 10 °C min⁻¹ to 600 °C under a nitrogen atmosphere. Calorimetric studies were performed using a TA Instruments DSC 2500. IR measurements were performed using a Bruker Alpha FT-IR with the following abbreviations: weak, w medium, m strong, s and broad, br. Single crystal X-ray diffraction was performed on a Bruker D8 Venture diffractometer equipped with a PHOTON 100 detector, Kappa goniometer and collected using a CuK_α (λ = 1.54178 Å) high brilliance IμS microfocus source or MoK_α (λ = 0.7107 Å) sealed tube source. Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N₂. Reflection data were integrated from frame data using APEX III software. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.^{S1} Final unit cell parameters were determined by least-squares refinement taken from the data set. Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by intrinsic phasing with SHELXT.^{S2} Subsequent difference Fourier calculations and full-matrix least-squares refinement against |F²| were performed with SHELXL-2014^{S3} using OLEX2.^{S4} All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealized positions and refined using a riding model.

Synthesis of Axle 2



1 (55 mg, 0.10 mmol), 4-tritylphenylboronic acid pinacol ester (223 mg, 0.50 mmol), K_2CO_3 (691 mg, 5.0 mmol) and $[Pd(PPh_3)_4]$ (66 mg, 0.04 mmol) were placed in a screw cap pressure vessel and degassed by vacuum/nitrogen cycles (3x). A separately degassed solution (5 mL) of toluene/1,4-dioxane/ H_2O (2/2/1; v/v/v) were added to the vessel and sealed with a Teflon screw cap under nitrogen. The reaction mixture was heated with stirring in a pre-heated oil-bath at 120 °C for 3 days. Afterwards, the reaction was brought to room temperature and all organic solvents were evaporated. The solid residue was filtered and washed with diethyl ether. The residue was washed with hot CH_3CN , filtered, and then washed again with CH_3CN followed by hexanes. Recrystallization from dichloromethane yielded pure **2** as a crystalline solid (39 mg, 26 %). Single crystals of **2** suitable for single crystal X-ray diffraction were obtained by slow cooling of a saturated CH_2Cl_2 solution under pressure. M.P. >350 °C dec. Due to the poor solubility of **2** at room temperature, the 1H NMR spectrum was obtained by adding 5% TFA to CD_2Cl_2 . 1H NMR of $[2H][CF_3COO]$ (CD_2Cl_2 , 300 MHz) δ 7.68 (4H, s), 7.60 (8H, d, $J = 8.5$ Hz), 7.46 (8H, d, $J = 8.5$ Hz), 7.34 – 7.16 (m, 60 H); NH^+ not observed. Neither a suitable ^{13}C NMR spectrum nor a HR-ESI-MS could be obtained due to the very poor solubility of **2**. The identity of **2** is however, verified from the SCXRD structure, matching PXRD of the bulk material, in addition to IR, TGA, DSC and successful conversion to **2c-24C6** which was fully characterized by SCXRD, PXRD, TGA, DSC, IR, 1H NMR, HR-ESI-MS and 2H SSNMR.

Synthesis of [2]Rotaxane **2**-**24C6**



2 (753 mg, 0.50 mmol) was suspended in CH₂Cl₂/CH₃CN (1/1) (250 mL) and heated to reflux temperature. To the refluxing reaction mixture, HBF₄·Et₂O (340 μL, 2.5 mmol) was added in one portion to give a yellow solution. Evaporation of the CH₂Cl₂ at its boiling temperature resulted in the precipitation of a yellow solid. The mixture was then cooled to room temperature and the yellow precipitate filtered, washed with CH₃CN (3 × 5 mL) and dried in air (775 mg, 92 %). The resulting salt, [H₂][BF₄] was used directly in the next step without further characterization. [H₂][BF₄] (210 mg, 0.125 mmol) and **3** (70 mg, 0.188 mmol) were dissolved in 5 mL MeNO₂/CH₂Cl₂ (1/4) and heated at 40 °C under nitrogen for 30 min. At that temperature, Grubbs I catalyst (10 mg, 0.0125 mmol) in CH₂Cl₂ (2 mL) was added and heating continued under nitrogen. After 28 h, Et₃N (87 μL) was added to the reaction mixture to precipitate the unsaturated-ring version of [2]rotaxane **2**-**24C6**. The white solid was filtered and washed exhaustively with CH₃CN and then hexanes (3 × 5 mL). (227 mg, 98 %). Since this compound is a mixture of isomers it was used directly in the next step without further purification. This product mixture (the unsaturated-ring version of [2]rotaxane **2**-**24C6**) (250 mg, 0.135 mmol) was dissolved in hot THF (70 mL) and 10% Pd/C (14 mg, 0.0135 mmol) was added to the solution. The mixture was stirred at 50 °C under D₂(g). After 18 h, the mixture was cooled to room temperature and filtered through Celite. The Celite was further washed with THF (3 × 10 mL). The solvents were evaporated, and the residue dissolved in CH₃CN with addition of a few drops of Et₃N. The resulting white solid was filtered and washed with CH₃CN followed by hexanes and Et₂O. (250 mg, 100 %). Single crystals of **2**-**24C6** suitable for single crystal X-ray diffraction were obtained by slow cooling of a saturated CH₂Cl₂ solution. M.P. >350 °C dec. ¹H NMR (CD₂Cl₂, 500 MHz) δ 12.53 (2H, s), 8.22 (4H, d, *J* = 8.0 Hz), 7.66 (4H, d, *J* = 7.9 Hz), 7.53 (2H, d, *J* = 7.8 Hz), 7.36-7.11 (70H, m), 3.02 (4H, s), 2.77 (8H, s), 2.66 (4H, s), 2.62 (4H, s), 2.42 (4H, s), 0.99 – 0.88 (8H, m), 0.49 (2H, s). A suitable ¹³C NMR spectrum could not be recorded due to the poor solubility of **2**-**24C6**. HR-ESI-MS: [M]⁺, [C₁₃₂H₁₁₆D₂N₄O₆]⁺ calc. 1856.9177 obs. 1856.9178.

