Supplementary Information

Dampened Circumrotation by CH···π Interactions in Hydrogen Bonded [2]Rotaxanes

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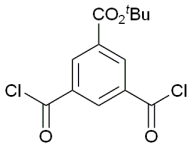
1. General Experimental Section

Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. HPLC grade solvents (Scharlab) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Column chromatography was carried out using silica gel (60 Å, 70-200 μm, SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminun cards (0.25 mm thick, with fluorescent indicator 254 nm, Fluka) and observed under UV light. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded as nujol emulsions on a Nicolet Impact 400 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded at 298 K on a Bruker Avance 300, 400 MHz and 600 MHz instruments. ^{1}H NMR chemical shifts are reported relative to Me_4Si and were referenced via residual proton resonances of the corresponding deuterated solvent whereas ^{13}C NMR spectra are reported relative to Me_4Si using the carbon signals of the deuterated solvent. Signals in the ^{1}H and ^{13}C NMR spectra of the synthesized compounds were assigned with the aid of DEPT, APT, or two-dimensional NMR experiments (COSY, HMQC and HMBC). Abbreviations of coupling patterns are as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. Mass spectra were recorded with Agilent 5973 (EI), Agilent VL (ESI) and HPLC/MS TOF 6220 mass spectrometers. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

2. Materials

Compounds 5-(*tert*-butoxycarbonyl)isophthalic acid,[1] 3,5-pyridinedicarbonyl dichloride,[2, 3] *N,N,N',N'*-tetrakis[(cyclohexyl)methyl]succinamide[4] and *N,N,N',N'*-tetrabenzylsuccinamide[5] and rotaxane **1d**[5] were prepared following previously reported procedures.

3. Synthesis of *tert*-butyl 3,5-bis(chlorocarbonyl)benzoate

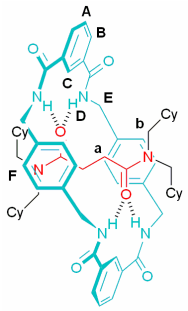


To a suspension of 5-(*tert*-butoxycarbonyl)isophthalic acid (2.12 g, 7.95 mmol) in dry dichloromethane (50 mL) under nitrogen was added oxalyl chloride (1.5 mL, 17.5 mmol). Then a few drops of DMF were added to the reaction mixture. After the reaction mixture was stirred for 22 h at 40ºC, a clear solution was obtained. The evaporation of excess oxalyl chloride and solvent gave a solid residue, which was recrystallized, from hexane to yield the titled compound (2.4 g, 85%) as colorless needles. $C_{13}H_{12}Cl_2O_4$ (MW 302.14). M.p.: 248-250 °C (hexane). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.56 (s, 9H, $(CH_3)_3$), 8.82-8.84 (m, 3H, Ar); ^{13}C NMR (100 MHz; $CDCl_3$): δ = 166.6 (C=O), 162.4 (C=O), 137.2 (Ph), 136.1, 134.6, 134.4, 83.4 ($C(CH_3)_3$), 27.9 ($C(CH_3)_3$).

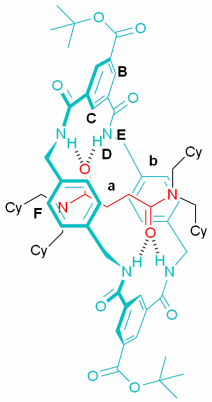
4. Experimental procedure and characterization of the succinamide-based [2]rotaxanes 1a-e

The thread (1 equiv.) and Et_3N (24 equiv.) in anhydrous $CHCl_3$ (150 mL) were stirred vigorously whilst solutions of *p*-xylylenediamine (8 equiv.) in anhydrous $CHCl_3$ (20 mL) and the corresponding acid dichloride (8 equiv.) in anhydrous $CHCl_3$ (20 mL) were simultaneously added over a period of 4 h using motor-driven syringe pumps. After a further 4 h the resulting suspension was filtered through a Celite pad and the solvent removed under reduced pressure. The resulting solid was subjected to column

chromatography (silica gel) using $CHCl_3$/MeOH (95/5) mixture as eluent to give the [2]rotaxanes.

