

Supporting Information

[4]Pseudorotaxanes with Remarkable Self-Sorting Selectivities

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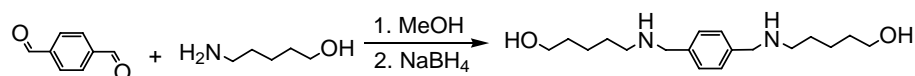
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Experimental Section

General Methods. All reagents were commercially available unless otherwise noted. Solvents were either employed as purchased or dried prior to use by usual laboratory methods. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). ¹H NMR, ¹³C NMR, and ¹H,¹H COSY spectra were recorded on Bruker ECX 400 MHz, Jeol Eclipse 500 MHz or Bruker AVANCE III 700 MHz NMR spectrometers. The ¹H NMR signal assignment for all assemblies was made through 2D NMR experiments. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an Agilent 6210 ESI-TOF, Agilent Technologies. The electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a superconducting 7 Tesla magnet and a micromass Z-spray ESI ion source utilizing a stainless steel capillary with a 0.65 mm inner diameter. The synthesis and characterization of host **2**¹ and guest **7-2H·2PF₆**² has been reported earlier. The dimerization of two crowns can favorably be performed by joining two benzo groups with butanal under strongly acidic conditions (82% H₂SO₄). In order to prevent oligo- or polymerization, the 24-crown-8 subunit carries a quinoxaline moiety which prevents this reaction to occur a second time on the same crown ether. At the same time, it facilitates the synthesis of the precursor crown through rigidifying the scaffold.

Synthesis:

Compound 8



Terephthalaldehyde (1.34 g, 10.0 mmol) and 5-aminopentanol (2.18 mL, 20.0 mmol) were dissolved in methanol (120 mL) and heated to reflux under argon atmosphere for 30 h. After cooling down to r. t., NaBH₄ (1.90 g, 50.0 mmol) was added in small portions. The resulting mixture was stirred at r. t. for another 24 h. The solvent was evaporated and the residue partitioned between H₂O and CH₂Cl₂ followed by the extraction of the aqueous phase with CH₂Cl₂ (three times 100 mL). The organic phases were combined and dried over anhydrous Na₂SO₄, and the solvent was removed to give the crude product, which was subjected to column chromatography (SiO₂, CH₂Cl₂ : MeOH : NH₃ (25 wt%), 50:1:0.1 to 50:5:0.1) to afford **8** (0.90 g, 29%) as a yellowish oil. ¹H NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 1.34-1.44 (m, 4H), 1.48-1.59 (m, 8H), 2.62 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 4H), 7.25 (s, 4H); ¹³C NMR (100 MHz, CDCl₃, 298 K): δ [ppm] = 23.4, 29.7, 32.5, 49.2, 53.8, 62.7, 128.4, 139.1; ESI-TOF-HRMS: *m/z* calcd for [M+H]⁺ C₁₈H₃₃N₂O₂, 309.2537; found, 309.2532 (100%).