Powder X-Ray Diffraction (PXRD)

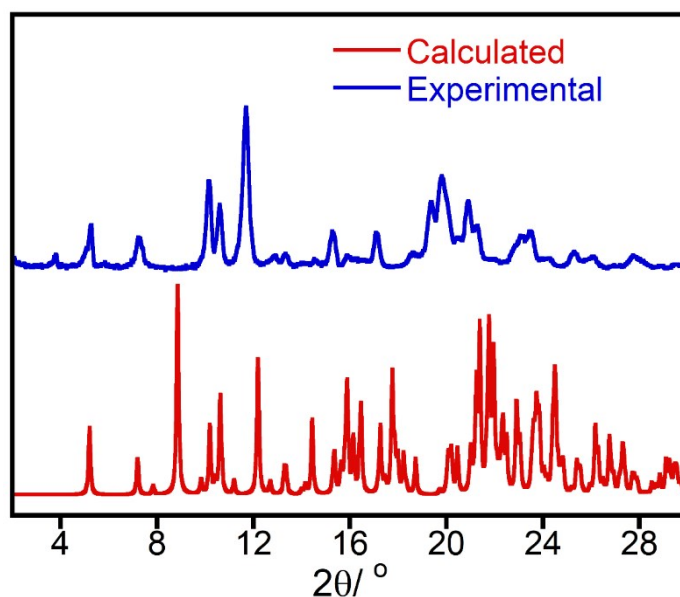


Figure S1. Comparison of calculated (red) and experimental (blue) PXRD for **2** at 298 K. (Note: the simulated PXRD is derived from the single crystal X-ray data solution which contains 7 molecules of CH_2Cl_2 , but the experimental PXRD is obtained from desolvated material – desolvation is instantaneous upon removal of the crystals from the mother liquor. Rather than losing crystallinity upon desolvation, the material converts to a slightly different crystalline phase. This is a testament to the stability of the material and the phenyl-embrace design feature that allows formation of such highly crystalline materials.)

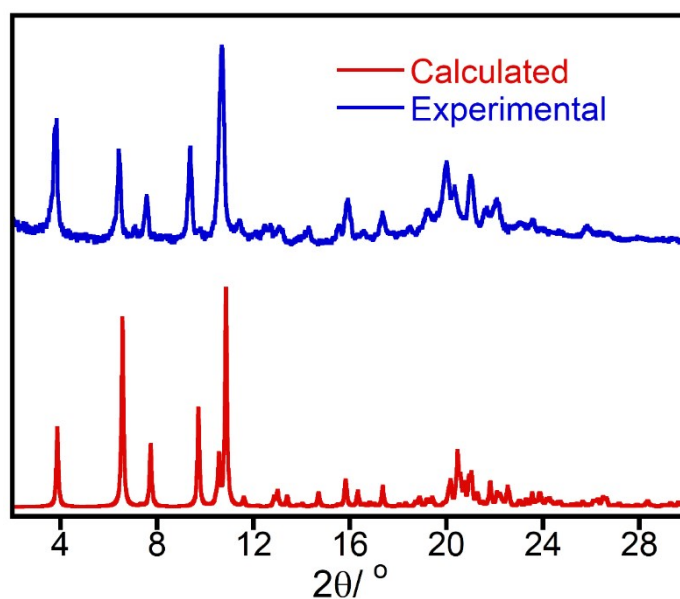


Figure S2. Comparison of calculated (red) and experimental (blue) PXRD for **2-24C6** at 298 K.