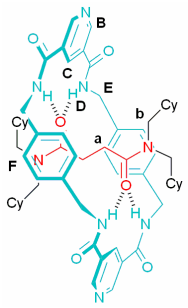


Rotaxane 1a: Yield: 23%; M.p. 212 - 214 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 2H, CH_C), 8.38 (dd, J = 7.8 Hz, 2H, CH_B), 7.68 (t, J = 5.7 Hz, 4H, NH_D), 7.66 (t, J = 7.8 Hz, 2H ,CH_A), 7.11 (s, 8H, CH_F), 5.43 (s, 4H, CH_E), 3.72 (s, 4H, $CH_{E'}$), 3.11 (d, J = 6.9 Hz, 4H, CH_b), 2.64 (d, J = 7.5 Hz, 4H, $CH_{b'}$), 1.77-1.15 (m, 21H, H_{Cy}), 1.10 (s, 4H, CH_a), 1.01-0.68 (m, 19H, H_{Cy}), 0.32-0.22 (m, 4H, H_{Cy}).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.76 (CO_{thread}), 165.13 ($CO_{macrocycle}$), 138.59 (*q*), 133.27 (*q*.), 132.50, 129.45, 128.91, 122.33, 56.10 (CH_2N), 54.71 (CH_2N), 43.13 ($ArCH_2N$), 37.46 (CH), 36.80 (CH), 31.49, 30.89, 28.46 (CH_2CO), 26.03, 25.93, 25.66, 25.41; IR (Nujol): ν = 3387 (w), 3331 (w), 3020 (s), 2950 (w), 1664 (m), 1590 (m), 1556 (m), 1425 (w), 1225 (vs), 767 (s) cm^{-1}; HRMS (ESI) calcd for $C_{64}H_{85}N_6O_6$ $[M + H]^+$ 1033.6531, found 1033.6529.

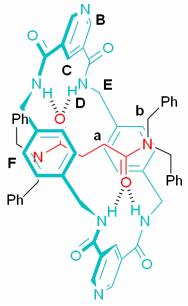


Rotaxane 1b: Yield: 10%; M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (br s, 6H, CH_C + CH_B), 7.66 (t, J = 5.1 Hz, 4H, NH_D), 7.10 (s, 8H, CH_F), 5.40 (br s, 4H, CH_E), 3.74 (br s, 4H, $CH_{E'}$), 3.10 (d, J = 6.6 Hz, 4H, CH_b), 2.61 (d, J = 7.3 Hz, 4H, $CH_{b'}$), 1.63 (s, 18H, $(CH_3)_3$), 1.82-1.45 (m, 21H, H_{Cy}), 1,35-1,10 (m, 8H, H_{Cy}), 1.06 (s, 4H, CH_a),

0.99-0.73 (m, 11H, H_{Cy}), 0.17-0.28 (m, 4H, H_{Cy}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.8 (CO_{thread}), 164.4 ($CO_{macrocycle}$), 164.3 (COO^tBu), 138.5 (*q*), 133.9 (*q*), 133.7 (*q*), 133.3, 128.9, 125.6, 81.95 ($C(CH_3)_3$), 56.1 (CH_2N), 54.6 (CH_2N), 43.2 ($ArCH_2N$), 37.5 (CH), 36.7 (CH), 31.5, 30.9, 28.5 (CH_2CO), 28.2 ($C(CH_3)_3$), 26.0, 25.9, 25.6, 25.4; IR ($CHCl_3$): ν = 3351 (w), 2921 (s), 2842 (w), 1719(s), 1658 (s), 1589 (s), 1537 (m), 1451 (w), 1276 (m), 761 (m) cm^{-1}; HRMS (ESI) calcd for $C_{74}H_{101}N_6O_{10}$ $[M + H]^+$ 1233.7579, found 1233.7593