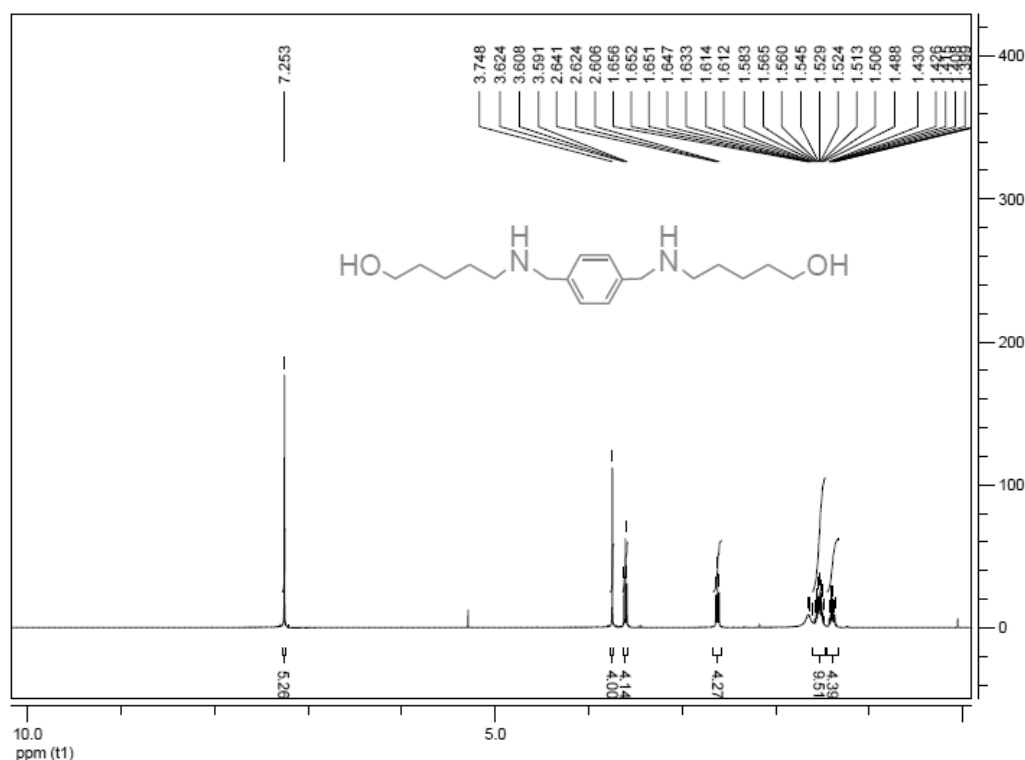


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **8**.

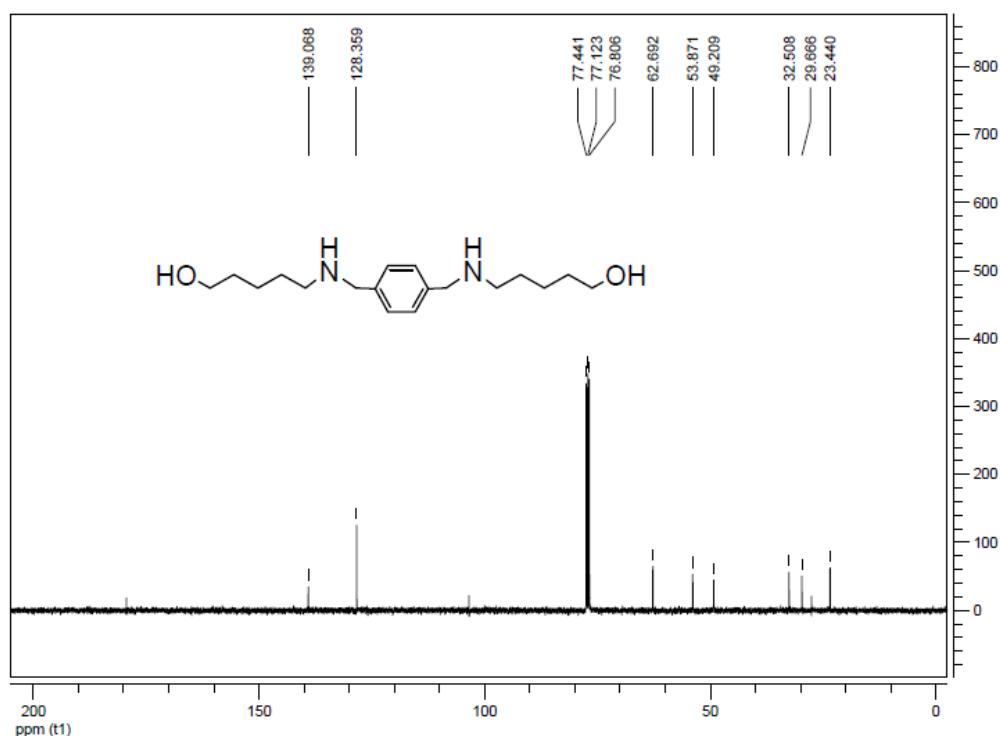
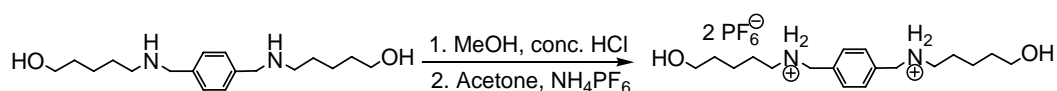


Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **8**.