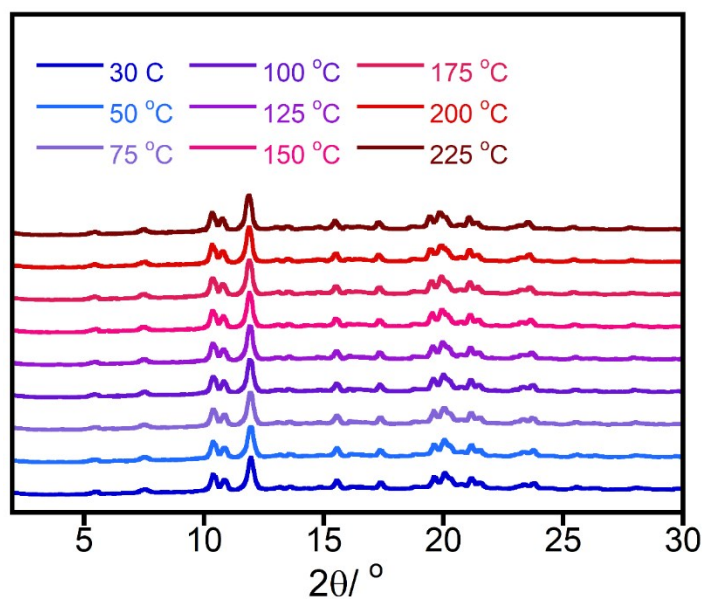


Figure S3. Variable temperature PXRD for **2** from 25 °C to 225 °C. Sample was heated under ambient atmosphere at 10 °C min⁻¹ and the temperature allowed to stabilise for 2 min. prior to collection.

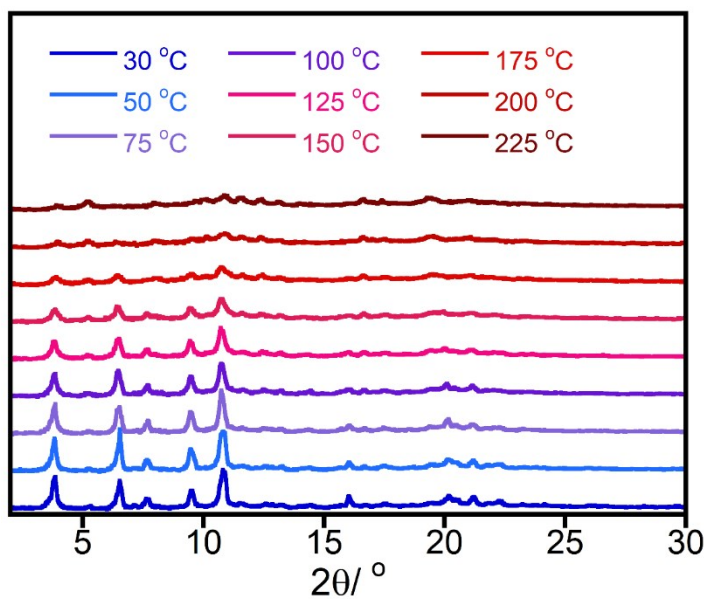


Figure S4. Variable temperature PXRD for **2** \cdot **24C6** from 25 °C to 225 °C. Sample was heated under ambient atmosphere at 10 °C min⁻¹ and the temperature allowed to stabilise for 2 min. prior to collection.

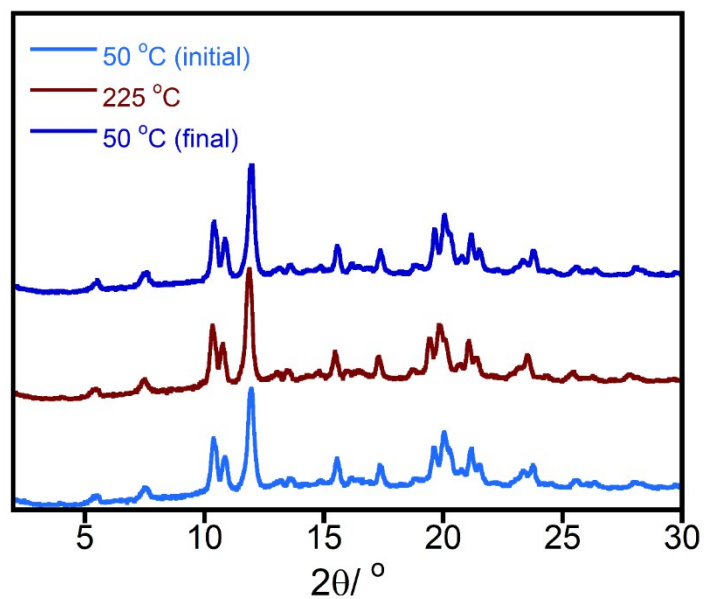


Figure S5. Comparison of PXRD for **2** after heating to 50 °C then 225 °C followed by cooling back to 50 °C .

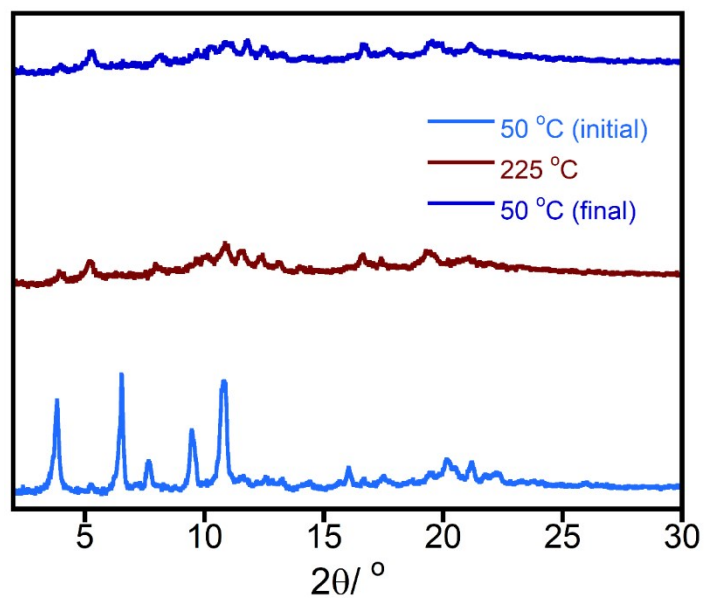


Figure S6. Comparison of PXRD for **2c24C6** after heating to 50 °C then 225 °C followed by cooling back to 50 °C .