Rotaxane 1c: Yield: 21%; M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (d, *J* = 1.9 Hz, 4H, CH_B), 9.16 (t, *J* = 2.0 Hz, 2H, CH_C), 7.51 (t, *J* = 5.6 Hz, 4H, NH_D), 7.13 (s, 8H, CH_F), 5.31 (br s, 4H, $CH_{E'}$), 3.95 (br s, 4H, CH_E), 3.11 (d, *J* = 6.7 Hz, 4H, CH_b), 2.65 (d, *J* = 7.3 Hz, 4H, $CH_{b'}$), 1.82-1.50 (m, 16, H_{Cy}), 1.33-1.14 (m, 12, H_{Cy}) 1.11 (s, 4H, CH_a), 1.03-0.71 (m, 12, H_{Cy}), 0.40-0.25 (m, 4H, H_{Cy}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.61 (CO_{thread}), 163.65 ($CO_{macrocycle}$), 153.42, 138.27 (*q*), 129.83, 129.11, 127.70 (*q*), 55.93 (CH_2N), 54.31 (CH_2N), 43.18 ($ArCH_2N$), 37.34 (CH), 36.85 (CH), 31.43, 31.08, 28.42 (CH_2CO), 25.96, 25.89, 25.71, 25.34; IR (Nujol): ν = 3387 (w), 3358 (w), 3023 (s), 2937 (m), 2852 (w), 1667 (s), 1593 (m), 1556 (m), 1540 (m), 1425 (w), 1213 (vs), 767 (s) cm^{-1}; HRMS (ESI) calcd for $C_{62}H_{83}N_8O_6$ $[M + H]^+$ 1035.6436, found 1035.6442.



Rotaxane 1e: Yield: 12%; M.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.40 (br s, 4H, CH_B), 8.65 (br s, 2H, CH_C), 7.40-7.16 (m, 12H, Ph), 7.08-7.00 (m, 4H, Ph), 7.04 (t, J = 7.0 Hz, 4H, NH_D), 6.86 (s, 8H, CH_F), 6.72 (d, J = 7.4 Hz, 4H, Ph), 4.46 (s, 4H, CH_b), 4.31 (br s, 8H, H_E + $H_{E'}$), 4.19 (s, 4H, $CH_{b'}$), 0.97 (s, 4H, CH_a); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.65 (CO_{thread}), 163.75 ($CO_{macrocycle}$), 153.22, 138.28 (*q*), 136.41, 134.32, 129.41 (*q*), 129.23, 129.04, 128.69, 128.41, 127.76 (*q*), 125.13, 51.75 (CH_2Ph), 51.63 (CH_2Ph), 43.21 ($ArCH_2N$), 28.13 (CH_2CO).; IR (Nujol): v = 3387 (w), 3326 (w), 3023 (vs), 1707 (m), 1667 (m), 1614 (m), 1531 (m), 1425 (m), 1365 (w), 1221 (vs), 1078 (w), 1029 (w), 953 (w), 755 (vs) cm^{-1}; HRMS (ESI) calcd for $C_{62}H_{59}N_8O_6$ $[M + H]^+$ 1011.4558, found 1011.4560.