Axle **8**-2H \cdot 2PF $_6$



Conc. HCl was added to the solution of **8** (0.50 g, 1.62 mmol) in EtOH (50 mL) to adjust the pH to < 2 . The resulting solution was stirred for another 2 h and the solvent was then evaporated under reduced pressure. The residue was suspended in acetone (50 mL). Saturated aqueous NH_4PF_6 solution was added until the suspension became clear. The solvent was removed in *vacuo*, and water (20 mL) was added to the residue. After 2 h stirring, the mixture was then filtered, washed with copious amounts of H_2O , and dried to yield **8**-2H \cdot 2PF $_6$ as a white solid (0.27 g, 28%). ^1H NMR (400 MHz, CD_3CN , 298 K): δ [ppm] = 1.32-1.42 (m, 4H), 1.43-1.51 (m, 4H), 1.61-1.71 (m, 4H), 3.98-3.07 (m, 4H), 3.47 (t, $J = 6.4$ Hz, 4H), 4.17 (t, $J = 6.4$ Hz, 4H), 6.62-6.90 (m, 4H; NH_2^+), 7.51 (s, 4H); ^{13}C NMR (100 MHz, CD_3CN , 298 K): δ [ppm] = 22.5, 25.3, 31.5, 48.1, 51.0, 61.2, 130.8, 132.1; ESI-TOF-HRMS: m/z calcd for $[\text{M}-2\text{PF}_6-\text{H}]^+$ $\text{C}_{18}\text{H}_{33}\text{N}_2\text{O}_2$, 309.2537; found, 309.2534 (100%); calcd for $[\text{M}-\text{PF}_6]^+$ $\text{C}_{18}\text{H}_{34}\text{F}_6\text{N}_2\text{O}_2\text{P}$, 455.2268; found, 455.2261 (5%).