Thermal Gravimetric Analysis (TGA)

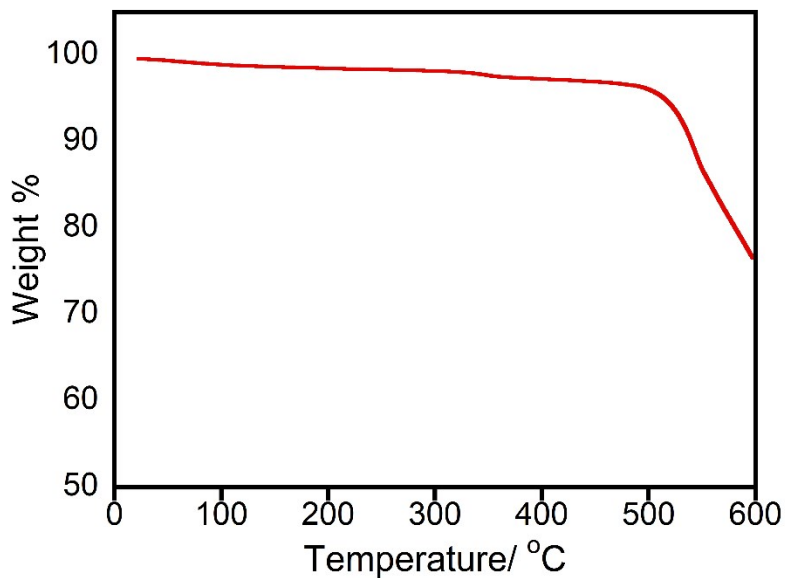


Figure S7. TGA for **2** performed under a nitrogen atmosphere with a ramp rate of 10 K min^{-1} . An isotherm was performed at ambient temperature for 10 minutes prior to the measurement.

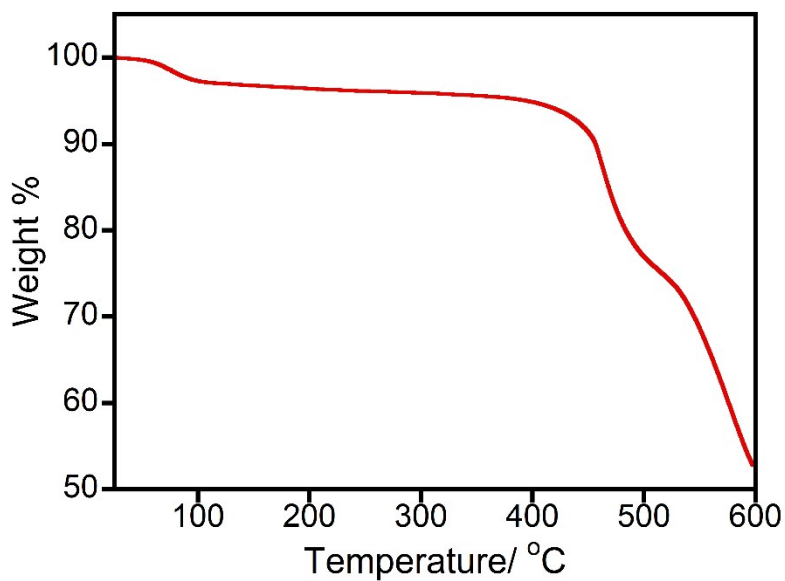


Figure S8. TGA for **2C24C6** performed under a nitrogen atmosphere with a ramp rate of 10 K min^{-1} . An isotherm was performed at ambient temperature for 10 minutes prior to the measurement.

Differential Scanning Calorimetry (DSC)

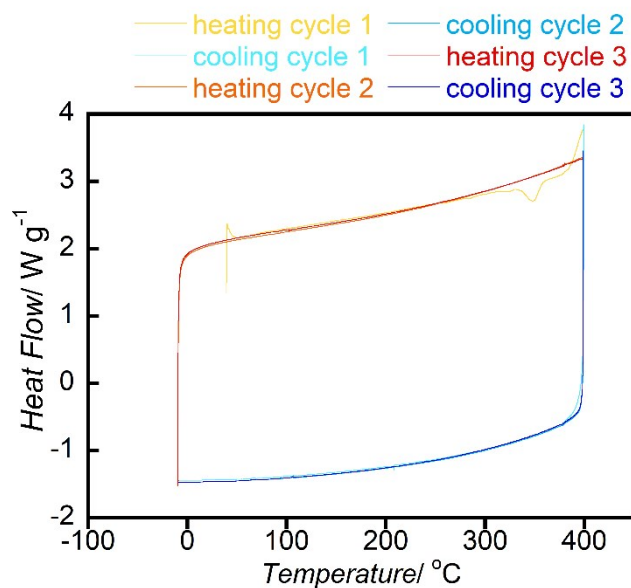


Figure S9. DSC for **2** performed under a nitrogen atmosphere with a ramp rate of 10 K min⁻¹.