5. Stacked plot of the ^{1}H-NMR spectra of rotaxanes 1c and 1e and their corresponding threads.

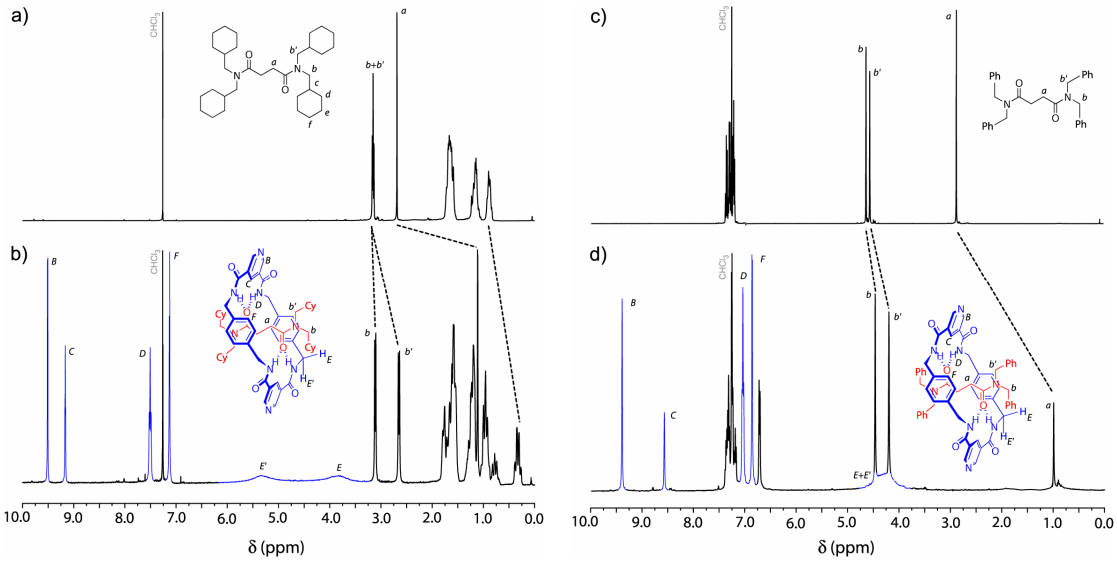


Figure S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of a) *N,N,N',N'*-tetrakis[(cyclohexyl)methyl]succinamide, b) rotaxane **1c**, c) *N,N,N',N'*-tetrabenzylsuccinamide and d) [2]rotaxane **1e**.

6. 2D ROESY spectrum of rotaxane 1a.

The ROESY spectrum was measured on a solution of rotaxane **1a** in $CDCl_3$ by using a 400 MHz Bruker AVANCE spectrometer at 293K. A spin-lock pulse of 500 ms was used. The number of scans per increment was 80, and 240 experiments were acquired in the second dimension. Total experimental time was approximately 8 h.

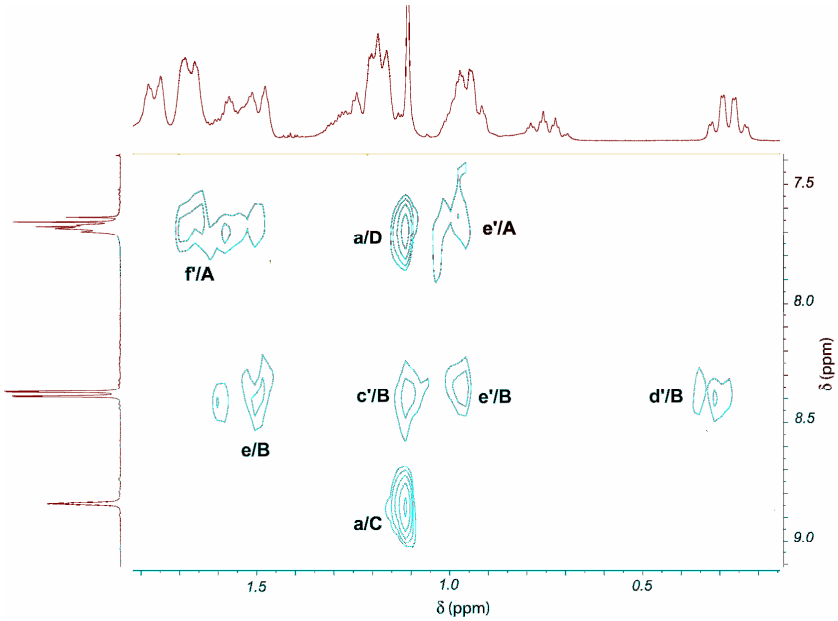
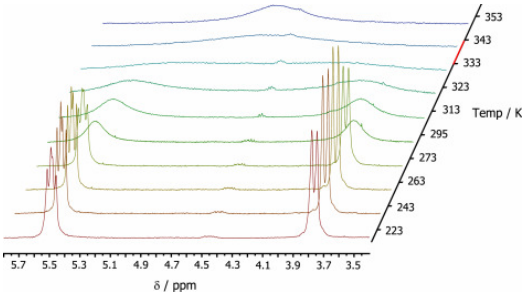


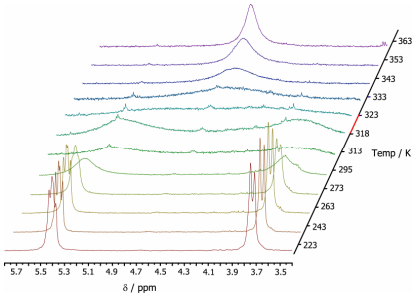
Figure S2. Section of the $^1H,^1H$ ROESY spectrum of a solution of rotaxane **1a** in $CDCl_3$ at 293 K. The cross peaks corresponding to the resonances assigned to the protons of the cyclohexyl group (in lower-case letters) and the protons of the isophthalimide moiety (in upper-case letters) of **1a** are shown. The assignments correspond to the lettering shown in Fig. 2 of the main text.