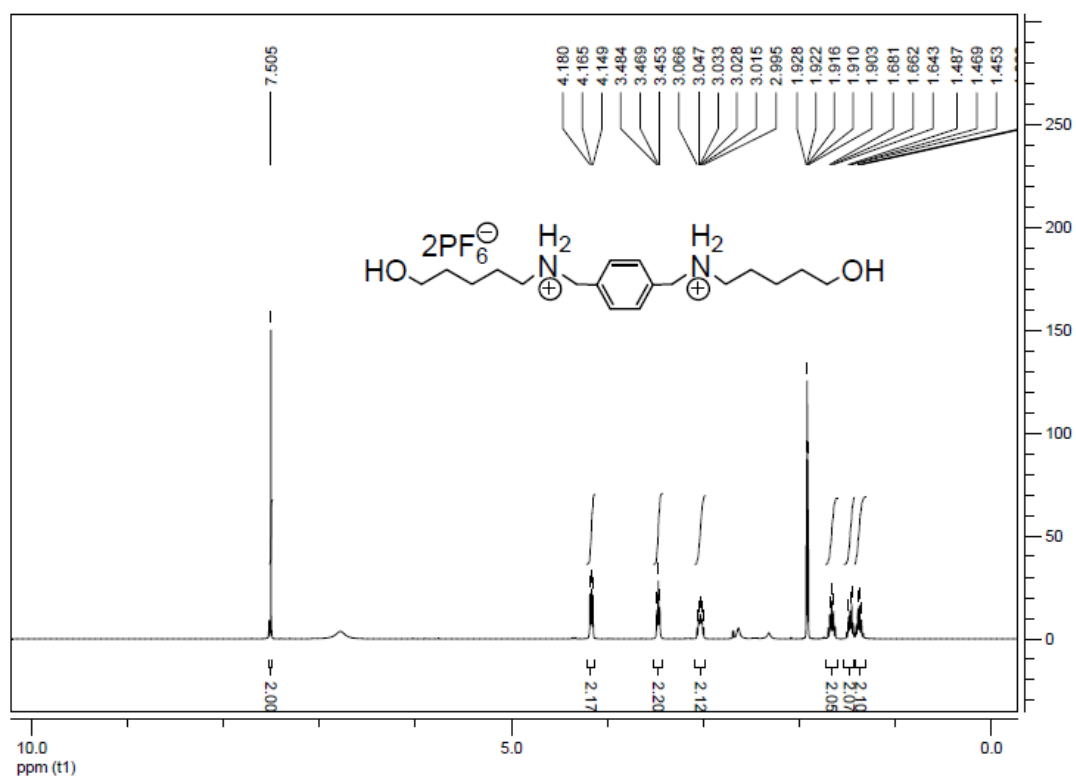


Figure S3. ¹H NMR spectrum (400 MHz, CD₃CN, 298 K) of **8-2H·2PF₆**.

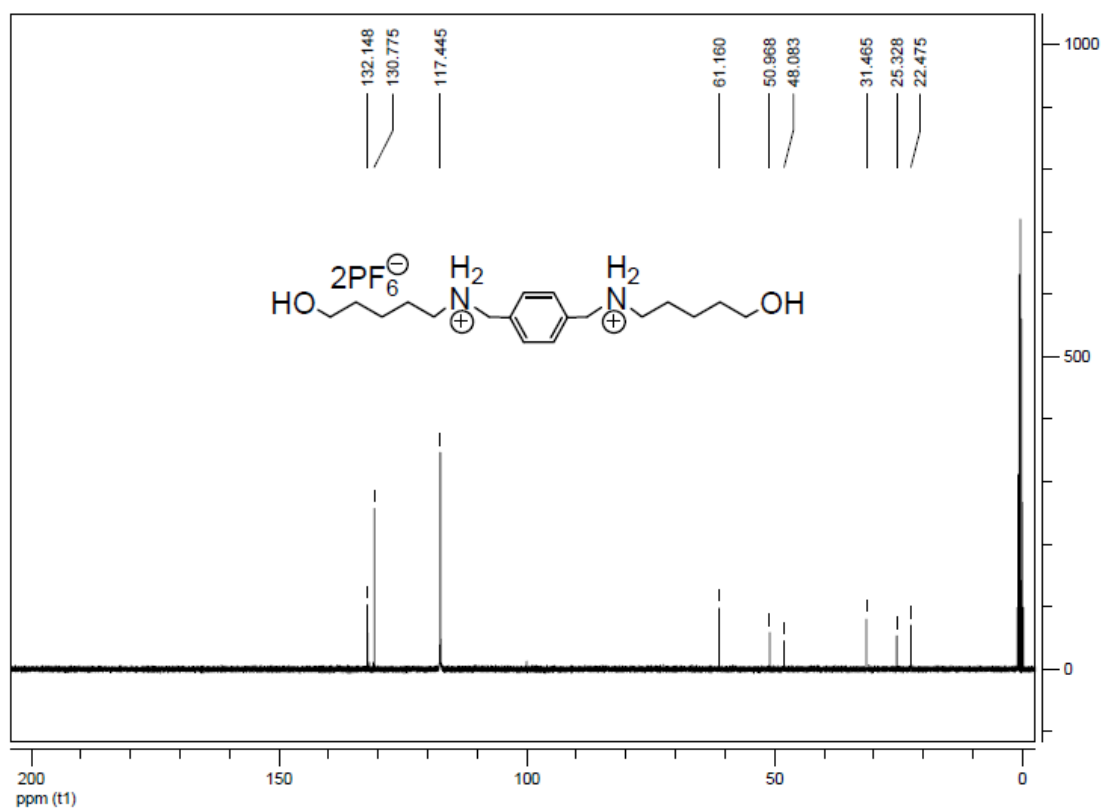


Figure S4. ¹³C NMR spectrum (100 MHz, CD₃CN, 298 K) of **8-2H·2PF₆**.

Preparation of the Pseudorotaxanes **9-4H•4PF₆** - **11-4H•4PF₆**

For the preparation of the [4]pseudorotaxanes, the components were mixed in amounts reflecting their stoichiometries (**7-2H•2PF₆**:**8-2H•2PF₆**:**2** = 1:1:2 for **9-4H•4PF₆** and **8-2H•2PF₆**:**2** = 1:1:2 for **10/11-4H•4PF₆**) in CDCl₃:CD₃CN = 2:1. The solutions were left to equilibrate over night, since the threading and error correction processes require some time in particular for the 21-crown-7 complexes. Then subjected to characterization without further purification.