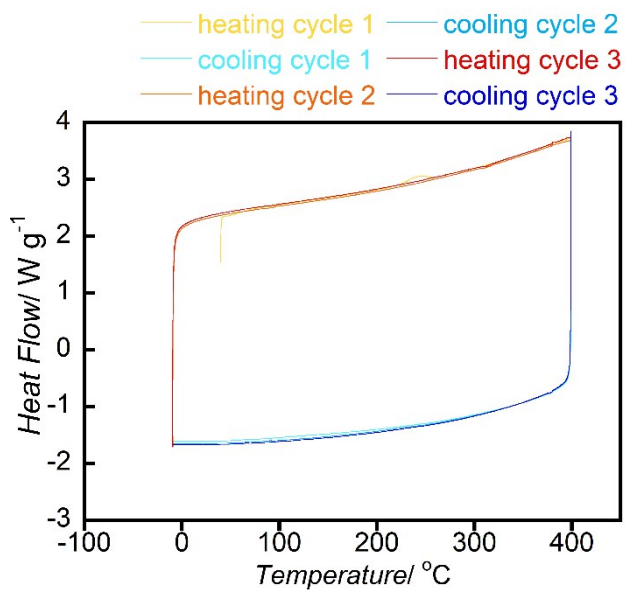
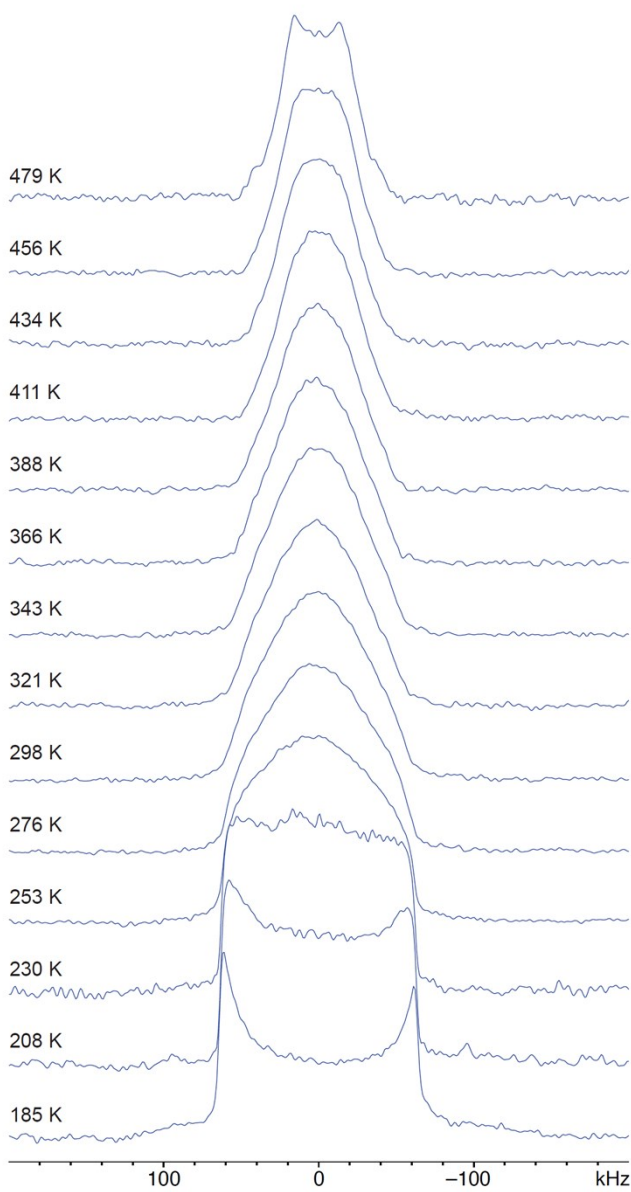


Figure S10. DSC for **2C24C6** performed under a nitrogen atmosphere with a ramp rate of 10 K min⁻¹.

Solid-State NMR (SSNMR)

Experiments were conducted on a Bruker Avance III HD spectrometer equipped with a 9.4 T Oxford magnet ($\nu_0(^1\text{H}) = 399.7$ MHz, $\nu_0(^2\text{H}) = 61.4$ MHz). A Chemagnetics 5 mm double resonance (HX) static probe was used. Spectra were acquired with a quadrupolar echo pulse sequence ($90^\circ - \tau_1 - 90^\circ - \tau_2 - \text{acquire}$) with an optimized pulse length of $3.3 \mu\text{s}$ ($\nu_1 = 75.8$ kHz), a 0.5 s recycle delay and either 30 or $60 \mu\text{s}$ pulse spacings. 50 kHz of continuous-wave ^1H decoupling was used. ^2H chemical shifts were referenced to D_2O ($\delta_{\text{iso}}(^2\text{H}) = 4.8$ ppm). The quadrupolar parameters of the SML spectra were determined using the SOLid Lineshape Analysis (SOLA) tool within TopSpin 4.0. Simulations of the dynamics were completed using EXPRESS.⁵⁴ Temperatures were calibrated



using the temperature-dependent ^{207}Pb chemical shift of $\text{Pb}(\text{NO}_3)_2$.^{S5,S6}