7. Variable temperature ^{1}H NMR spectra of the [2]rotaxanes 1a-c and 1e

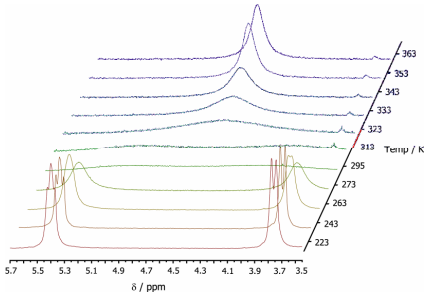
a) [2]Rotaxano **1a**



b) [2]Rotaxano **1b**



c) [2]Rotaxano **1c**



b) [2]Rotaxano **1e**

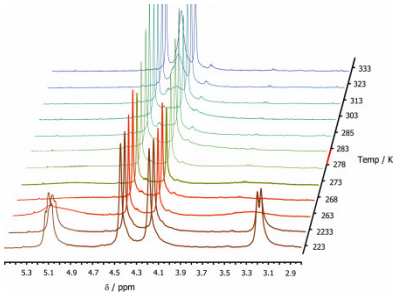


Figure S3. Variable temperature ^{1}H NMR spectra (stacked expansions of the aliphatic region, 400 MHz) of **1a-c** and **1e** in CD_2Cl_2 at 223-300 K and $C_2D_2Cl_4$ at 300 - 370K.

Free energies of activation were calculated using the Eyring equation, $\Delta G_c^{\neq} = -RT_c \cdot ln(k_c h/k_b T_c)$, where $k_c = (\pi\Delta\upsilon)/\sqrt{2}$ or $k_c = \pi\sqrt{(\Delta\upsilon^2 + 6J^2)}/\sqrt{2}$ and R, h and k_b are the gas, Planck and Boltzmann constants, respectively.[6-8]

8. General crystal data and structure refinement for the [2]rotaxane 1a

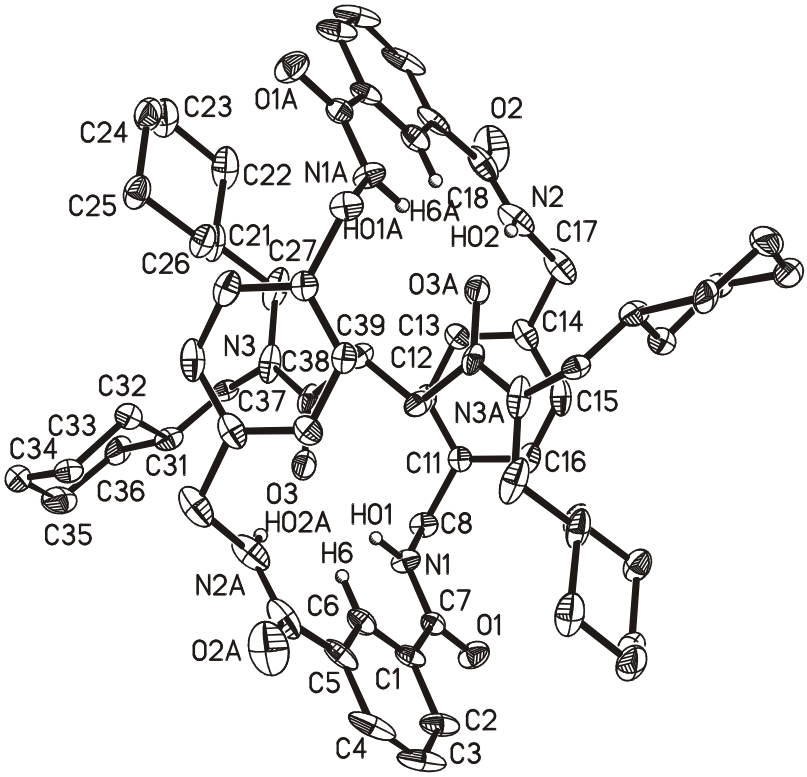


Figure S4: Molecular structure of **1a** (hydrogen atoms omitted for clarity) with thermal ellipsoids drawn at 50% probability.