¹H and ¹H,¹H COSY NMR Spectra Supporting the Formation of **9-4H•4PF₆**

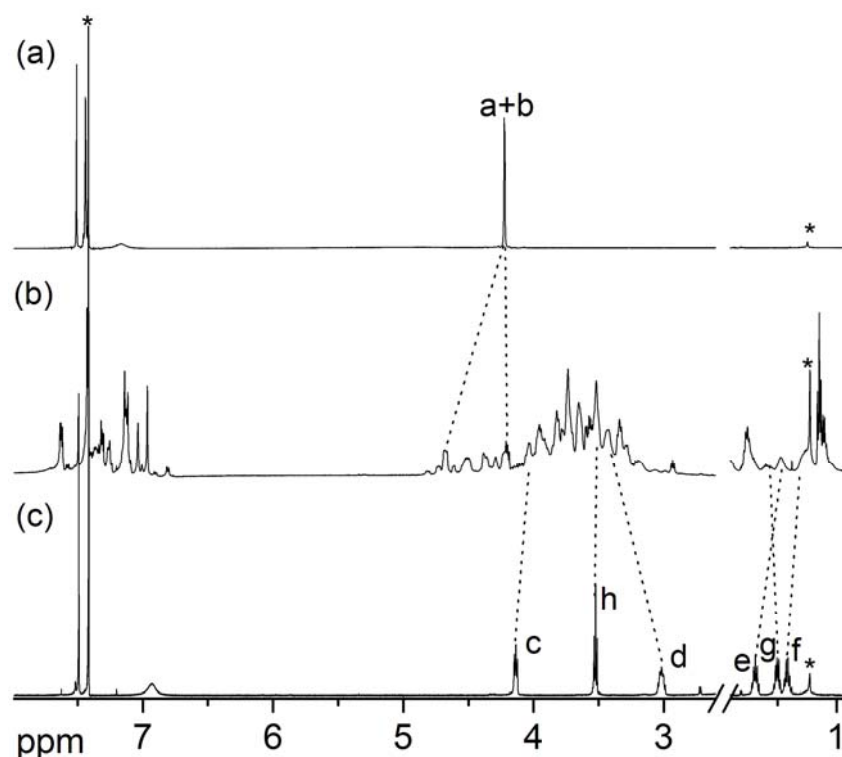


Figure S5. ¹H NMR spectra (500 MHz, 298 K, CDCl₃:CD₃CN = 2:1, 2.0 mM) of (a) **7-2H•2PF₆**, (c) **8-2H•2PF₆**, and (b) the 1:1:2 mixture of **7-2H•2PF₆**, **8-2H•2PF₆**, and **2**. The dotted lines indicate the shifting of the protons on the guests after complex formation. Asterisk = solvent residue.