Figure S11. Full set of experimental VT ^2H SSNMR spectra for [2]rotaxane **2C24C6**
Single Crystal X-ray Diffraction (SCXRD)

Table S1. Single Crystal XRD Data for **2·(CH₂Cl₂)₇** and **2C24C6**

Compound	2·(CH₂Cl₂)₇	2C24C6
CCDC Number	2079257	2079258
Empirical formula	C ₁₂₁ H ₉₆ Cl ₇ N ₄	C ₁₃₂ H ₁₁₈ N ₄ O ₆
Formula weight	2091.65	1856.30
Temperature/K	170.0	170.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.2864(7)	9.0214(9)
b/Å	12.6134(7)	13.7471(13)
c/Å	17.4682(10)	22.9679(19)
α/°	76.476(3)	94.140(7)
β/°	89.608(4)	93.355(8)
γ/°	89.864(3)	100.854(8)
Volume/Å ³	2632.0(3)	2782.6(5)
Z	1	1
ρ _{calc} /cm ³	1.320	1.108
μ/mm ⁻¹	3.270	0.520
F(000)	1082	986
Crystal size/mm ³	0.40 × 0.16 × 0.13	0.20 × 0.10 × 0.20
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2θ range for data collection/°	7.20 to 117.86	3.86 to 120.0
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 13, -19 ≤ l ≤ 19	-10 ≤ h ≤ 10, -14 ≤ k ≤ 15, 25 ≤ l ≤ 25
Reflections collected	28330	66583
Independent reflections	7454 [R _{int} = 0.043, R _{sigma} = 0.0489]	8161 [R _{int} = 0.1314, R _{sigma} = 0.1984]
Data/restraints/parameters	7454/91/703	8161/694/145
Goodness-of-fit on F ²	1.041	0.901
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1323, wR ₂ = 0.1573	R ₁ = 0.0817, wR ₂ = 0.1798
Final R indexes [all data]	R ₁ = 0.3131, wR ₂ = 0.3326	R ₁ = 0.1925, wR ₂ = 0.2472
Largest diff. peak/hole / e Å ⁻³	1.74/-0.82	0.34/-0.31

References

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NMR Spectra of New Compounds