Table S1. Crystal data and structure refinement for **1a**.[§]

Empirical formula	$C_{66}H_{86}Cl_6N_6O_6$ [**1a**·2$CHCl_3$]	
Formula weight	1272.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9123(13) Å	α= 73.492(2)°
	b = 11.7727(16) Å	β= 73.172(2)°

	c = 14.746(2) Å γ = 86.333(2)°
Volume	1578.9(4) Å^3
Z	1
Density (calculated)	1.338 Mg/m^3
Absorption coefficient	0.329 mm^{-1}
F(000)	674
Crystal size	0.33 x 0.28 x 0.06 mm^3
Theta range for data collection	1.80 to 28.68°
Index ranges	-13<=h<=13, -15<=k<=15, -18<=l<=18
Reflections collected	19245
Independent reflections	7391 [R(int) = 0.0402]
Completeness to theta = 26.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9805 and 0.8992
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7391 / 16 / 416
Goodness-of-fit on F^2	1.153
Final R indices [I>2sigma(I)]	R1 = 0.0830, wR2 = 0.1629
R indices (all data)	R1 = 0.1065, wR2 = 0.1736
Largest diff. peak and hole	0.663 and -0.582 e.Å^{-3}

§ CCDC reference number 872249

X-ray Structure Determinations. Intensities were registered at low temperature on a Bruker SMART APEX CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were based on multiscans (program SADABS). The structure was refined anisotropically on F^2 using SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112). The refinement of hydrogen atoms was carried out using the riding model except for those of the NH groups which were refined freely. A CH_2 fragment of the cyclohexane in s-*cis* disposition to the carbonyl oxygen atom of the amide function was disordered over two positions (ca 55:45%) and the carbon atoms of the disordered part were refined isotropically.

Table S2. Hydrogen bonds for **1a** [Å and (°)].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(01)...O(3)	0.87(4)	2.21(4)	3.084(3)	173(3)
N(2)-H(02)...O(3)#1	0.82(4)	2.40(4)	3.204(4)	165(3)
C(6)-H(6)...O(3)	0.93	2.27	3.193(4)	175.6
C(37)-H(37A)...O(2)#2	0.97	2.49	3.385(6)	154.2
C(99)-H(99)...O(1)	0.98	2.17	3.000(4)	141.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z #2 -x+2,-y+2,-z

9. Hirsfield surface analysis for the visualization of CH/π interactions in rotaxane 1a.

A convenient way to view and quantify CH/π interactions is by mapping a Hirshfeld surface[9] onto the thread of rotaxane **1a** using the program CrystalExplorer[10] and then rendering the corresponding 2D fingerprint plot.[11, 12]

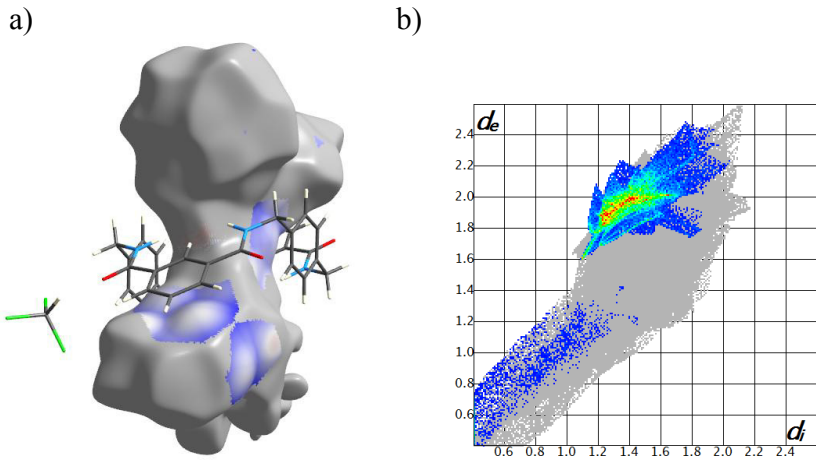


Figure S5: Hirshfeld surface (a) and its fingerprint plot (b) of crystal structure of [2]rotaxane **1a**.

10. References

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