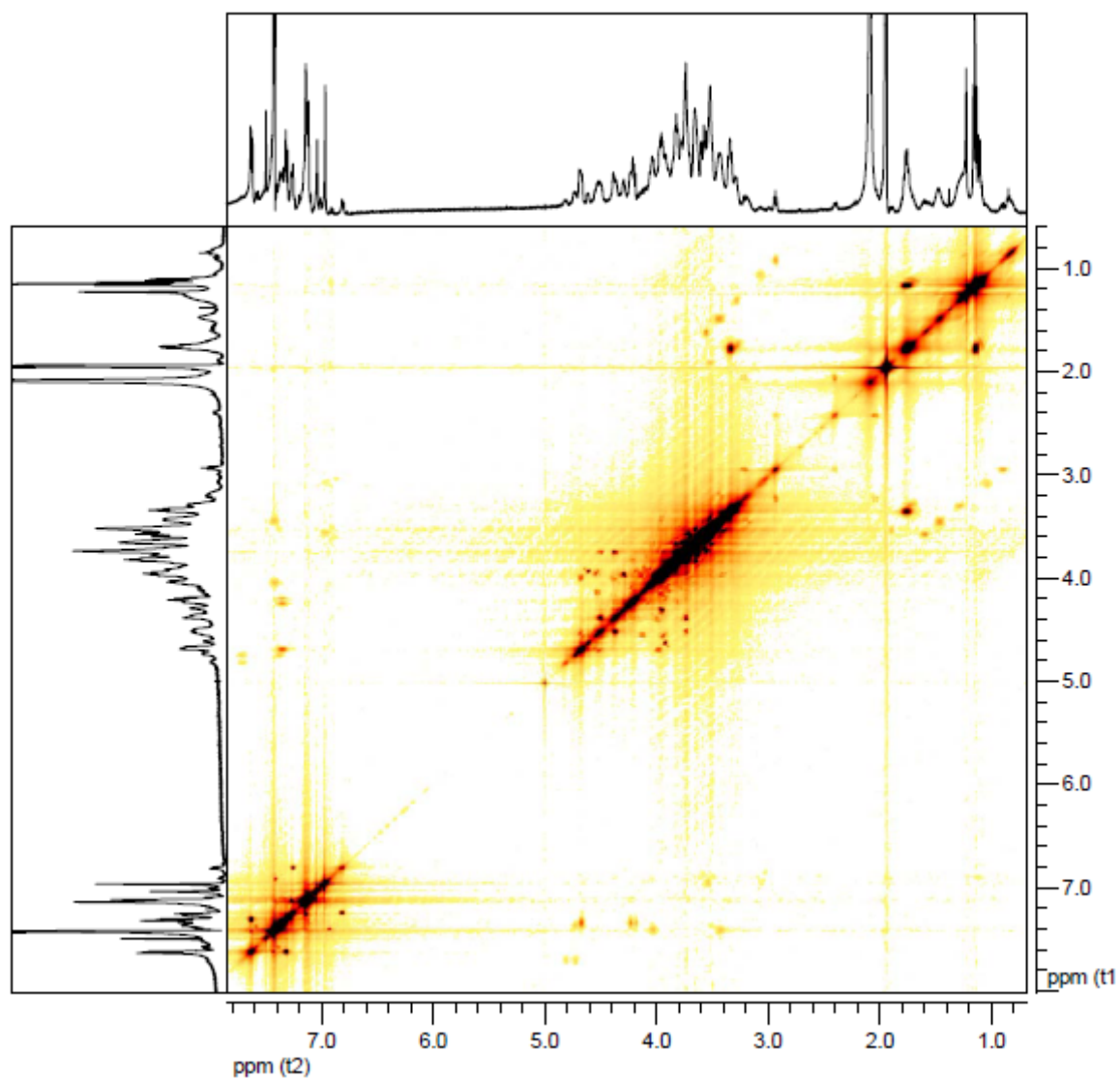


Figure S6. ^1H - ^1H COSY spectrum (500 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 2:1$, 2.0 mM) of the pseudorotaxane **9-4H**· 4PF_6 .