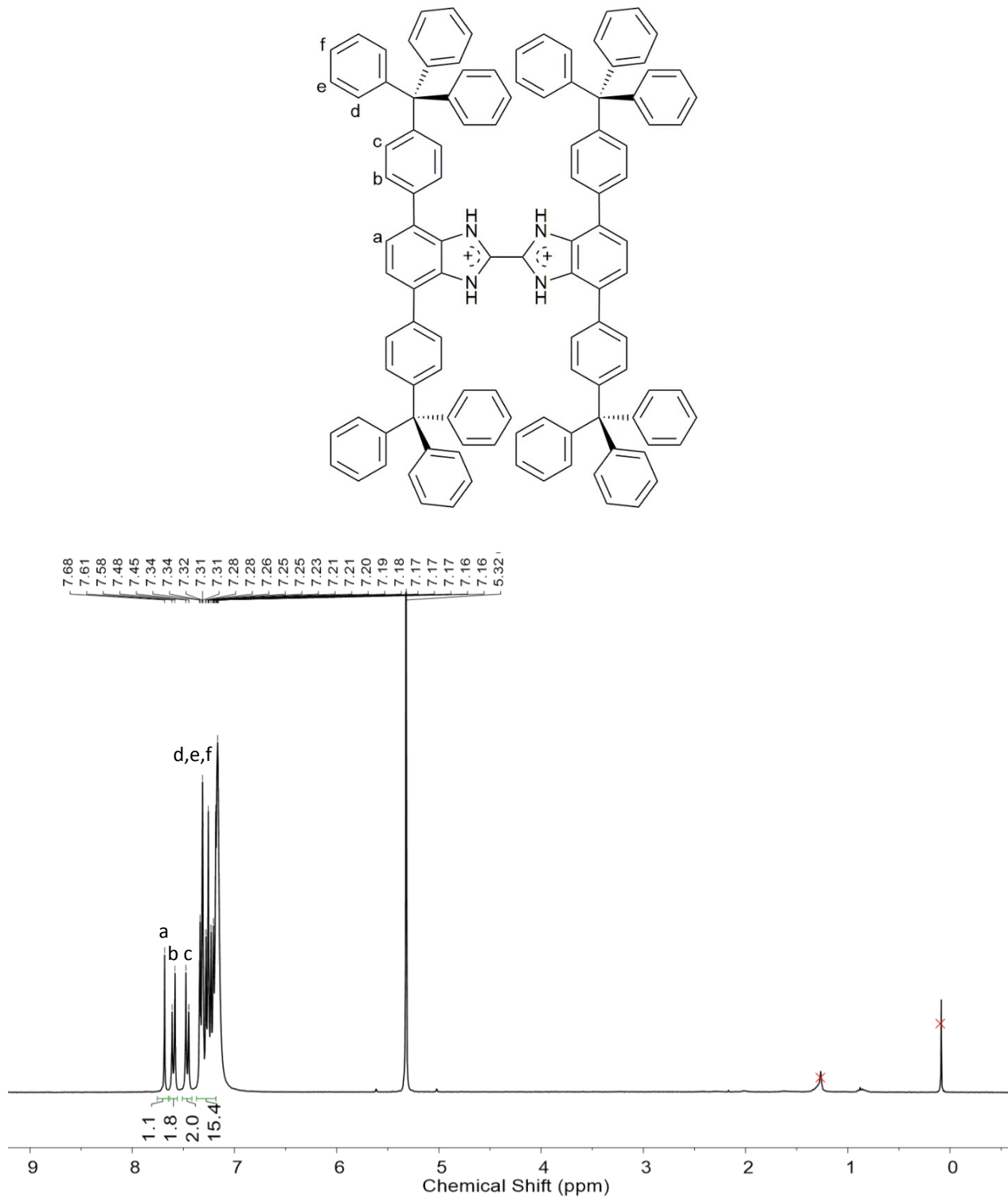


Figure S12. ¹H NMR of axle [2H][CF₃COO] (CD₂Cl₂, 300 MHz, 298 K). β = H-grease; NH⁺ peaks not observed.

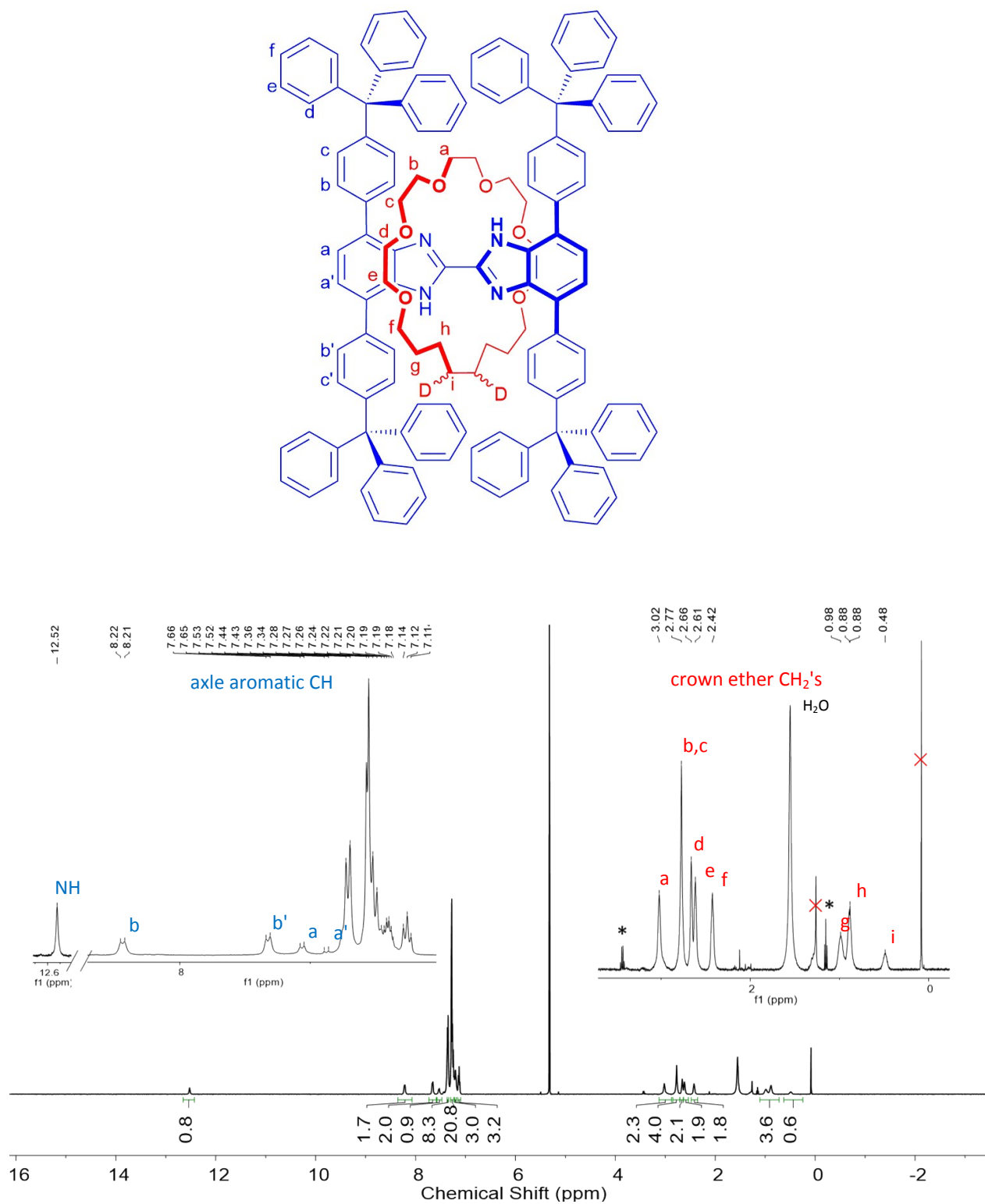
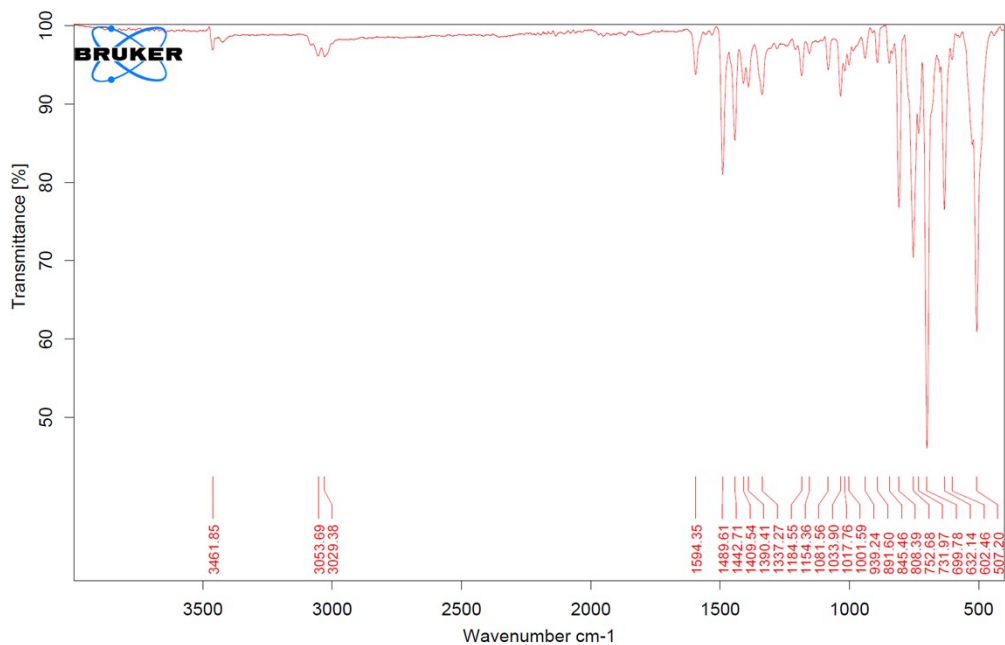