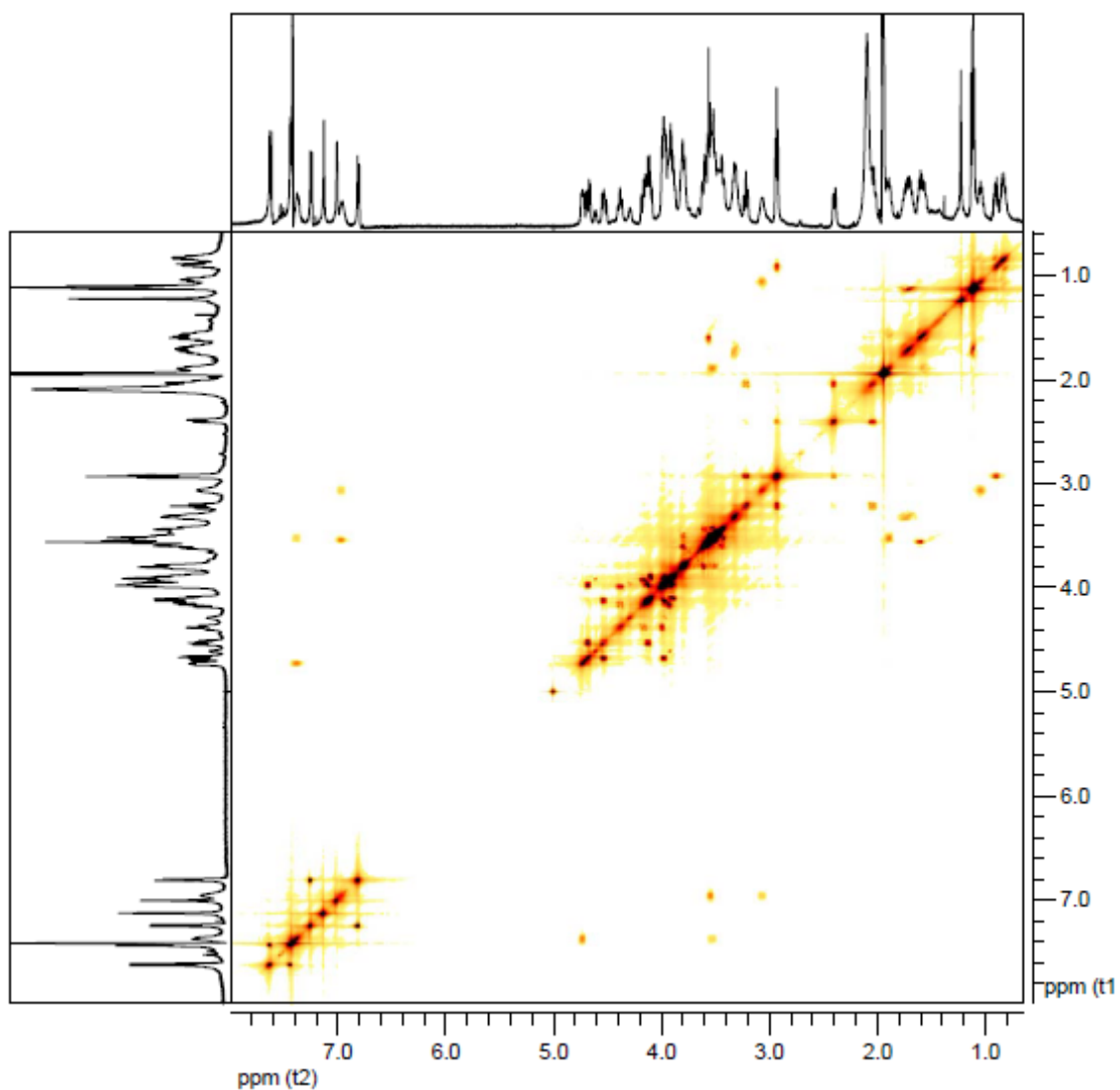


Figure S7. Full ¹H-¹H COSY spectrum (500 MHz, 298 K, CDCl₃:CD₃CN = 2:1, 2.0 mM) of the equimolar mixture of **8-2H-2PF₆** and **2**.

Crystallography

Colorless crystals of **11-4H•4PF₆** were obtained by (vapor diffusion of diethylether into a saturated CHCl₃:acetonitrile (3:1) solution of **11-4H•4PF₆**. The structural analysis was performed using a Bruker Kappa Apex II diffractometer with graphite-monochromatized Cu-*Kα* ($\lambda = 1.54183 \text{ \AA}$) radiation. Collect software³ was used for the data measurement and DENZO-SMN⁴ for the processing. The structure was solved by the charge flipping method with SUPERFLIP⁵ and refined by full-matrix least-squares methods using the WinGX-software,⁶ which utilizes the SHELXL-97 module.⁷ Multi-scan absorption correction by SADABS2008.⁸ All C-H hydrogen positions were calculated using a riding atom model with $U_H = 1.2 \times U_C$. The crystals were very fragile and had a very low diffraction quality (86.4% of data until $2\theta = 58.11^\circ$) and coupled with severe disorders of the ends of the axle and on the smaller crown ether moiety of the pseudorotaxane, altogether 81 restraints (DFIX, EADP) were used to make the disordered parts chemically reasonable. Some residual electron density could not be fitted to any model and were thus included in the final refinements as isolated carbon atoms with fractional occupancies. All non-H atoms, despite of their apparent disorder, were refined anisotropically. The severe thermal movement and disorder of the ends of the axle, lead to two physically unreasonably short H...H distances. This could not, however, be treated properly and was left as they were and no attempt to model this disorder was done. The remaining residual electron density, which could not be modeled, was treated with the SQUEEZE protocol inside PLATON⁹ to remove the void electron density. Crystal data for **11-4H•4PF₆**: $M = 2981.2$, colorless prisms, $0.10 \times 0.10 \times 0.15 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 14.1502(6) \text{ \AA}$, $b = 21.638(1) \text{ \AA}$, $c = 27.734(1) \text{ \AA}$, $\beta = 95.860(4)^\circ$, $V = 8446.9(6) \text{ \AA}^3$, $Z = 2$, $D_c = 1.172 \text{ g/cm}^3$, $F(000) = 3172$, $\mu = 0.929 \text{ mm}^{-1}$, $T = 173(2) \text{ K}$, $2\theta_{\text{max}} = 116.22^\circ$, 10216 reflections used, 4715 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.1290$, 917 parameters, 81 restraints, $\text{GoF} = 1.336$, $R = 0.1646 [I_o > 2\sigma(I_o)]$, $wR = 0.4406$ (all reflections), $0.824 < \Delta\rho < -0.472 \text{ e/\AA}^3$. CCDC-829618 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif;

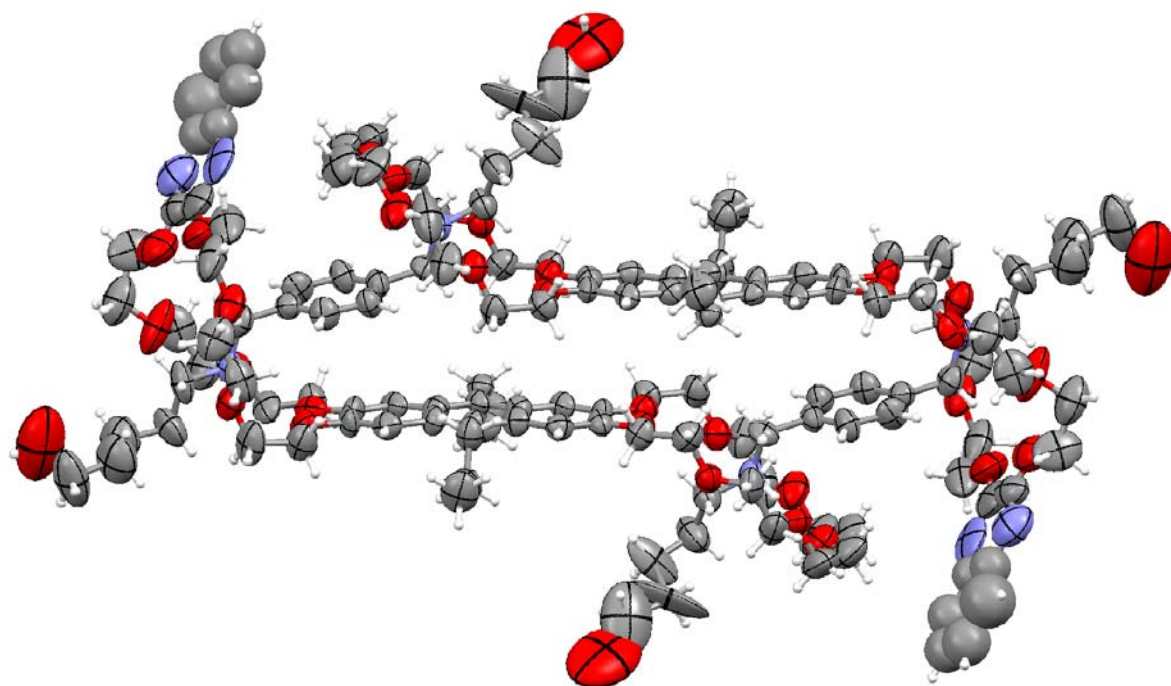


Figure S9: ORTEP plot (50% probability level)

References

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