Figure S13. ¹H NMR of [2]rotaxane **2C24C6** (CD₂Cl₂, 500 MHz, 298 K). β = H-grease, \ominus = Et₂O



IR Spectra of New Compounds

Figure S14. IR spectrum of axle 2.

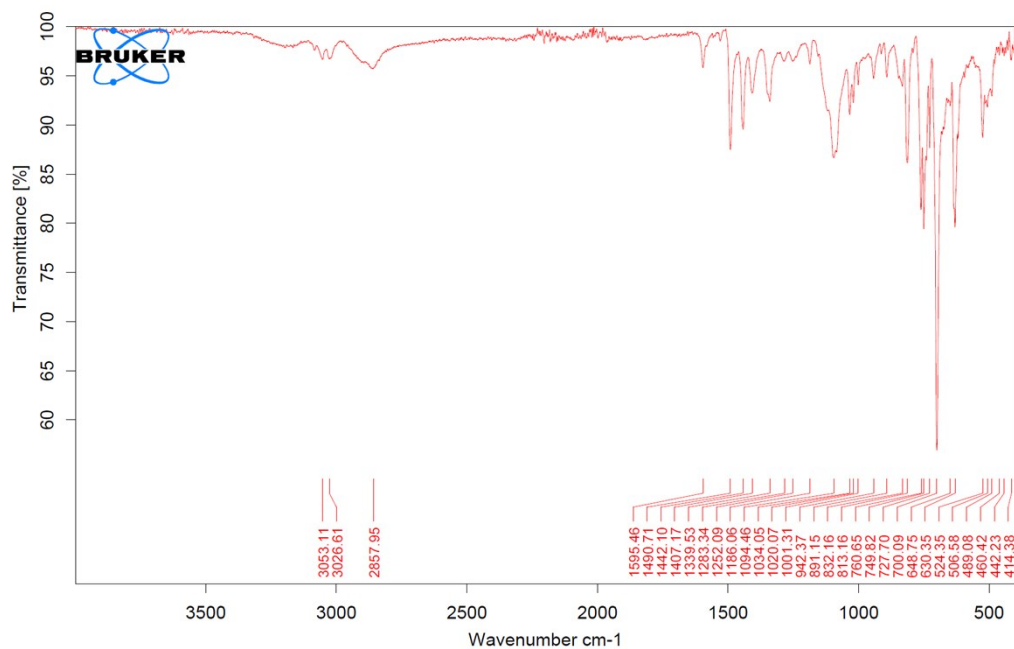


Figure S15. IR spectrum of [2]rotaxane 2C24C6